

CRANFIELD UNIVERSITY

Junfeng Chen

Combinatorial sputtering and degradation behaviour of
photoluminescence Europium Titanium Oxide thin films

School of Aerospace, Transport and Manufacturing
PhD in Manufacturing

PhD Thesis
Academic Year: 2020 - 2024

Supervisor: Dr. Adrianus Indrat Aria
Associate Supervisor: Dr. Jeff Rao
March 2024

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ABSTRACT

The most common type of solar cell is the crystalline silicon (c-Si) cell, which has a low cost of production and a high efficiency of energy conversion and is widely used in various applications that require solar power. Inefficiencies associated with PV devices mainly stem from energy conversation mismatches between solar radiation and the PV spectral response. Photoluminescent (PL) thin films possess the capability to absorb and re-emit specific photons, thereby minimising energy losses within the PV system. In this thesis, PL thin films have been fabricated using the physical vapour deposition (PVD) method, synthesised Europium oxide and Titanium oxide coating. A range of Europium Titanium Oxide (ETO) luminescence thin films, with concentrations varying from 0 at% to 100 at% in Eu/(Eu+Ti), were fabricated using combinatorial sputtering. The samples underwent heat treatment annealing at 450°C and 600°C, resulting in changes to the phase, structure, and optical properties. The effect of composition and annealing temperature on the characterisations of the ETO thin film samples were comprehensively studied using SEM, EDX, XRD, UV–Vis spectrophotometer, Raman spectrometer, fluorescence spectrometer, and solar simulator. Transmittance and bandgap variations are observed and influenced by annealing temperature and europium ratios. The bandgap energy variation is identified as a crucial factor affecting photon absorption and the luminescent properties of the films. Fluorescence spectroscopy was used to examine the photoluminescence properties of the thin films. Excitation peaks at 394 nm ($^7F_0 \rightarrow ^5L_6$) and 464 nm ($^7F_0 \rightarrow ^5D_2$) are identified as the most intense in excitation spectra, while in emission spectra the strongest emission intensity peak at 613 nm ($^5D_0 \rightarrow ^7F_2$) exhibits a higher branching ratio in fluorescence spectra. Furthermore, an investigation into the optical and fluorescence properties of luminescence thin films comprising Eu(dbm)₃ and CuInS₂/ZnS in conjunction with PMMA and PVA matrices has been conducted. The characteristics of these films were analysed both before and after degradation testing, with a comparative assessment made against ETO thin films. In addition, an intriguing correlation between bandgap values and power conversion efficiency is established. Films with narrower bandgaps demonstrate reduced power conversion efficiency due to increased photon absorption, scattering and escape from the substrate edge. These

findings contribute valuable insights into tailoring the properties of luminescence thin films for potential applications, particularly in the realm of optoelectronic devices.

Keywords: lanthanide materials, down-conversion, combinatorial sputtering, fluorescence, degradation

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LIST OF ABBREVIATIONS

Europium Titanium Oxide	ETO
PV	Photovoltaic
c-Si	Crystalline Silicon
QD	Quantum dot
PCE	Power Conversion Efficiency
EQE	External Quantum Efficiency
PLQY	Photoluminescence Quantum Yield
PL	Photoluminescence
PVD	Physical Vapour Deposition
RF	Radio-Frequency
DC	Direct-Current
RE	Rare-Earth
Eu(dbm) ₃	Dibenzoylmethane Europium(III)
CuInS ₂ /ZnS	Copper Indium Disulfide/Zinc Sulfide
UV	Ultraviolet
E _g	Bandgap
NC	Nanocrystal
FWHM	Full Width at Half Maximum
VIS	Visible
FF	Fill Factor
V _{oc}	Open Circuit Voltage
I _{sc}	Short Circuit Current
J _{sc}	Shor Circuit Current Density

$P_{\max}$	Maximum Power
V_{mp}	Maximum Power Peak Voltage
I_{mp}	Maximum Power Peak Current
J_{mp}	Maximum Power Peak Current Density
I-V	Current—Voltage
P-V	Power—Voltage
PMMA	Poly (methyl methacrylate)
PVA	Polyvinyl acetate
SEM	Scanning Electron Microscopy
EDX	Energy-Dispersive X-ray Spectroscopy
XRD	X-ray diffraction
NIR	Near Infra-red

1 Introduction

1.1 Background and motivation

Solar energy is one type of green, renewable energy that can be converted to electrical energy by photovoltaic (PV) devices. PV devices exhibit differing performance characteristics depending upon the makeup of the device, which could be either a crystalline silicon solar cell (c-Si), a dye-sensitised solar cell (DSSC), a perovskite solar cell, etc.[1–3] The c-Si solar cell is the most mature technology, and it is the one employed most frequently.

Inefficiencies associated with PV devices mainly stem from energy conversation mismatches between solar radiation and the PV spectral response. The band-gap energy of c-Si is 1.12 eV, corresponding to an equivalent spectral response of 1000 nm. However, the power of sunlight has a maximum spectral irradiance at around 500 nm.[4] This spectral mismatch produces thermalisation losses and sub-bandgap losses in the PV material. There are two approaches to reduce the losses, the first approach is to match the spectral response to the incident spectral irradiance by stacking different band gap materials into >1 junctions, such as two-terminal perovskite/silicon tandem solar cells.[3] The second approach is to match the incident spectral irradiance to the spectral response by down-shifting/converting.[5] The second approach can improve the power conversion efficiency of the existing solar cells without changing their materials. Luminescent materials are fabricated by introducing dopants into the host semiconductor materials. Dopants include lanthanide elements such as Tb^{3+} , Ce^{3+} , Eu^{3+} , Er^{3+} , Pr^{3+} and Yb^{3+} . [6] Lanthanide ions have a 4fⁿ ($0 < n < 14$) electron structure. Therefore, a lot of energy levels are created by lanthanide ions, which have sharp lines in the UV to NIR light range offering unique spectroscopic properties.[7] Lanthanide elements can provide Up/Down-conversion mechanism properties. Moreover, the down-conversion mechanism can provide photoluminescent quantum yields (PLQY) >100% to compensate for optical losses. The photoelectric performance of solar cells can be improved by doping with lanthanide materials, thereby increasing the conversion mechanisms. Host materials selection includes common oxide thin films (e.g. ZnO and TiO₂). [8,9] The Host materials offer a specific bandgap to absorb the photons close to the maximum

spectral irradiance of sunlight and low phonon energies that enable RE ions to emit specific wavelengths effectively.[9,10]

Photoluminescence materials with several specific compositions were studied in the last decades, but the seamless variation in composition and crystalline phase is missed. Drop-casting is the most simple and economical process, with no need for expensive and industrially non-compatible instruments.[11] However, drop-casting is not for the rapid discovery of material characteristics and properties. High-quality luminescent thin films can be fabricated by physical vapour deposition, which is more stringent control and reproducible in a low temperature surrounding.[12] more importantly, magnetron sputtering can be utilised for combinatorial synthesis to rapidly vary material characteristics and properties with a low number of experimental iterations. Moreover, complex and various character materials can be quickly fabricated by combinatoric co-sputtering that can handle large amounts of data, such as more than three samples per substrate. In addition, the combinatorial co-sputtering is applied to fabricate co-dopant samples, which can cover a broader range of radiation spectra.

1.2 Scope of research

Drawing upon an extensive review of the existing literature, this study aims to delineate and address pertinent research gaps:

1. Combinatorial sputtering offers a significant various concentration during each deposition run. However, the precise composition of the thin film necessary to achieve the desired PL properties has not yet been thoroughly investigated and requires further elucidation.
2. An existing gap in knowledge pertains to whether thin films must exhibit crystallinity to demonstrate PL or if amorphous structures suffice. Furthermore, the potential impact of thin film microstructure on PL remains undetermined.
3. The lifetime of luminescence thin films remains unexplored within the existing literature. Furthermore, the influence of both material composition and microstructure on the degradation properties of these thin films has yet to be investigated.

1.3 List of Publications

Junfeng Chen, Adrianus Indrat Aria, Jeff Rao

Combinatorial Sputtering of Luminescent Europium Titanium Oxide Thin Films.

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1.4 List of Conferences

There are three conferences that participated during the PhD research, which are detailed in Table 1-1. The conferences are numbered from 1 - 3 for reference with details of their name and their date.

Table 1-1 List of conferences linked to the chapters.

Conference number	Conference name	Conference date	Presentation title	Link to chapter
1	Advances in Photovoltaics: Tandems and Bifacial PV Conference	07/12/2022	Combinatorial synthesis of lanthanide-doped luminescent films for photovoltaics	4
2	Quantum Technologies for Fundamental Physics Engagement Event	02/02/2023— 03/02/2023	Combinatorial synthesis and degradation mechanism of quantum dots and lanthanide-doped luminescent thin film to improve photovoltaic performance	3,4, 6
3	PVSAT-17 & Super Solar Conference	26/06/2023— 28/06/2023	Synthesis and degradation of photoluminescent films	4,5,6

1.5 Aims and Objectives

1.5.1 Aims:

Investigate the effect of Eu^{3+} doping concentration and annealing temperature on PL properties and degradation behaviour.

1.5.2 Objectives:

Firstly, combinatorial sputtering holds the promise of attaining the precise composition of thin films necessary to achieve the desired PL properties.

Secondly, a combinatoric sputtering synthesis method is used to develop and identify key processing parameters for rapid variation of doping concentration and film characteristics, such as microstructure and cross-sectional morphology. And to elucidate the effect of such characteristics on PL and optical properties.

Thirdly, the degradation properties of these thin films synthesised by combinatorial sputtering with various concentrations will be measured and compared with the luminescence films from the chemical method to understand further development of the degradation behaviour impacted by materials and fabrications.

1.6 Thesis Structure

This research project is structured to align its objectives with specific chapters within this thesis, as outlined in Table 1-2. The primary focus of this thesis is to elucidate the characteristics of luminescence thin films, with a particular emphasis on lanthanide materials. Additionally, the investigation delves into the degradation properties associated with luminescence thin films.

Chapter 2 is dedicated to an extensive literature review encompassing various facets, including different types of solar cells, photoluminescence mechanisms, lanthanide materials, and fabrication methodologies. Chapter 3 outlines the methodological framework employed throughout the research, detailing aspects such as materials suppliers, synthesis parameters for sample preparation, characterisation techniques, and degradation testing protocols.

Chapter 4 endeavours to elucidate the microstructure of ETO synthesised via combinatorial sputtering, employing SEM, EDX, XRD and Raman spectroscopy.

Chapter 5 presents the optical and fluorescence properties of ETO thin films fabricated using combinatorial sputtering, including analyses of transmittance, fluorescence spectra, and the PCE of c-Si solar cells.

Chapter 6 delves into the degradation properties of ETO thin films, $\text{Eu}(\text{dbm})_3$ and $\text{CuInS}_2/\text{ZnS}$ with polymer thin films facilitating a comparative assessment of optical, fluorescence properties, and PCE before and after degradation testing.

Chapter 7 serves to conclude the research endeavour, providing insights into future directions aimed at enhancing performance and advancing the utilisation of luminescence thin films in industrial and commercial applications.

Table 1-2 List of chapters linked to the objectives.

Chapter	Objective covered
4	1, 2
5	2,
6, 7	3

2 Literature review

2.1 Introduction

The power conversion efficiency (PCE) of current PV devices remains relatively low, primarily constrained by the Shockley-Queisser limit, which sets the theoretical maximum efficiency for a single-junction solar cell at 33% considering only radiative recombination.[13] Despite advancements, the maximum PCE achieved by single-junction c-Si solar cells is $26.7\% \pm 0.5\%$ and stands at around 27% due to the Shockley-Queisser limit.[3,13] This fundamental limitation is attributed to five main mechanisms: thermalisation, sub-bandgap, optical, recombination, and spatial relaxation losses. These factors collectively hinder the attainment of higher efficiencies in solar energy conversion technologies.[14] A significant portion of research efforts is directed towards enhancing the conversion efficiency of solar cells, with the aim of bolstering their commercial viability, reducing costs, and extending their operational lifespan. Much of this research concentrates on improving the solar cell itself, exploring more efficient alternative materials and optimising the device configuration. However, this approach often entails high costs and long-term research. As an alternative strategy, the application of PL thin films atop solar cells has garnered interest in mitigating or eliminating fundamental losses, consequently augmenting conversion efficiencies. By overlaying external PL thin films onto solar cells, it is possible to enhance their PV performance, especially in instances where solar cells exhibit inefficiencies or are characterised by high production costs. This approach offers a promising avenue for improving solar cell efficiency while circumventing some of the challenges associated with traditional device-centric optimisation strategies, which include luminescent solar concentrator (LSC), quantum dots thin film and lanthanide-doped thin film.[7,15,16]

A diverse array of materials can be utilised in the fabrication of PL thin films, including metallic quantum dots (QD), perovskite QD or lanthanide elements, among others.[7,17,18] These materials, along with the configuration of the PL thin film, exhibit distinct mechanisms such as down-shifting, down-conversion, and up-conversion.[5] Luminescence, a phenomenon introduced by Wiedemann in 1888, refers to the ability of materials to absorb energy and emit specific light.[19] This emission can be triggered by various energetic sources, including electromagnetic radiation, electric fields, X-rays, and charged particles resulting from radioactive decay.

PL, on the other hand, is specifically linked to photo-excitation. By employing luminescent materials as spectral converters, it becomes possible to mitigate inherent thermalisation and non-absorption losses, thereby enhancing the efficiency of light conversion processes.[7] Luminescence, defined as the emission of light by a material subsequent to the absorption of energy, finds its etymological roots in the Latin term "lumen," signifying "light." Coined by Eilhard Wiedemann, a distinguished German physicist and science historian, in 1888, the term encompasses all light phenomena not primarily influenced by temperature elevation, distinguishing it from incandescence.[19]

Among the RE elements, the Eu^{3+} ion distinguishes itself as a premier pure red-emitter, attributing to its distinct $^5D_0 \rightarrow ^7F_2$ transition under UV radiation. This characteristic emission, confined to the red spectrum, renders it particularly noteworthy for various applications. Moreover, the PL emission of Eu^{3+} ions is highly sensitive to their surroundings within the host matrix, offering versatility in optical properties. Europium, a well-established RE material, is often chosen to achieve enhanced colour purity and luminescence efficiency, underscoring its significance in luminescence research and applications.[20,21] Copper indium sulfide colloidal quantum dots ($\text{CuInS}_2/\text{ZnS}$ QDs) have attracted significant interest due to their advantageous features, such as the utilisation of non-toxic elements, cost-effective synthesis methods, and tunable bandgap properties.[22] $\text{CuInS}_2/\text{ZnS}$ is acknowledged as a direct semiconductor with a bulk bandgap of around 3 eV. The emission wavelength of CuInS_2 QDs can be finely adjusted through size or composition manipulation, covering a wide spectral range from visible to NIR regions.[23] Each mechanism plays a pivotal role in augmenting the performance of PV devices. The techniques utilised in PV manufacturing hold significant sway over the microstructure of thin films, thus exerting a profound influence on their efficiency. The performance characteristics of both crystalline and amorphous thin films are markedly affected by the chosen manufacturing methodology, which encompasses processes such as drop casting and sputter coating.

The utilisation of lanthanide elements as luminescent materials in the fabrication of PL thin films offers paths for both down-conversion and up-conversion mechanisms, thus enhancing the performance of PV systems. Consequently, this review seeks to elucidate the significance, progression, and deposition techniques associated with

lanthanide-doped luminescent materials tailored for solar PV applications via sputtering deposition. Various sputtering methods enable the production of high-quality luminescent thin films, with PVD standing out as a prominent and sophisticated thin film deposition technique widely embraced across diverse industries and research domains.[24] Combinatorial sputtering emerges as an advanced technique in thin film deposition, revolutionising material exploration and property characterisation. By concurrently sputtering multiple materials onto a substrate, this method enables the creation of compositional gradients across the deposited film, expediting the investigation of diverse material combinations and their resultant properties in a single deposition process.[25] Radio-frequency (RF) magnetron sputtering and direct-current (DC) magnetron sputtering are commonly employed in the fabrication of luminescent thin films due to their cost-effectiveness and efficiency, particularly in low-temperature environments.[26] Drop casting, widely recognised as a simple and rapid coating technique, holds substantial utility across various fields globally, particularly in the modification of electrode surfaces using nanoparticles. This method entails the application of a liquid-phase chemical process, offering a straightforward and cost-effective approach to thin film fabrication. Its versatility and ease of implementation make it a preferred choice for numerous applications requiring efficient and uniform nanoparticle deposition on surfaces.[27]

This research focuses on investigating the current advancements in solar cell technology, particularly concerning the utilisation and performance of Eu-doped and $\text{CuInS}_2/\text{ZnS}$ luminescent materials in PV applications, along with the fabrication techniques for luminescent thin films. Initially, an overview is provided of various materials and process methods employed in the production of diverse PV devices, each exhibiting distinct performance characteristics. Additionally, the study offers insights into the efficacy of state-of-the-art up-conversion and NIR quantum-cutting thin films designed for c-Si solar cells, highlighting the use of single and co-doped pairs of lanthanide elements. The investigation encompasses a comprehensive examination of lanthanide materials integrated into different host matrices. Furthermore, two distinct manufacturing processes for fabricating luminescent thin films are discussed and compared.

2.2 State-of-the-art solar cells

The release of pollutants caused by fossil fuels reflects the daily human need for energy, which leads to an unsustainable equilibrium between pollution and nature. A source of renewable energy is one of the most important drivers for global development in the twenty-first century. Solar energy is one of the most commonly exploitable renewable energy sources currently utilised. Nonetheless, efficiently capturing and converting solar energy into a usable form of energy for humans is challenging. Even though thin film and emerging solar cells have made significant progress, the c-Si PV technology currently dominates the global PV market with a market share of 95% in 2019. This is due to its combination of high-power conversion efficiencies, stability, use of non-toxic and abundant materials, and well-developed scaled manufacturing methods. So, the second most prevalent element in the earth's crust is the huge supply of silicon used by the semiconductor industry.[28] Due to their high efficiency of 26.7%, long life duration of more than 20 years, and mature manufacturing process, c-Si solar cells have been successfully commercialised among other types of solar cells.[4]

PV devices are produced using several different materials and process methods producing PV devices with different performance characteristics, such as c-Si solar cell, GaAs, CZTS/CdS, perovskite and Dye-sensitized solar cell (DSSC).[1–3,29,30] The key performance attributes include excitation, emission, dopant concentration, transmission, reflection, photoluminescent quantum yield (PLQY) and external quantum efficiency (EQE).

2.2.1 Single junction Silicon: mono-crystalline, multi-crystalline, amorphous

PV solar cells are devices that convert solar energy directly into electricity. There are various PV technologies existing, and the most widely used and mature technology is c-Si in the current commercial solar cells market owing to its advantages of high conversion efficiencies and ample materials supply.[1]

For the manufacturing of c-Si heterojunction solar cells, an as-cut n-type solar grade (99.9999% (6N) to 99.999999% (8N)) c-Si wafer with a (100) orientation, possessing a resistivity ranging from 1 to 5 Ωcm and a thickness of approximately 180 μm , was

utilised. The front transparent conductive oxide (TCO) layer of these solar cells consisted of an 80 nm thick Indium tin oxide (ITO) film. Additionally, a p-type microcrystalline silicon oxide (p- μ c-SiO:H) layer, with a thickness of 30 nm, served as the emitter layer. Both sides of the wafer were coated with a 6 nm thick intrinsic amorphous silicon oxide (i-a-SiO:H) film, employed as the passivation layer.[31]

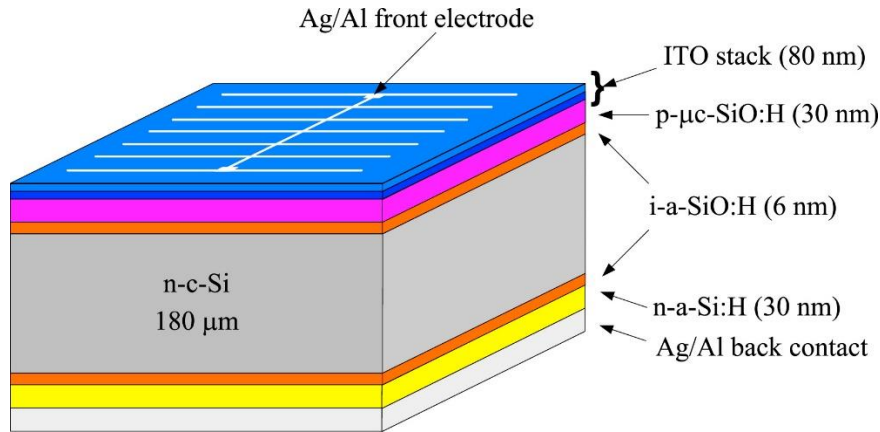


Figure 2-1 Structure of crystalline silicon heterojunction PV cell with the ITO stack layer.
[31]

The fill factor (FF) serves as a crucial parameter in evaluating solar cell performance, representing the ratio of the maximum power output of the cell to the product of its open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}). [32] The proposed configuration not only showcases the advantages typical of single-junction solar cells, such as simplified design and absence of tunnel connections but also exhibits features like a reduced active layer thickness, minimising material requirements and costs. Moreover, the structure's composition lacks harmful components, utilises band gap tailoring, and demonstrates desirable cell characteristics, collectively positioning the suggested device as a promising candidate for single-junction amorphous silicon PV structures.[33] In 2018, Fang et al. introduced a novel approach utilising a crystal silicon heterojunction (HIT) bottom cell to construct a double-junction solar cell characterised by a high V_{oc} , rendering it suitable for applications such as solar-to-hydrogen conversion and chemical battery replacement.[34] The fabrication process involved a specific etching technique to create a double-junction PV device, integrating n-i-p type single-junction hydrogenated amorphous silicon (a-Si:H) and HIT solar cells. The substrate employed for this device was a smooth stainless steel devoid of a back reflector coupled with monocrystalline Czochralski (Cz) silicon (100) wafers. The n-

type layer of the wafer exhibited a diameter of 2 inches and a thickness of $300 \pm 10 \mu\text{m}$, with a resistivity ranging from 1 to $3 \Omega\text{cm}$, as depicted in Figure 2-2. Figure 2-3 (a) illustrates the structure of the a-Si:H/HIT double-junction solar cells. Notably, the a-Si:H solar cell demonstrated a high V_{oc} of 0.919V alongside a low short circuit current density (J_{sc}) of 11.34 mA/cm^2 , attributed to the wide bandgap of the a-Si:H intrinsic layer and the absence of a light-trapping structure. Conversely, the HIT device exhibited a significantly higher J_{sc} of 39.26 mA/cm^2 , V_{oc} of 0.692V, and a fill factor of 60.7%, resulting in a power conversion efficiency of 16.5%. [34]

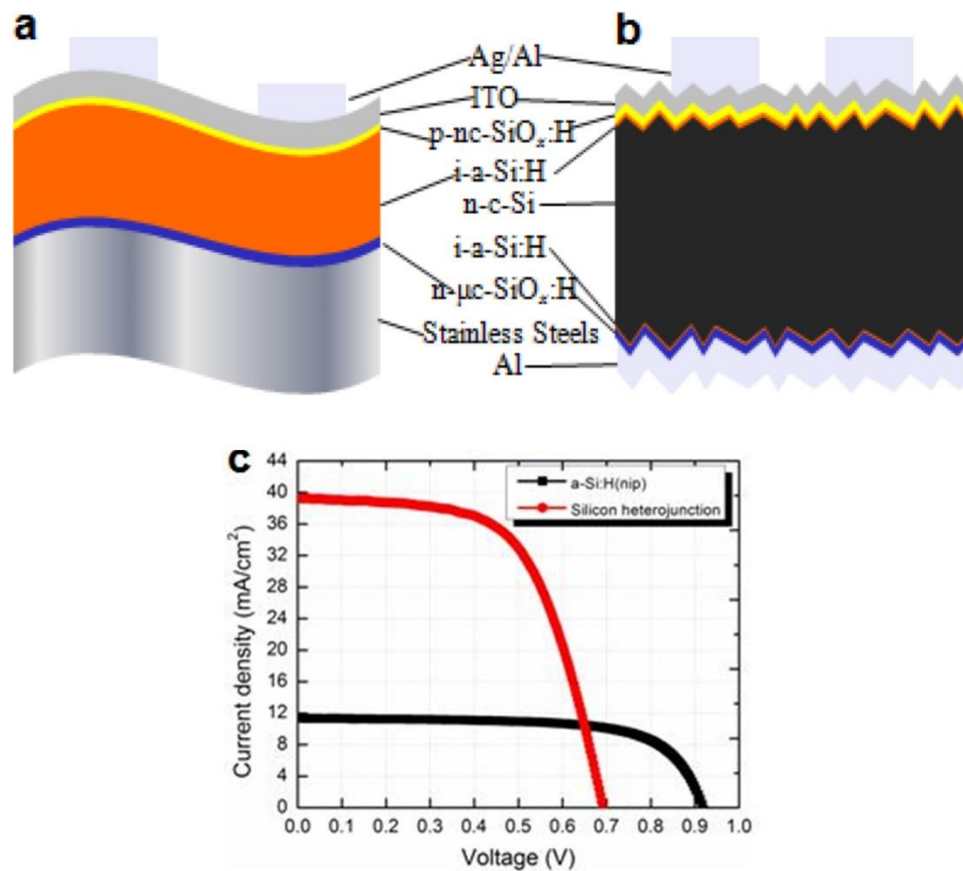


Figure 2-2 (a) Structure of PV cell, (b) n-i-p type single junction PV cell, (c) J-V curves of a PV cell. [34]

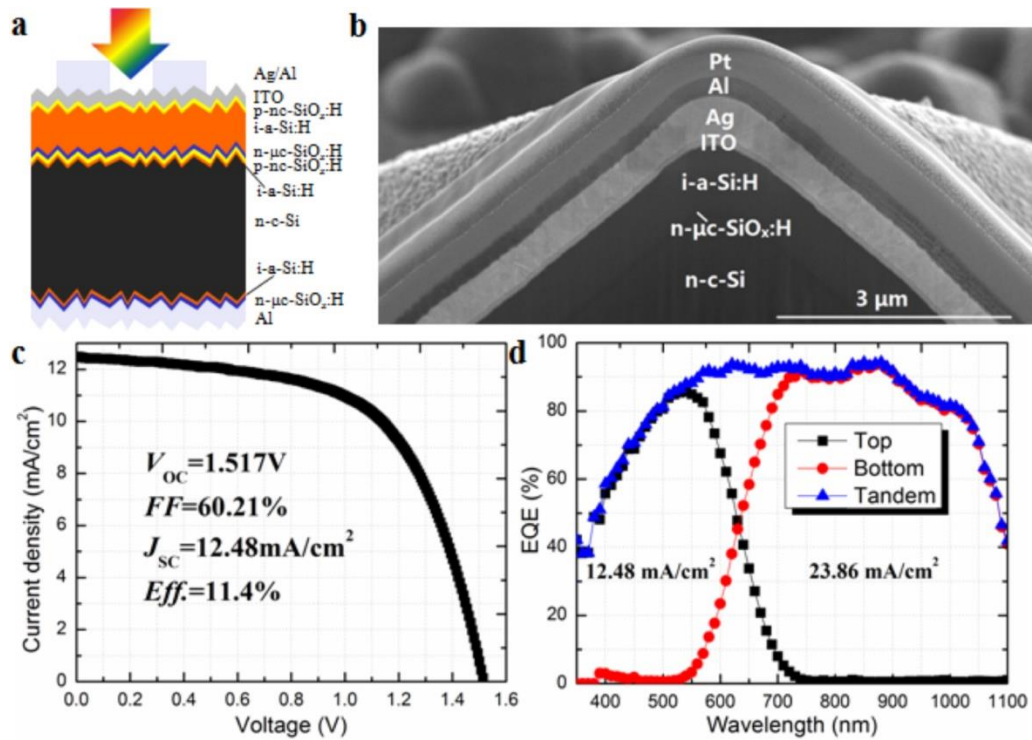


Figure 2-3 (a) Structure of double junction PV cell, (b) image of cross-sectional of double-junction PV cell taken by SEM, (c) J-V curve of this cell, (d) EQE of this cell.[34]

2.2.2 Tandem solar cells

The Shockley-Queisser limit imposes constraints on the PCE of single-junction solar cells, motivating the exploration of alternative strategies, such as multi-junction cells to achieve higher efficiencies. To date, single-junction c-Si, GaAs, CZTS/CdS, Perovskite and Dye sensitised solar cells have achieved various efficiencies at 26.1%, 25.1%, 48.05%, 29.8% and 12.25%, respectively.[30,35]

The tunable bandgaps inherent in III-V compound semiconductors offer a pathway to realising exceptionally high efficiencies in multi-junction solar cells. Nevertheless, the widespread adoption of organic-inorganic perovskite solar cells has been impeded by their comparatively high production costs when contrasted with c-Si solar cells. Despite this challenge, perovskite solar cells have garnered increasing attention in recent years due to their notable PCE of 25.5%. Fang et al. (2021) have proposed two common configurations for tandem solar cells: the four-terminal (4-T) and two-terminal (2-T, or monolithic) configurations, as illustrated in Figure 2-4.[36]

The integration of a semi-transparent wide-bandgap front (or top) cell atop a narrow-bandgap rear (or bottom) cell results in the formation of a four-terminal (4-T) tandem

cell configuration. In this arrangement, the front and back cells remain electrically segregated, allowing for independent optimisation of each component. Moreover, power outputs can be extracted autonomously from each sub-cell. Alternatively, a 2-T configuration involves directly growing either the front or rear sub-cell onto the opposing sub-cell, necessitating stringent fabrication compatibility and current matching between the interconnected sub-cells. The 2-T configuration benefits from fewer transparent electrodes compared to the 4-T configuration, reducing both reflection and parasitic absorption. Tandem cells employing perovskite/Si combinations have exhibited the potential to surpass 30% in PCE. Notably, the latest advancement in this field, a perovskite/Si tandem solar cell with a PCE of 29.1%, has been reported by Helmholtz-Zentrum Berlin (HZB), surpassing the efficiency of both single-junction perovskite and Si solar cells.[36]

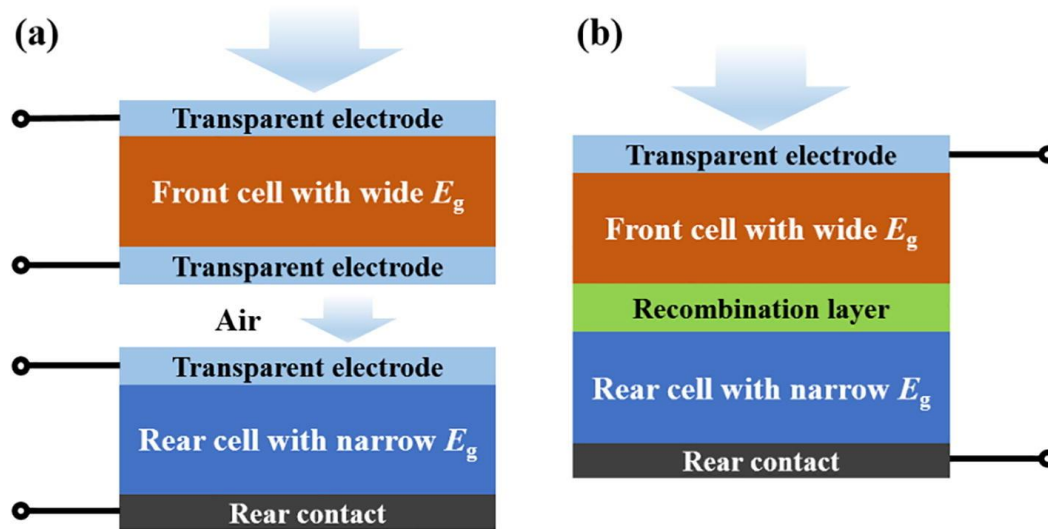


Figure 2-4 (a) is 4-T tandem PV cell, (b) is 2-T tandem PV cell.[36]

In 2018, Shen et al. devised an ultra-high efficiency and cost-effective all-thin-film perovskite/CIGS tandem solar cell.[37] This tandem configuration achieved a remarkable efficiency of 23.9%, wherein a semi-transparent perovskite solar cell with a bandgap of 1.62 eV, boasting a maximum efficiency of 18.1%, was combined with a 16.5% efficient CIGS cell through mechanical stacking. Furthermore, the authors proposed an alternative tandem configuration featuring a semi-transparent perovskite solar cell with a higher bandgap of 1.75 eV, achieving a top efficiency of 16% and a tandem efficiency of 23.4%. The implementation of a high-bandgap perovskite top cell in this configuration led to optical modelling forecasts predicting a perovskite/CIGS

tandem efficiency exceeding 30%. Additionally, to mitigate reflectance across the entire wavelength range from 350 nm to 1200 nm, a custom-textured foil was utilised on the front side of the perovskite solar cell.[37]

Illustrated in Figure 2-5, is a mechanically stacked two-terminal perovskite/silicon tandem solar cell, wherein the sub-cells are independently fabricated, optimised, and subsequently interconnected by establishing contact between the front contact and back electrode of the silicon bottom cell and the mesoscopic perovskite top cell. The leading tandem device in this configuration achieves an efficiency of 26.3% (stabilised at 25.9%) across an active area of 1.43 cm². This impressive efficiency is attributed to the reduction of optical losses, achieved through the engineering of the hole-selective layer/rear contact structure and the implementation of a graphene-doped mesoporous electron-selective layer for the perovskite top cell.[3]

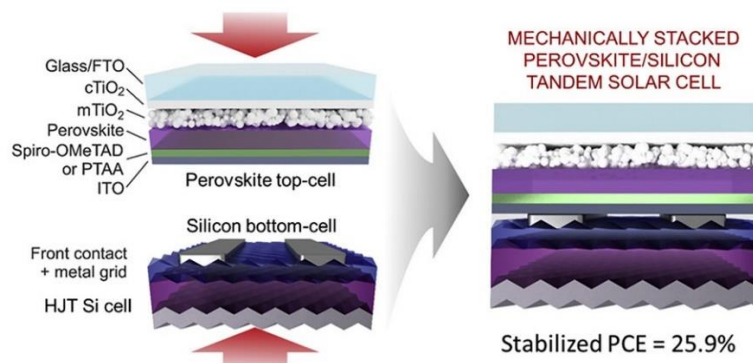


Figure 2-5 The structure of perovskite solar and silicon solar cells.[3]

2.3 Characteristics of solar cells

Various types of solar cells have been extensively studied and utilised globally. However, each solar cell is subject to specific fundamental losses, encompassing five distinct mechanisms. The collective impact of these intrinsic loss mechanisms has been demonstrated to impose fundamental limits on efficiency. Accounting for all incident solar radiation provides a comprehensive understanding of solar energy conversion in an ideal device.[38] The EQE, which quantifies the number of electrons

generated per incident photon on the device, serves as a pivotal metric for analysing the efficacy of solar cells.

2.3.1 Fundamental losses of PV

In 2018, Da et al. conducted a comprehensive analysis of energy losses in planar perovskite solar cells, focusing on the underlying physical mechanisms.[14] The study entails a meticulous comparison between simulation results and experimental data across diverse operational conditions. By scrutinising and contrasting the fundamental losses, the disparity between the maximum efficiency limit and actual PCE is delineated. These fundamental losses encompass five primary mechanisms, namely thermalisation losses, below bandgap losses, optical losses, recombination losses, and spatial relaxation losses, as illustrated in Figure 2-6 and Figure 2-7.[14]

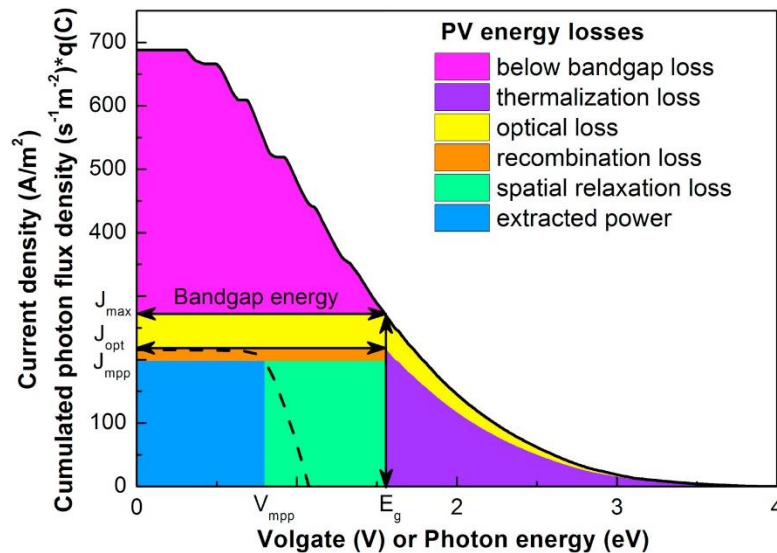


Figure 2-6 Fundamental losses of the PV devices and each loss is shown in a different colour.[14]

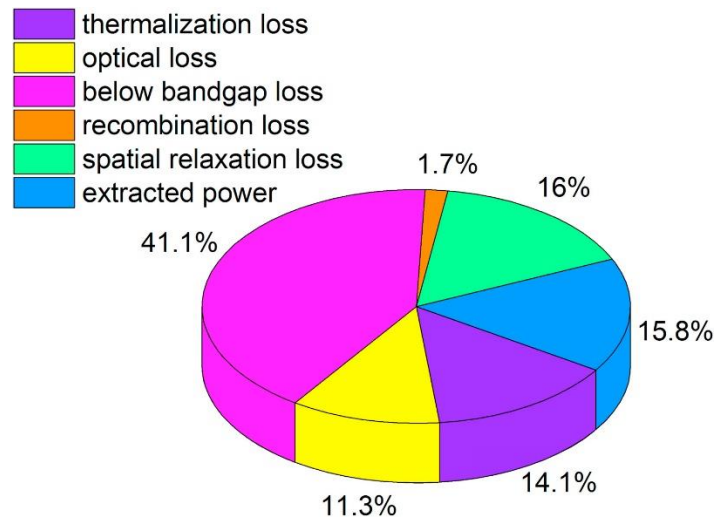


Figure 2-7 Fundamental losses of the PV devices are quantified and separated as below bandgap (41.1%), thermalisation (14.1%), optical(11.3%), recombination(1.7%), spatial relaxation (16%) losses and extracted power (15.8%).[14]

2.3.1.1 Below bandgap (sub-bandgap) loss

When the energy of photons falls significantly below the bandgap of the PV device, termed as $E_{ph} \ll E_g$, these photons remain unabsorbed and fail to generate electron-hole pairs, resulting in what is known as below bandgap loss. In essence, these photons contribute negligibly to photoelectric conversion. Theoretical studies indicate that sub-bandgap loss constitutes approximately 41.1% of the energy within the total solar spectrum, emerging as the predominant energy loss mechanism for single-junction perovskite solar cells.[39] Consequently, strategies aimed at mitigating this loss, such as increasing the bandgap of incident photons, employing dopants, or adjusting the bandgap of PV devices to alleviate bandgap mismatch, hold significant promise for enhancing conversion efficiencies.

2.3.1.2 Thermalisation loss

Thermalisation loss manifests when the energy carried by photons exceeds the bandgap of the solar cell. In this scenario, photons possessing energy levels surpassing the bandgap of the PV material have the capability to generate charge carriers characterised by elevated kinetic energy, adhering to the concept of a single photon initiating an electron-hole pair, denoted as $E_{ph} \gg E_g$. However, these photoexcited carriers undergo swift relaxation from their initial excited states to the

band edges to attain a state of thermal equilibrium, thereby dissipating their excess energy through interactions with the crystal lattice.[14] Furthermore, the surplus energy can be discharged through interactions between the excited carriers and lattice photons. Lowering the photon energy to align with the bandgap energy may mitigate thermalisation loss, for instance, through photon red-shifting. Several research endeavours have demonstrated that tandem PV devices exhibit diminished thermalisation losses compared to single-junction PV devices.[13]

2.3.1.3 Optical loss

Photons possessing energy levels exceeding the bandgap of PV materials hold potential utility within PV cells. However, their absorption is hindered by optical losses, comprising reflection, transmission, and parasitic absorption, which collectively diminish photon absorption within the device. This phenomenon, known as optical loss, undermines the efficiency of the photoelectric conversion process. Consequently, the generation of electron-hole pairs within the solar cell is contingent upon the photons successfully absorbed.[14] Parida et al. in 2020 presented a method aimed at mitigating optical losses.[40] Their study demonstrated that Al-doped NiOx thin films deposited on indium tin oxide (ITO) substrates exhibited an average optical transmittance exceeding 81% within the 400 to 800 nm range. The notable transparency of these NiOx films suggests a potential reduction in optical losses, thereby potentially enhancing carrier production within perovskite solar cells. Strategies such as applying antireflective coatings or nanostructured films can further curtail losses attributable to reflection. Moreover, the reduction in thickness of transparent conducting oxide (TCO) substrates, as well as hole transport layer (HTL) or electron transport layer (ETL) layers, holds promise for minimising parasitic absorption losses.[40]

2.3.1.4 Recombination loss

Recombination loss represents a significant form of electrical loss in PV devices, arising from the degradation of internal carriers during their transit through the device. As photogenerated carriers undergo separation and collection in the transport process, a portion of them may undergo recombination, leading to recombination loss. This loss mechanism encompasses several common processes, including radiative recombination, Auger recombination, Shockley-Read-Hall (SRH) recombination, and

surface recombination.[14] Xue et al. (2020) provided insights into the recombination loss mechanisms within perovskite solar cells, particularly elucidating variations under V_{oc} and I_{sc} conditions, as illustrated in Figure 2-8.[41] Radiative recombination emerges as the predominant contributor, constituting approximately 83% of the total recombination loss within the perovskite layer. SRH recombination within the perovskite layer is reported at 8%, indicating its significance in influencing device performance. Moreover, recombination occurring at the interface between the perovskite layer and the hole-transporting layer accounts for 7% of the total loss. Conversely, recombination at the interface between the perovskite layer and the hole-transporting layer is comparatively lower, representing only 2% of the overall recombination loss.[41]

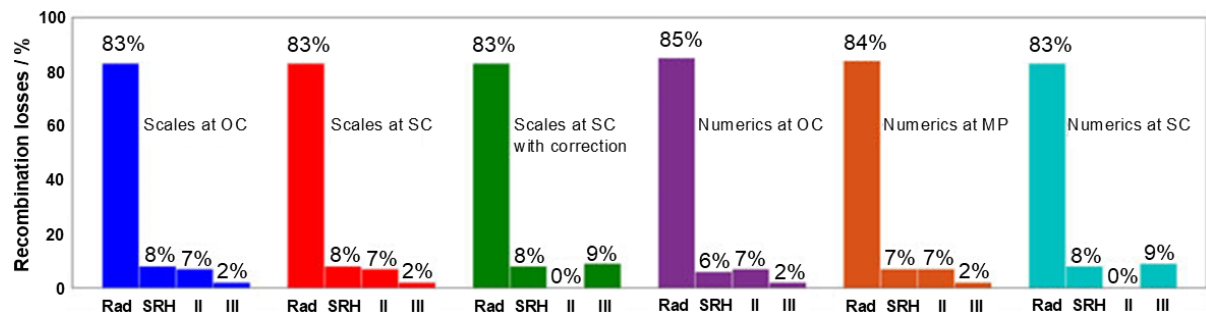


Figure 2-8 Different recombination losses are quantification, including simulations at the conditions of an open-circuit voltage, a maximum power point, and a short-circuit.[41]

2.3.1.5 Spatial Relaxation loss

Spatial relaxation loss and recombination loss represent significant components of electrical losses within PV devices, both intricately linked to the fate of internal carriers during the electrical transfer process. Therefore, spatial relaxation loss also falls under the purview of electrical losses.[42] Spatial relaxation loss occurs when the potential energy of photogenerated carriers is insufficient to traverse from the band-edges to the contacts, thus impeding their effective collection. The bias voltage applied to solar cells emerges as a critical determinant for these losses. Variation in the bias voltage can significantly influence the ratio of energy loss attributed to these two mechanisms.[14]

2.3.2 Spectral Response and External Quantum Efficiency (EQE)

The EQE of a device quantifies the number of electrons produced per incident photon, elucidating its photoelectric conversion efficiency. It is computed as the ratio between the number of charge carriers generated and the number of incident photons. Prior to determining the EQE, the spectral response (SR) of the device is measured, denoting the relationship between the current output and incident power. Karmalawi et al. (2020) provided an equation delineating the interconnection between EQE and SR, facilitating the comprehensive analysis of the device's performance characteristics and its response to incident light stimuli.[43]

$$EQE = \eta_{ext}(\lambda) = \frac{hc}{nq\lambda} \frac{s(\lambda)}{a} \quad (2-1)$$

Within the equation, key parameters are defined: h represents Planck's constant, c denotes the speed of light, q signifies the electronic charge, λ represents the wavelength in nanometres, $s(\lambda)$ indicates the spectral sensitivity in amperes per watt, n signifies the refractive index, and a represents the device's area. These parameters collectively elucidate the relationship between spectral sensitivity and key physical constants, offering insights into the device's behaviour under varying spectral conditions.[43]

At wavelengths below 400 nm, bare c-Si solar cells typically demonstrate a modest optical response, resulting in a low EQE of 11%. However, the inclusion of a quantum dot luminescent down-shifting (QD-LDS) layer enhances the EQE to 23% at these wavelengths. This improvement can be attributed to the absorption of photons by QDs, followed by their reemission at longer wavelengths. Notably, the incorporation of a plasmonic layer, denoted as QD-pLDS, yields a more substantial enhancement, elevating the EQE to 52%. This enhancement is attributed to the presence of silver (Ag) nanoparticles within the composite layer, which augment QD absorption, emission, and PLQY. As reported by Ahmed et al. in 2016, the EQE measured at absorption wavelengths can be raised to levels approaching those measured at emission wavelengths, resulting in a value of 12.6%, after accounting for losses associated with non-ideal PLQY, self-absorption, and absorption in host materials.[44] McIntosh et al. in 2009 noted that edge losses could be disregarded if the incident beam is uniformly emitted from all directions, particularly when the beam is centred on

the cell.[45] Figure 2-9 illustrates that the observed increase in EQE is primarily attributed to the QD-pLDS composite layer. Notably, in Figure 2-9, EQE ranges from 50% to 90% at wavelengths where QDs absorb (300-500 nm), only slightly below the EQE at emission wavelengths of 450-550 nm.[44]

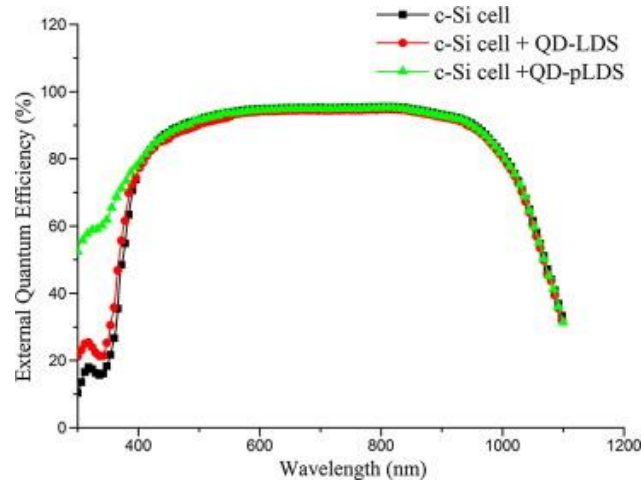


Figure 2-9 The EQE of pure c-Si cell only, QD-LDS layer added on top of the c-Si cell and QD-pLDS layer added on top of the c-Si cell.[44]

The EQE serves as a distinctive metric for differentiating between various types of solar cells, given its pivotal role in spectral responsivity determination, which is integral to solar cell characterisation. The EQE is computed by integrating the spectral responsivity over the entire solar spectrum, with the incident solar radiation standardised at $P_{\text{solar}}=1000\text{W m}^{-2}$. The numerator of the EQE equation represents the J_{sc} utilising the upper limit of EQE set at 100%. By contrast, the denominator encapsulates the incident solar radiation. J_{sc} values derived from EQE spectra, computed by weighing with the AM 1.5G spectrum, align closely with those obtained from J-V (current-voltage) curves. This congruence underscores the reliability and utility of EQE measurements in providing accurate insights into solar cell performance characteristics. Green et al. recorded and summarised the EQE of different types of solar cells, which are crystalline Si heterojunction, CZTSSe, perovskite, organic and Cd-free buffer CIGSSe InGaP/GaAs/InGaAs and CdTe solar cells.[35]

The investigation of EQE across various solar cell types reveals distinctive spectral response patterns, with each exhibiting high EQE within specific wavelength ranges. Si solar cells, for instance, demonstrate broad coverage across the solar irradiation spectrum, spanning from 300 to 1200 nm in EQE spectra, thus representing a wide

wavelength range within single-junction solar cells. In contrast, multi-junction solar cells leverage the combination of two or more distinct solar cell materials to augment EQE. Furthermore, the EQE outcomes are closely linked to the PLQY, which denotes the probability of photon emission subsequent to photon absorption. This correlation underscores the intricate relationship between EQE measurements and PL properties, elucidating crucial insights into solar cell performance and efficiency enhancement strategies.[46]

2.3.2.1 Spectral response

The efficiency of a PV device is fundamentally constrained by its spectral response when compared to the entirety of the solar spectrum. PV technologies are discerned by the materials constituting the PV cells, alongside their associated parameters such as I_{sc} , V_{oc} , and FF. The efficacy of these devices is pivotal in determining the efficacy of solar cells. Essential parameters including spectral response, photocurrents, I-V curve, PCE, EQE, and FF, assume significance when evaluating and contrasting PV performance characteristics.[47] Various factors contribute to the quality of solar cells, including enhanced EQE and FF performance, which can bolster conversion efficiency. However, the paramount determinant of energy conversion remains the spectral irradiance of sunlight. Spectral irradiance exhibits significant variability across different air mass (AM) and temporal conditions. Figure 2-11 illustrates the spectrum of direct normal irradiance for several ideal scenarios: (1) the default AM0 spectrum; (2) a sea-level site depicting both AM1 and AM5.6, utilising a rural aerosol model with $\tau_{a500} = 0.084$; and (3) a sea-level location under a desert aerosol model with $\tau_{a500} = 0.54$, for both AM1 and AM5.6. A notable red shift in the direct spectrum is observed with an increase in air mass from 1 to 5.6. The direct spectrum assumes a notably narrow profile owing to the combination of a high air mass (AM5.6) and significant aerosol optical depth (AOD) ($\tau_{a500} = 0.54$). Notably, AM0 pertains to the space region (Direct Normal Irradiation (DNI) $\approx 1.366 \text{ W/m}^2$), while AM1.5G / AM1.5D (DNI $\approx 986.8 \text{ W/m}^2$) are representative of the water surface. Additional parameters correspond to distinct scenarios, as delineated in Figure 2-10 and Figure 2-11. The peak energy of sunlight is typically around 500nm.[48]

The SMARTS 2.9.5 model is utilised to simulate hourly aggregated spectrally resolved data under Kanpur conditions, spanning from 8:00 AM to 4:00 PM, on selected days

throughout the year, ranging from September 2018 to August 2019. Over the course of the year, Chintapalli et al. operate the panel for 8 hours daily. As depicted in Figure 2-12, the peak global tilted irradiance occurs at 12:00 PM, as simulated by SMARTS 2.9.5 on May 15, 2019, under Kanpur conditions.[49]

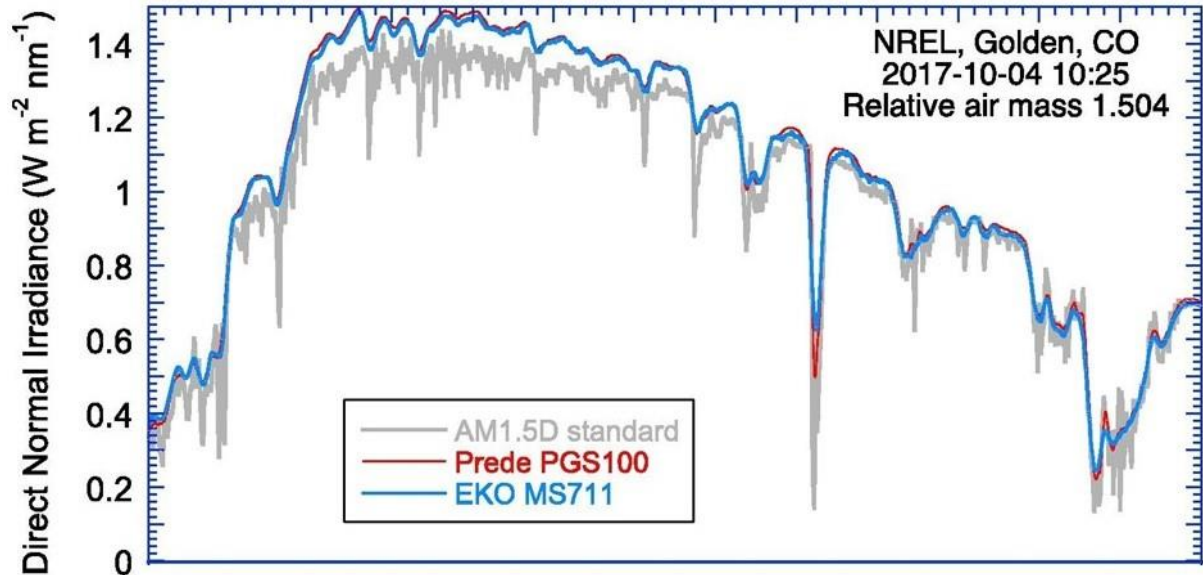


Figure 2-10 The results of the AM1.5D standard reference spectrum at SRRL-NREL on 2017-10-04.[48]

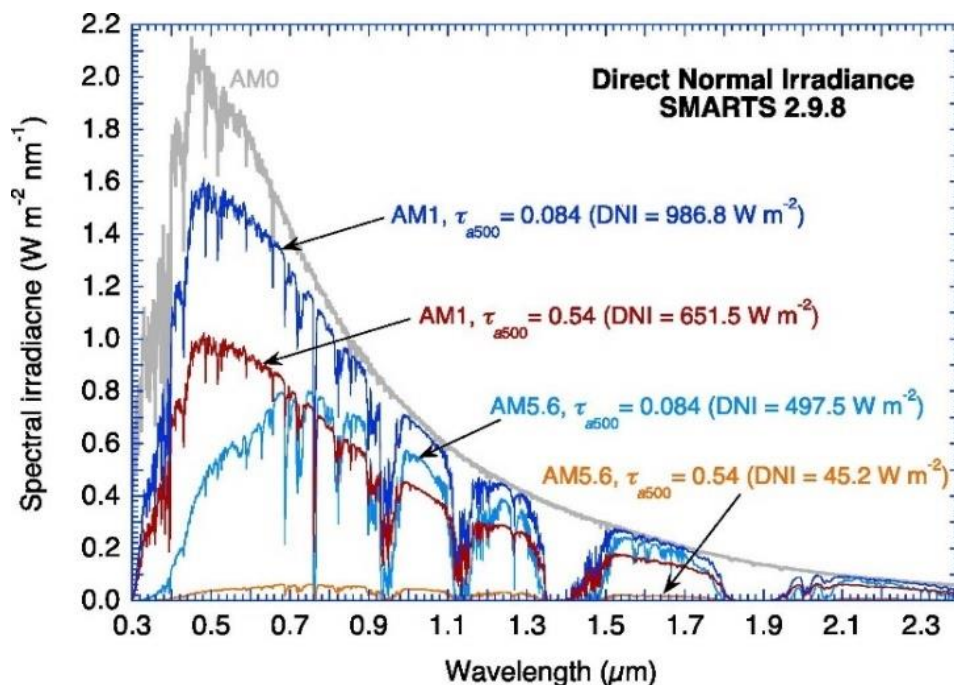


Figure 2-11 The forecast of the direct normal irradiance spectral distribution was detected SMARTS v2.9.8 in ET9 AM0 spectrum, and analysis of the influence of air mass and aerosol model.[48]

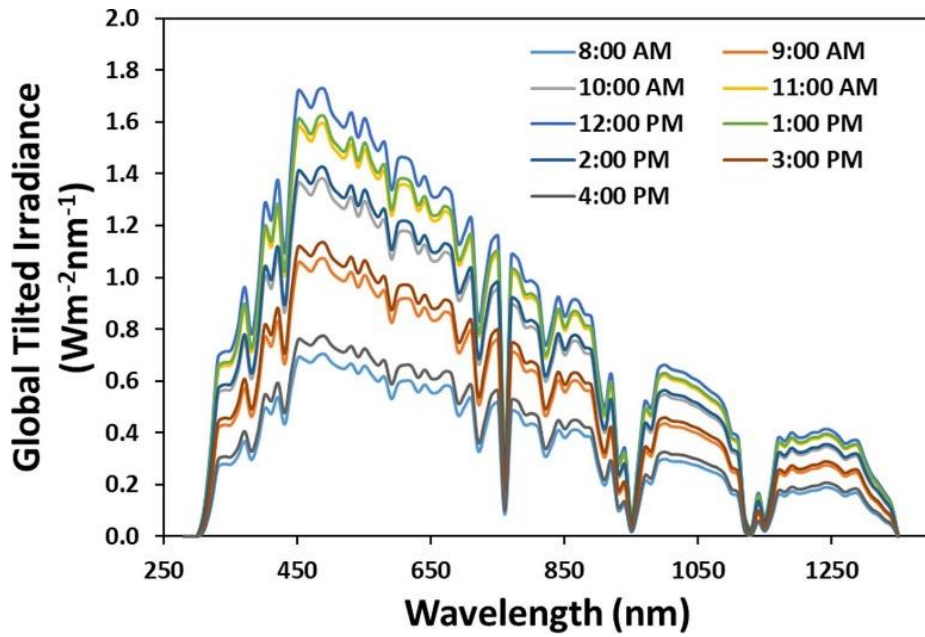


Figure 2-12 Spectral resolved irradiance in each hour on 2019-05-15 under Kanpur conditions.[49]

An influential factor contributing significantly to the efficiency of c-Si PV cells is the bandgap energy of the material. The bandgap of c-Si, measured at 1.12 eV, is remarkably close to ideal for effectively harnessing solar energy across the spectrum. This characteristic renders c-Si a highly proficient solar converter.[50] The band-gap energy of c-Si encompasses a spectral response wavelength ranging from 300nm to 1100nm, effectively spanning the ultraviolet, visible, and near-infrared regions of the solar spectrum. However, solar radiation exceeding 1200nm lies beyond the absorption capability of c-Si, as it surpasses the 'cut-off' wavelength of materials.[51] In Figure 2-13 illustrates the AM1.5 solar radiation spectrum alongside the spectral response of c-Si. While the peak energy of sunlight occurs around 500nm, the optimal spectral response for c-Si extends to approximately 1000nm, aligning with the material's bandgap of 1.12 eV, thereby representing the ideal absorption range for c-Si cells. Additionally, the UV region, spanning from 300nm to 450nm, exhibits a comparatively low spectral response in c-Si, posing challenges for efficient absorption and conversion by PV cells.[51] The primary cause of the low conversion efficiencies in c-Si solar cells persists due to the mismatch between the AM1.5 solar spectrum and the spectral response of c-Si, a phenomenon highlighted in Figure 2-13.[51] In addressing this challenge, a multitude of approaches have been developed. These encompass the creation of over ten distinct solar cells, including c-Si solar cells,

perovskite and DSSC, each designed to convert solar energy into electrical power efficiently.[4,52,53]

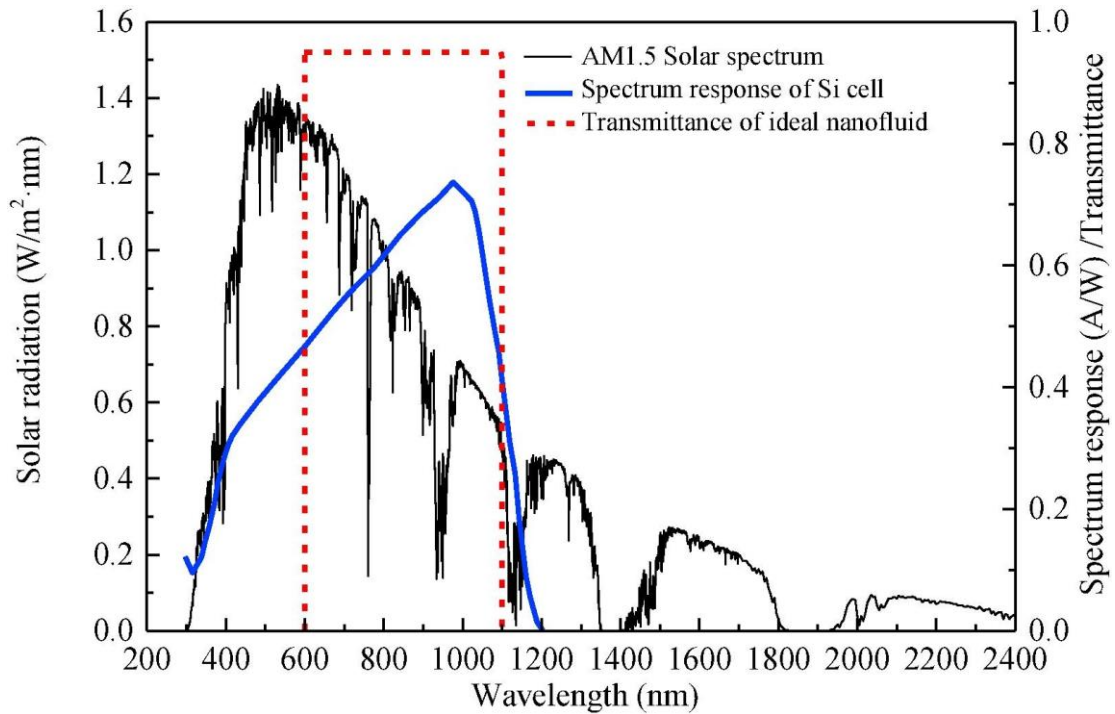


Figure 2-13 The mismatching between AM1.5 solar spectrum in black and spectrum response of Si solar cell in blue. The red-dotted line area is the transmittance of the ideal nanofluid.[51]

2.4 Beyond Shockley-Queisser limit

The maximum efficiency of each individual junction in PV solar cells is inherently constrained by its bandgap energy.[54] In essence, when a semiconductor within a PV device absorbs photons from solar radiation, it becomes excited. Electrons from the valence band transition to the conduction band across the bandgap, leaving behind positively charged holes. These holes, situated in the valence band, are drawn towards electrons in the conduction band, forming bound excitonic states.[55] Throughout the subsequent decay process, electrons transition from the conduction band back to the valence band, wherein electron-hole pairs recombine, emitting photons with energies equivalent to the semiconductor's bandgap.[56] The efficiency of this PL process is determined by the balance between photon emissions and absorptions, known as the PLQY.[57,58], Illustrated in Figure 2-14 is the journey of photoelectric conversion from absorption to emission. Shockley and Queisser have

demonstrated that under one sun (AM1.5G, 1000 W/m²), a single material with an optimal bandgap of approximately 1.3 eV can achieve a PCE nearing 31%.^[59]

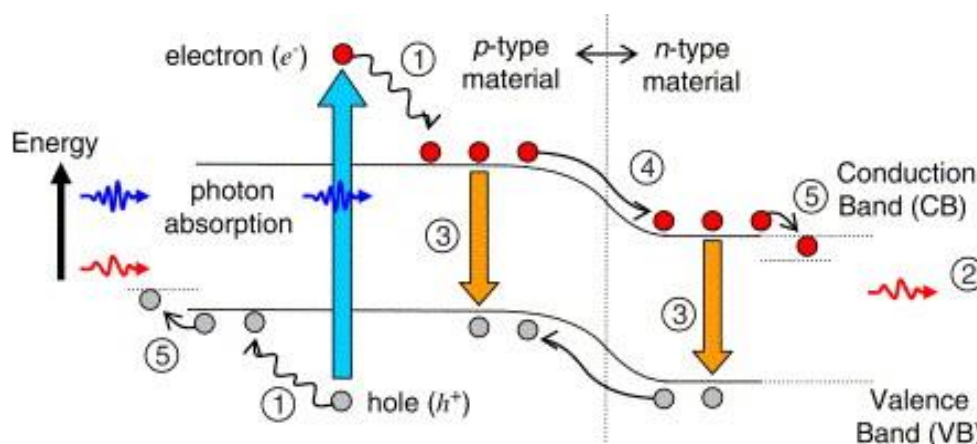


Figure 2-14 The photoelectric conversion process of semiconductor solar cell.^[59]

2.4.1 Singlet fission

Singlet fission represents a down-conversion mechanism with the potential to enhance the efficiency of silicon solar cells by leveraging the solar spectrum more effectively. This process involves the absorption of high-energy photons by singlet-fission materials, leading to the formation of a spin-singlet exciton. Subsequently, this singlet exciton undergoes a division into two spin-triplet excitons, each possessing roughly half the energy of the original singlet exciton. Notably, certain organic compounds such as poly-acenes and perylene diimides (PDIs) exhibit this singlet fission phenomenon. In the case of pentacene, singlet fission can be remarkably efficient, with efficiencies approaching 200%, indicating that the quantum yields reach 200%.^[60] The transport of triplet excitons into a quantum dot initiates Förster resonance energy transfer (FRET), followed by FRET into silicon. Achieving the most efficient implementation based on a record-efficiency silicon solar cell involves the transfer of charge from triplet excitons into silicon, with a maximum theoretically estimated efficiency of 34.6%. This efficiency peak is reached with a low singlet exciton energy of 1.85 eV and a realistic entropic gain of 100 meV. Comparing singlet fission cells to perovskite-silicon tandem solar cells reveals that singlet fission yields the greatest efficiency improvements for highly efficient silicon-based cells, while tandem solar cells offer greater efficiency enhancement for less efficient silicon-based cells.^[61]

Singlet exciton fission represents an organic semiconductor phenomenon where a single photogenerated spin-singlet exciton converts into two spin-triplet excitons on

adjacent chromophores. Figure 2-15 illustrates singlet exciton fission in pentacene. Within pentacene, the green arrow signifies the photoexcitation of ground-state molecules (S_0), resulting in singlet excitons (S_1), which subsequently undergo fission into two triplet excitons (T_1) within a remarkably short duration of 80 femtoseconds.[62] Singlet exciton fission, paired with a low bandgap inorganic semiconductor, offers a route to surpassing the Shockley-Queisser limit in single-junction PV. Figure 2-15 b demonstrates the transfer of triplets from a thin organic singlet exciton fission layer to sensitise inorganic solar cells to singlet fission. It enables the generation of two triplet excitons for every high-energy photon absorbed, addressing thermalisation losses. These triplets can efficiently transfer their energy to the inorganic semiconductor for charge separation and extraction, augmenting overall efficiency.[62]

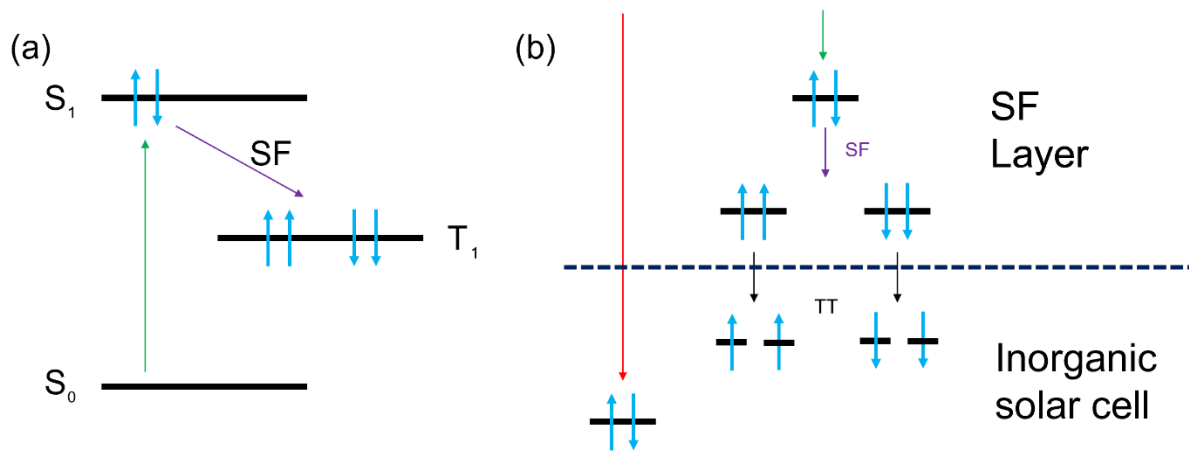


Figure 2-15 Singlet exciton fission and triplet transfer.

Jiang et al. (2021) applied the model to two established multiple threshold devices: a perovskite on silicon tandem and a tetracene-based singlet fission device. The perovskite/Si tandem cell operates at 1.4 V, with 0.8 V for the perovskite and 0.6 V for the Si junctions. Singlet fission's energy threshold is at 530 nm, with a mildly endothermic nature ($\Delta E=0.2$ eV).[63]

One challenge in creating commercially viable devices is the degradation of singlet-fission layers. Unlike multi-junction devices, singlet fission devices will not face current matching issues or top cell degradation. Both perovskite-based tandems and singlet fission cells reduce heat load and extend the primary silicon module's lifespan at low degradation rates. Even with high degradation, tetracene-based singlet fission cells outperform conventional cells because their degradation product doesn't harm the main silicon cell's performance.[63]

Singlet fission in polyacenes like tetracene (Tc) offers a route to enhance solar cell efficiency beyond the Shockley-Queisser limit. Tabernig et al. (2018) explored the use of lead sulphide (PbS) QDs as an interlayer to enable FRET from Tc to Si, facilitating efficient down-conversion of high-energy photons.[64] FRET is distance-dependent and involves molecules acting as point dipoles. Förster's equation for FRET rate considers factors like emission and absorption spectra, donor lifetime, and donor-acceptor distance. Even small changes around R0 yield efficiency gains up to 75%, reaching nearly 100% for slightly larger bandgaps. Despite a low quantum yield (QY) of 20%, substantial FRET efficiency (>65%) can be achieved at practical distances of 1nm. To optimise FRET for enhancing silicon solar cells with singlet fission, precise control over QD size, bandgap, and emission yields is crucial.[64]

2.4.2 UP-Conversion, Down-conversion and Down-shifting

In downshifting, high-energy photon excitation leads to nonradiative relaxation followed by radiative relaxation, emitting a lower-energy photon. In contrast, quantum-cutting involves a two-step radiative relaxation process, emitting two or more lower-energy photons after high-energy photon excitation. Up-conversion converts multiple low-energy photons into a single higher-energy photon. While both processes tap into the high-energy solar spectrum, they differ in quantum efficiencies. Downshifting has a theoretical efficiency below 100%, while quantum cutting exceeds 100%. These materials are typically applied to the front surface of mono-facial solar cells to absorb photons. For sub-bandgap sunlight collection, up-conversion materials are positioned between a bifacial solar cell and a light-reflection layer.[7]

The efficiency of c-Si solar cells has seen enhancements through the introduction of lanthanide-doped porous silicon layers. These material configurations demonstrate both down-conversion and up-conversion mechanisms, leveraging the unique properties of lanthanides to improve performance.[5] The FULLSPECTRUM project, funded by the European Commission under the Sixth Framework Programme, has undertaken research on photon conversion processes for PV applications. This investigation has uncovered three primary mechanisms involved in the photon conversion process: down-shifting, down-conversion, and up-conversion. These mechanisms are visually represented in Figure 2-16.[65]

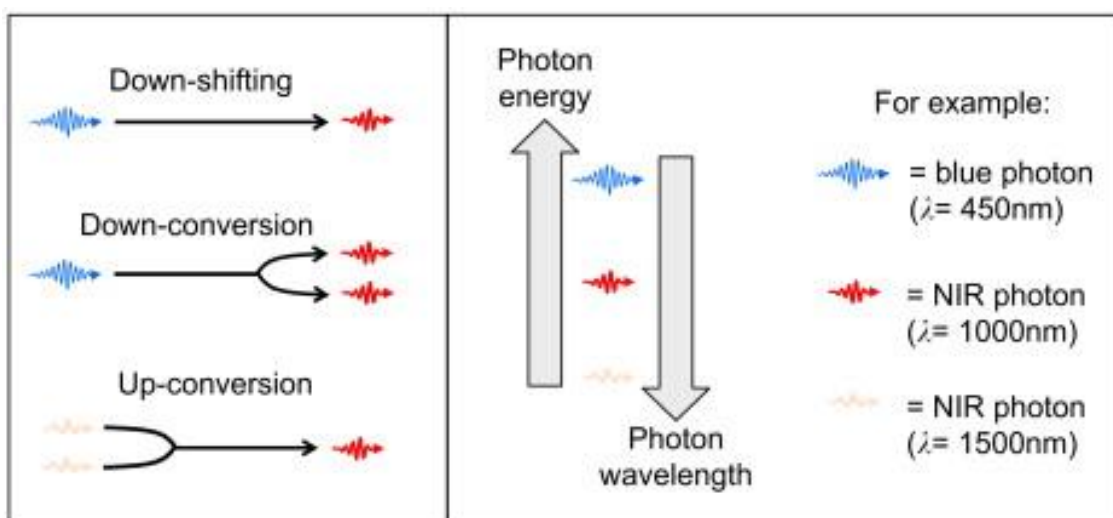


Figure 2-16 Photoluminescent conversion processes, which include down-shifting, down-conversion and up-conversion.[65]

2.4.2.1 Up-conversion

An up-conversion layer facilitates the generation of a high-energy photon from one or a few low-energy photons. Bifacial solar PV technology, a well-established approach, leverages light absorption to enhance efficiency. In bifacial solar cells, photons from both incident radiation and albedo, reaching both the front and back sides of a solar module, are simultaneously harvested.[66] In conventional PV devices, the up-conversion layer is typically positioned at the bottom to capture sub-bandgap photons, thereby augmenting the PCE of the device. Without this layer, sub-bandgap photons may directly pass through the PV device. In scenarios where sunlight is not concentrated onto the solar cell, the utilisation of an up-conversion layer can potentially elevate the PCE to approximately 47.6%.[5]

Lanthanide materials are commonly employed in the construction of up-conversion layers. Possessing unique luminescent properties and non-toxic characteristics, lanthanide elements find extensive utility across a spectrum of current commercial applications. Their suitability for single-wavelength near-infrared up-conversion in Si-PV applications is underscored by their relatively uniform distribution of energy levels.[69] On the Yb-Er co-doped bilayer WSe₂ excited by a 980 nm laser, an intriguing up-converted luminescence has been achieved. For Er³⁺-doped layers, a $^4S_{3/2} \rightarrow ^4I_{15/2}$ energy level transition has a 550 nm up-conversion luminescence peak.[67] The anti-Stokes effect demonstrates that the up-conversion layer can

produce a high-energy photon from two or more incident low-energy photons, essentially absorbing longer wavelength photons and emitting shorter wavelength photons. This phenomenon finds application in various devices such as biological imaging, biological nanothermometers, solar energy harvesting, and infrared sensing.[65]

Various applications, including short-wavelength lasers, sensors, colour displays, and infrared viewers, harness up-conversion from infrared to visible light. An intriguing example involves a lanthanide element, Yb/Er co-doped bilayer WSe₂, capable of generating up-conversion luminescence. Upon excitation with a 980 nm laser, the Yb-Er co-doped bilayer WSe₂ exhibits visible light emission measured between 550 and 610 nm, and infrared emission between 755 and 817 nm. However, the pure bilayer WSe₂, when excited by a 980 nm laser, does not achieve the up-conversion luminescence peak.[68]

Yb³⁺/Ho³⁺/Mn⁴⁺ phosphors are synthesised by a high-temperature solid-state reaction of SrLaAlO₄ (SLA). A 980 nm wavelength laser radiates an SLA, producing an up-conversion luminescence between 600-800 nm. This emission is from the Mn⁴⁺: ${}^2E_g \rightarrow {}^4A_{2g}$ and Ho³⁺: ${}^5F_5 \rightarrow {}^5I_8$, ${}^5S_2/{}^5F_4 \rightarrow {}^5I_7$. Nowadays, lanthanide ion-doped materials are utilised in many up-conversion luminescence manufacturing. Ho³⁺, Er³⁺ and Tm³⁺ are special to fabricate the narrow bandgap up-conversion luminescent device.

Figure 2-17(a) shows that an increasing concentration of Ho³⁺ will increase the up-conversion luminescence intensity of Mn⁴⁺, reaching a peak intensity at a Ho³⁺ concentration=0.01. The luminescence intensity diminishes as the concentration of Ho³⁺ increases due to concentration quenching. In Figure 2-17(b) various up-conversion luminescence intensities of Mn⁴⁺: ${}^2E_g \rightarrow {}^4A_{2g}$ will be affected by different concentrations of Yb³⁺ in SLA.[69]

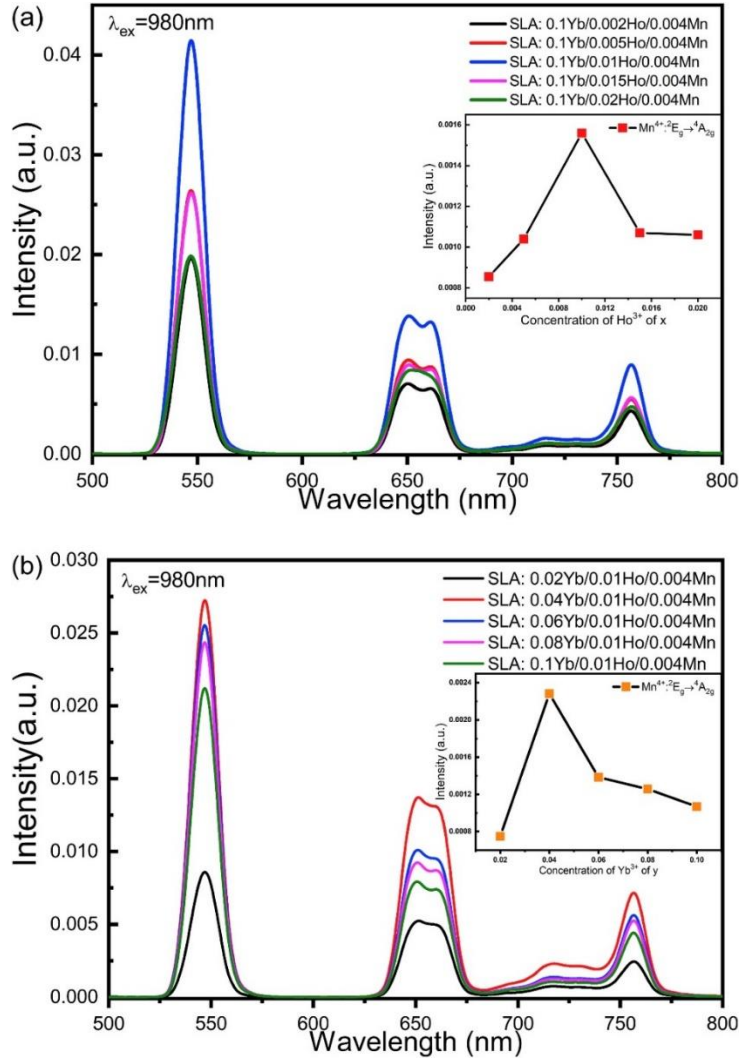


Figure 2-17 (a) Up-conversion spectrum of SLA and UC luminescence intensity of Mn^{4+} affected by Ho^{3+} concentration, (b) Up-conversion spectrum of SLA and UC luminescence intensity of Mn^{4+} affected by Yb^{3+} concentration.[69]

2.4.2.2 Quantum-cutting (Down-conversion)

Incorporating a down-conversion layer atop a PV device facilitates the conversion of one short wavelength, high-energy photon into two or more longer wavelength photons with lower energy. The introduction of a down-conversion layer significantly enhances the PCE of the PV device, with the PCE soaring to 39.6%, surpassing the theoretical Shockley–Queisser limit.[5]

Incorporating a down-conversion layer represents a straightforward yet impactful strategy to enhance solar cell performance. Typically, luminescent materials possess the ability to convert a wide spectrum of light into photons of specific wavelengths. Down-conversion luminescence refers to a single-photon conversion process where

high-energy photons are transformed into lower-energy photons upon absorption. Enhancements in emission can be achieved through energy transfer mechanisms between silicon nanoparticles and Erbium (Er^{3+}) ions.[70] Lanthanide elements, characterised by their distinctive $4f$ electronic structure, are frequently employed to fabricate luminescent down-shifting (LDS) or down-conversion layers. Various mechanisms contributing to NIR quantum cutting are illustrated in Figure 2-18. These layers serve to absorb ultraviolet light and convert it into visible and near-infrared light. Various down-conversion materials, including $\text{YVO}_4:\text{Eu}^{3+}$, Eu-complex, $\text{Sm}^{3+}\text{-Ce}^{4+}$, $\text{ZnGa}_2\text{O}_4:\text{Eu}^{3+}$, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$, and fluorescent carbon dots, have been investigated in numerous studies aimed at enhancing the PV performance of perovskite solar cells.[71] Researchers have shown a keen interest in leveraging rare earth ions within TiO_2 hosts to enhance down-conversion luminescence and optimise UV light utilisation. TiO_2 oxide, renowned for its stability, cost-effectiveness, and low phonon energies, provides an ideal platform for RE ions to emit specific wavelengths efficiently.[9] Doping with cerium (Ce) ions significantly enhances the PCE of the device, reaching 10.1%, compared to 8.1% in undoped devices. This represents a notable 24.6% improvement in PCE relative to undoped counterparts.[71] Additionally, investigations have demonstrated that doped samples exhibit reduced dark current densities and display hysteresis compared to undoped samples.[72] Upon Ce doping, the band gap of TiO_2 is raised from 2.92 eV to 3.00 eV, while the flat band potential shifts negatively by 50 mV. This alteration results in a higher Fermi level and a lower surface defect density, consequently elevating the V_{oc} of the perovskite solar cells.[71]

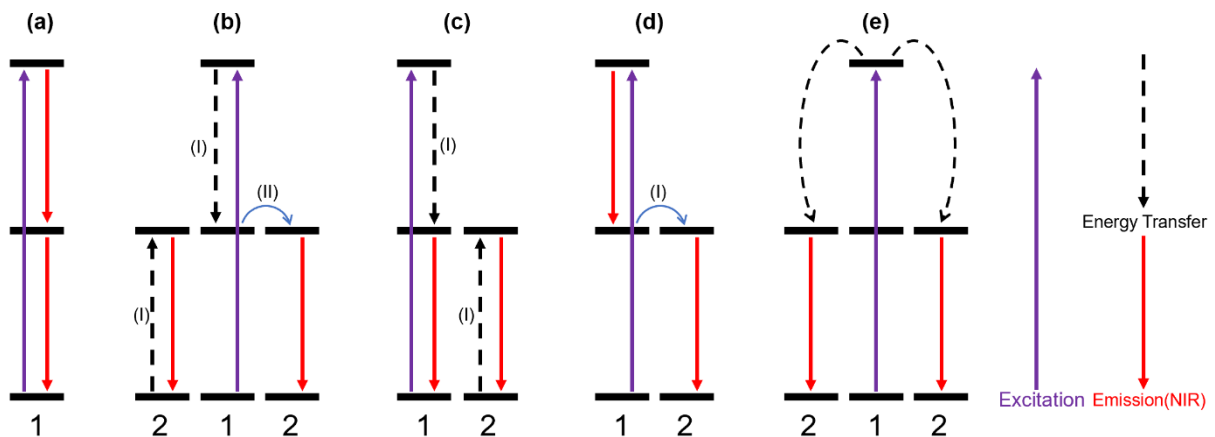


Figure 2-18 Energy level graph for 5 specific mechanisms of down-conversion for solar cell application.

2.4.2.3 Down-shifting

The process of spectral-shifting involves the absorption of photons with higher energy and their subsequent re-emission as lower energy photons, known as down-shifting, aimed at enhancing the PCE of solar cells. In this project, QDs are employed for this purpose. Positioned atop the solar cell, the down-shifting layer serves to augment the number of photogenerated charge carriers, thereby elevating both I_{sc} and PCE while concurrently reducing thermalisation effects.[73]

QDs integrated into a protective layer, commonly composed of a polymer or silica matrix, demonstrate enhanced stability even under elevated temperatures. This characteristic serves to diminish the risks associated with photobleaching, notably stemming from the photooxidation process.[74] To date, there is a paucity of research focusing on the temporal progression of both photo- and thermally induced degradation of QDs, underscoring a significant gap in our understanding in this area.[75] Prior studies have primarily focused on the modifications in PL properties observed as QDs transition from ambient to cryogenic temperatures.[76] The PL of QDs is intrinsically influenced by radiative electron-hole recombination processes. Essential factors including bandgap energy, particle size, and surface trapping mechanisms significantly contribute to the quenching of PL, resulting in a decrease in PL intensity.[77] Defects present within QDs have the potential to produce non-radiative surface states, characterised by energies lower than those within the bandgap. These states serve as trap centres for either electrons or holes, altering the process of excited-state relaxation and thereby diminishing the PLQY.[78] Furthermore, non-specific interactions initiated by solvents among QDs may promote nanoparticle aggregation, resulting in observable spectroscopic modifications. These alterations entail a reduction in the PL intensity of QDs and an additional blue-shift of the PL band, thereby exerting further influence on the optical characteristics of the QDs.[79]

2.5 Lanthanides luminescent materials

In luminescent materials, the majority of phosphors typically consist of a host crystalline structure. Introducing a modest concentration of foreign ions as dopants into the host materials induces characteristic luminescent properties. Often, a sensitizer ion is incorporated into the host material to transfer its excitation energy to the activator, enabling luminescence generation from an activator lacking sufficient

absorption for the available excitation energy. By adjusting the dopant concentration or composition, the emission colour can be easily modified without altering the host lattice. Many lanthanide activators exhibit emission spectra with spectral characteristics unaffected by their chemical environment.[7] Lanthanide materials have been extensively researched in the last decade due to their distinct properties, particularly their unique luminescent characteristics.[6]

2.5.1 Lanthanides dopant material

RE-doped materials such as Tb^{3+} , Tm^{3+} , Ce^{3+} , Eu^{3+} , Er^{3+} , Pr^{3+} , and Yb^{3+} have demonstrated enhancements in the PCE of c-Si solar cells by adjusting the solar radiation spectrum to match the spectral response of the PV cell closely. Among these, Yb^{3+} ions are prominently utilised in fabricating luminescent thin films. This preference is attributed to the $^2\text{F}_{5/2}$ single excited energy level of Yb^{3+} ions, which emits at approximately 980 nm, aligning well with the bandgap of c-Si solar cells.[80,81] However, certain RE-doped materials exhibit less effectiveness in altering solar spectra due to their narrow spectra and limited f - f electronic transitions. These lanthanide materials also typically feature sharp spectral lines.[82] Transition metal ions offer wideband absorption and emission characteristics, with Yb^{3+} ions particularly adept at converting UV-Vis light to the NIR light spectrum. However, their use in luminescent thin film fabrication is limited due to the low PLQY resulting from strong electron-phonon coupling.[83,84]

Trivalent lanthanide ions possess an abundant energy-level structure, as depicted in the Dieke diagram, making them highly suitable for spectral conversion applications. Spanning from lanthanum (La) to lutetium (Lu), the lanthanide series comprises 15 elements with $4f$ orbitals. These ions exhibit a $4f_n$ ($0 < n < 14$) electron configuration, leading to the creation of numerous energy levels.[7]

Metal-halide perovskite nanostructures, notably solution-processable cerium lead halide perovskite NCs, have emerged as key players in the realm of optoelectronic devices. Their appeal lies in their wide absorption range, elevated PLQY, and notably, their ability to emit narrowband and adjustable luminescence across the entire visible spectrum. In contrast, transition metal ions exhibit broadband emission with limited energies, emitting only at specific wavelengths. However, lanthanide ions present

sharp spectral lines spanning from UV to NIR wavelengths, offering distinct spectroscopic attributes.[85] These attributes offer the means to precisely adjust the PL of perovskite NCs to desired spectral positions. As one progresses across the lanthanide group from Cerium (Ce) to Lutetium (Lu), there is a reduction in ionic radius and alterations in electronic, magnetic, and chemical properties. Analysis through XRD and SEM demonstrated that phosphor thin films deposited or subjected to high-temperature annealing exhibited heightened crystallinity and acquired a pyramid-shaped morphology. PL characterisation underscored the significant impact of growth temperature on emission intensity, emphasising the sensitivity of emission properties to temperature variations during fabrication.[86,87] These variations enable the elucidation of the underlying mechanisms governing doping reactions and facilitate the development of tailored systems for incorporating lanthanide ions into perovskite NCs. The doping of lanthanide ions contributes to the enhancement of perovskite PV device performance.[88]

Doping solar cells with lanthanide materials offers a promising avenue for enhancing their photoelectric performance and augmenting conversion mechanisms. In recent years, lanthanide-doped materials have been utilised in down-conversion processes to bolster the performance and UV light stability of inorganic PV devices.[89] Lanthanide down-conversion materials have been investigated in prior studies to enhance both the PV performance and UV light stability of inorganic solar cells.[90]

2.5.2 Up-conversion films

The phenomenon of NIR down-conversion has been demonstrated in a variety of systems featuring co-doped lanthanide ions (Table 2-1). In 2006, Richards identified three advantages of applying an up-conversion layer to solar cells. Firstly, while previous research on up-conversion focused largely on achieving visible light output, their study aimed at utilising NIR light with energies exceeding the bandgap ($E > E_g$), particularly beneficial for Si solar cells. Secondly, the addition of an up-conversion layer at the bottom of a solar cell does not interfere with the device's performance concerning incident photons with energy $E > E_g$. However, it's important to note that up-conversion is a nonlinear optical process. In recent investigation presented insights gleaned from employing up-conversion layers based on RE luminescence centres.[59]

In 2018, Giedraityte et al. conducted a study involving a series of thin films with thicknesses ranging from 20 to 50 nm to investigate the impact of film thickness on up-conversion intensity. Their findings revealed that within this thickness range, up-conversion intensity remained largely unaffected by changes in film thickness. Figure 2-19 illustrates the response of the films to 974 nm radiation, exhibiting both green and red up-conversion emissions attributed to Er^{3+} transitions $^2\text{H}_{11/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$, respectively.[91]

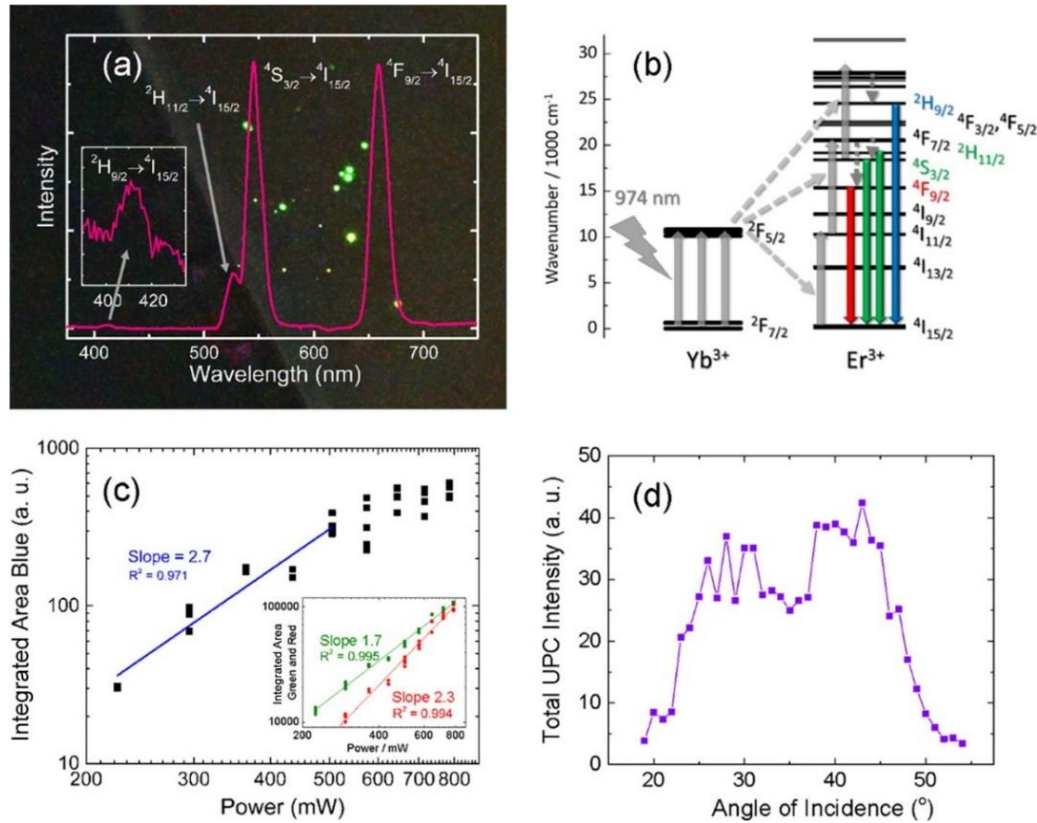


Figure 2-19 (a) Emission spectrum of upconversion for a typical (Y,Yb,Er)-pyrazine thin film produced on a Si substrate. (b) Schematic of the mechanism for up-conversion. (c) dependency of laser pump power on the (Y,Yb,Er)-pyrazine thin film, and (d) relationship of UPC emission intensity on incoming excitation angle.[91]

Table 2-1 Selected lanthanide-doped up-conversion materials applied for PV applications.

Dopant ion	Host materials	Manufacturing process	Excitation (nm)	Up-conversion		Crystalline phase	Application	Ref.
				Emission (nm)	Concentration			
Er ³⁺ –Yb ³⁺	HF/HNO ₃	Thermal doping process	980	550/660			Cz Si solar cell	[5]
Er ³⁺ –Yb ³⁺	ZnO	RF magnetron sputtering	980	550/660	0.5 at.% (Er), 2.5 at.% (Yb)	002, 004 (ZnO), 222 (Yb ₂ O ₃)	a-Si solar cell	[67]
Er ³⁺ –Yb ³⁺	Bilayer WSe ₂	Molten-salt assisted CVD	980	550/610	W:Yb:Er atomic ratio: 95:1.25:3.73, 95:3.75:1.25, 90:2.75:7.25, and 80:5:15	004, 103, 105 (2H-WSe ₂)	LED with architecture of Cr/Au electrodes	[68]
Er ³⁺ –Yb ³⁺	Y ₂ O ₃	Hydrothermal synthesis method	978	539.6/564.28	Y _{1.97} Yb _{0.02} Er _{0.01} O ₃	211, 222, 400, 411, 322, 134, 440, 611, 622, 136, 127, 800, 662, 048	LED, infrared detectors and scintillators	[92]
Er ³⁺ –Yb ³⁺	CaF ₂	Liquid-solid-solution strategy	980	524/541/654	CaF ₂ :Yb ³⁺ (20%)/Er ³⁺ (2%)	111, 200, 220, 311	Biological labelling and imaging	[93]
Er ³⁺ –Yb ³⁺	NaYF ₄	One-pot synthetic method	980	635, 540	20.24% (Y), 2.31%(Na), 2.44%(F), 4.82%(Yb), 1.446% (Er), (in parts per million)		Imaging of biological cells and tissues	[94]
Er ³⁺ –Yb ³⁺	NaGdF ₄	Drop-casting	980	523, 540, 653	18 mol% (Yb ³⁺), 2 mol% (Er ³⁺), 0, 5, 10, 20, 30, and 40 mol% (Fe ³⁺)	100, 110, 111, 201, 102	Fluorescent imaging HeLa cells	[95]

$\text{Er}^{3+}\text{--Yb}^{3+}$	LaF_3	Ethylene glycol (EG) based solvothermal synthesis route	980	543, 655	0.6 mM (Er^{3+}), 2.1 mM (Yb^{3+}), 21 mM (La^{3+}) in 70 mL	101 (TiO_2), 111 (LaF_3)	Dye sensitized solar cells	[96]
Er^{3+}	ZrO_2	Sol-gel process	962	545/680	0.16, 0.32, 0.98, 1.66, 3.46 mol% of Er_2O_3	101, 011, 211, 112, 110, -111, 111, 220	Photonics applications	[97]
Eu^{3+} , Er^{3+}	K_3YF_6	Melt-quenching	980	525/545	0.1 mol% (EuF_3), 0.5 mol% (ErF_3)	211, 022, 402	Optical temperature sensors	[98]
Er^{3+}	NaYF_4	Embedding process	1523	980	NaYF_4 :20% Er^{3+}		Silicon solar cells	[99]
$\text{Yb}^{3+}/\text{Tm}^{3+}$	NaYF_4	quenching process	980	802	0.2, 0.5, 1, 2, 4, 8 mol% (Tm^{3+}), 20 mol% (Yb^{3+})		Biodetection	[100]
$\text{Ho}^{3+}/\text{Yb}^{3+}/\text{Mn}^{4+}$	SrLaAlO_4	High-temperature solid state reaction	980	600-800	SrLaAlO_4 : $x\text{Ho}^{3+}/y\text{Yb}^{3+}/z\text{Mn}^{4+}$, x :0.002—0.02 (Ho^{3+}), y :0.02—0.1 (Yb^{3+}), z :0—0.01 (Mn^{4+})	101, 004, 103, 110, 112, 105, 114, 200, 211, 107, 213, 206, 118, 109, 217	tunable up-conversion laser/full color display	[69]
Ho^{3+} , Yb^{3+}	Fluorindate glass	melting glass	1155	550, 650, 980	0.25, 0.75 mol% (HoF_3), 0.1, 0.75, 2.25 mol% (YbF_3)		Silicon solar cells	[101]
Nd^{3+}	TiO_2	Ultra-high-vacuum RF magnetron sputtering, Sol-gel, electrodeposition	980	540-560	$2\text{Nd}_2\text{O}_3$:9 TiO_2	440, 282, 044, 391, 012 0	Photoelectrochemical cells	[9]

2.5.3 Quantum-cutting (Down-conversion) films

The phenomenon of NIR down-conversion has been demonstrated in a variety of systems featuring co-doped lanthanide ions (Table 2-2). The utilisation of lanthanide-based down-conversion active layer materials, such as PTB7-Th (poly[[2,6'-4,8-di(5-ethylhexylthienyl) benzo [1,2-b;3,3-b] dithiophene] [3-fluoro-2[(2-ethylhexyl) carbonyl] thieno [3,4-b] thiophenediyl]]) and PBDB-T-2F, has shown promise in enhancing the PV performance and UV light stability of solar cells. With a ZnO/ETP (Electron Transport Layer) configuration, photovoltaic cells have achieved PCE of 9.22% (PTB7-Th) and 13.12% (PBDB-T-2F). Spectral analyses, including absorption spectra processing and PL spectra of ZnO, are detailed in Figure 2-20. Upon excitation by UV light, the ETP complexes emit red light at 612 nm, indicating their role as the emission source. ZnO exhibits modest fluorescence across the 420-675 nm range, with a notable peak observed at 612 nm.[102]

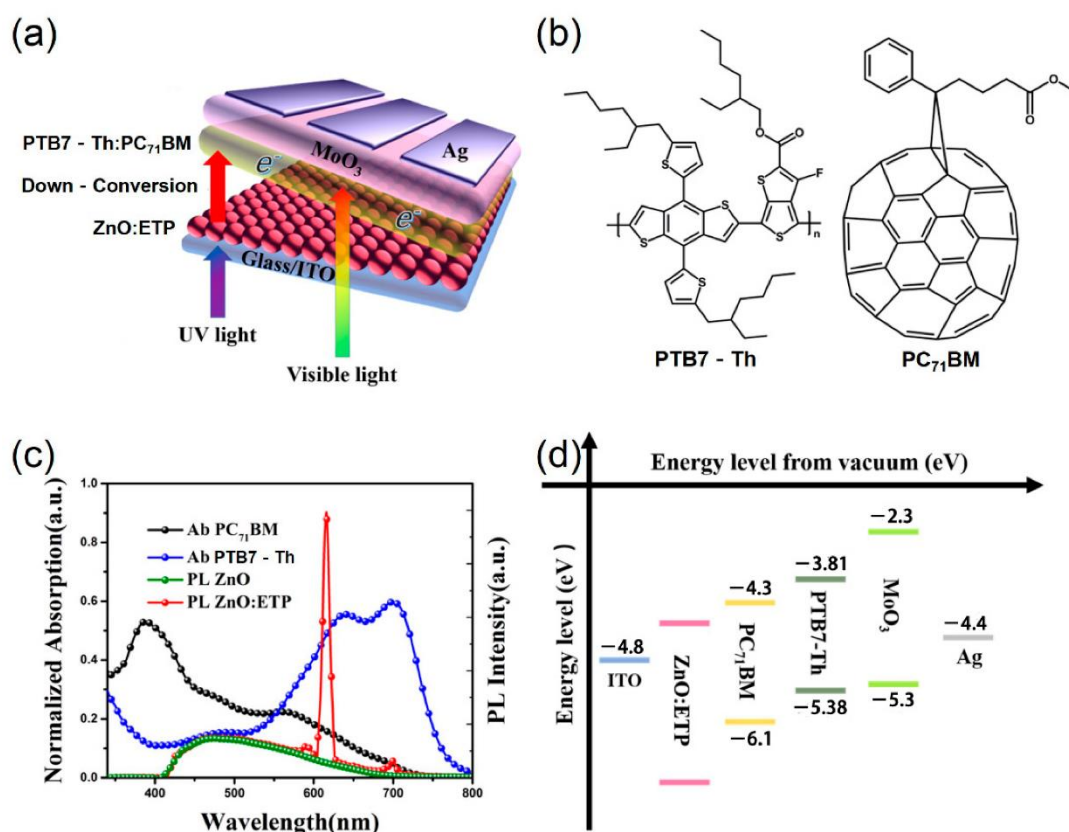


Figure 2-20 (a) The structure of PV device, (b) The molecular structure of polymer PTB7-Th and PC₇₁BM, (c) Absorption spectra of different materials, (d) Energy level of each material in PV device.[102]

Chromium (Cr^{3+}) and ytterbium (Yb^{3+}) ions were incorporated into oxyfluoride silicate glasses, renowned for their superior thermal stability compared to tellurite and germanate glasses. The absorption spectra of oxyfluoride silicate glasses reveal peaks at 430 nm ($\text{Cr}^{3+}:^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}$ (P)) and 627 nm ($\text{Cr}^{3+}:^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}$), while their emission occurs at 1010 nm ($\text{Yb}^{3+}:^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$) upon photoluminescence excitation, consistent with the down-conversion mechanism.[103] Further analysis via decay curves indicates an energy transfer efficiency of 33.5% and a quantum cutting efficiency of 133.5%.[104]

The transition between the energy levels $^4\text{A}_{2g}$ and $^4\text{T}_{2g}$ results in an emission peak near 970 nm in the Cr^{3+} -doped samples. In the $\text{Cr}^{3+}/\text{Yb}^{3+}$ co-doped sample, an emission peak at approximately 1010 nm is observed, attributed to the $^2\text{F}_{5/2}$ to $^2\text{F}_{7/2}$ transition. These two broadband emissions are concurrently observed in the $\text{Cr}^{3+}/\text{Yb}^{3+}$ co-doped sample. Figure 2-21 displays the PL spectra of Yb^{3+} -doped, Cr^{3+} -doped, and $\text{Cr}^{3+}/\text{Yb}^{3+}$ co-doped glass samples with varying concentrations of Cr^{3+} ions under 627 nm excitation.[104]

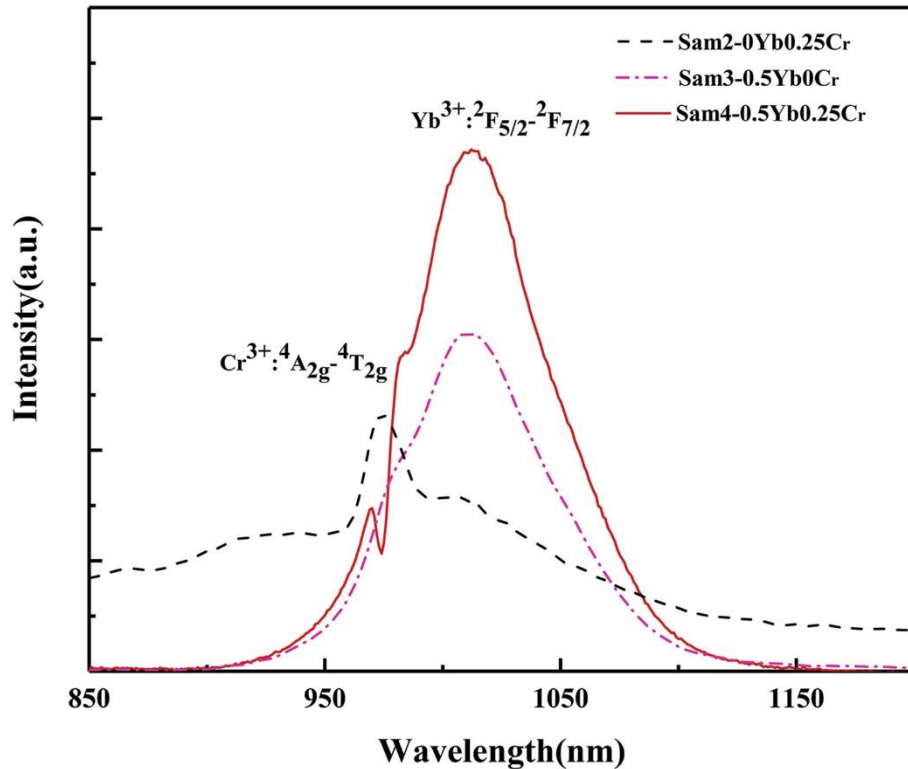


Figure 2-21 Excitation wavelength is 627 nm, and it shows photoluminescent spectra of Cr^{3+} -doped, Yb^{3+} -doped and Cr^{3+} , Yb^{3+} co-doped in glasses.[104]

Under excitation at 627 nm, Figure 2-22 displays the PL spectra of glass samples doped with Yb^{3+} , Cr^{3+} , and $\text{Cr}^{3+}/\text{Yb}^{3+}$ at various concentrations of Cr^{3+} ions. The broadband emission near 700 nm in samples containing Cr^{3+} ions is attributed to the energy level shift from ${}^4\text{T}_{1g}(\text{F})$ to ${}^4\text{A}_{2g}$. [104]

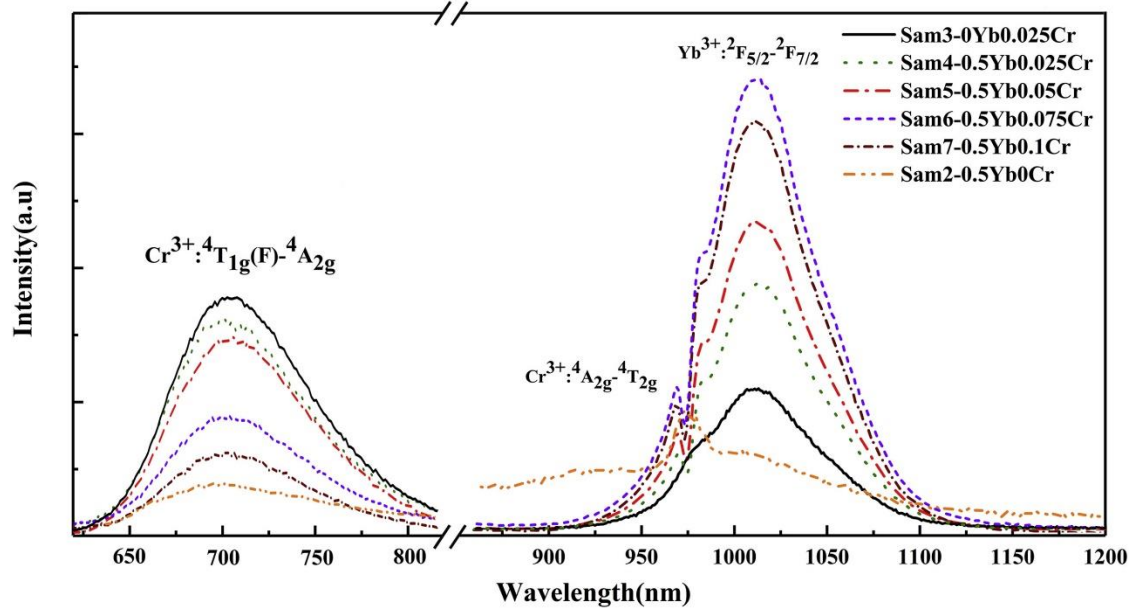


Figure 2-22 Under various Cr^{3+} ions concentrations at 627 nm excitation conditions, it shows the result of PL spectra of Cr^{3+} -doped, Yb^{3+} -doped and Cr^{3+} , Yb^{3+} co-doped in glasses. [104]

Among RE elements, Eu^{3+} emerges as a notable pure red-emitting ion. Its distinct and well-defined red emission during the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition under UV radiation renders it highly suitable. Moreover, the PL emission of Eu^{3+} ions is notably sensitive to their surroundings within the host matrix. Eu is a widely utilised RE material, is commonly chosen to achieve enhanced colour purity and luminescence efficiency. [105,106] The Judd-Ofelt (JO) theory stands as a valuable framework for assessing the intensity of such transitions, offering three sensitivity parameters denoted as Ω_λ ($\lambda = 2, 4$, and 6). These parameters provide valuable insights into the environment surrounding the Ln ion. [107] Upon excitation with visible light, the $\text{Eu}:\text{TiO}_2$ samples demonstrate unique PL, attributed to the ${}^5\text{D}_0 / {}^7\text{F}_i$ ($i = 0, 1, 2, 3, 4$) transitions of Eu^{3+} ions within the visible spectral range. [108] The excitation spectra (325–580 nm) reveal several distinct excitation peaks located at 344, 363, 377, 381, 393, 403, 414, 464, 526, 533, and 579 nm, corresponding to specific $f-f$ transitions of Eu^{3+} ions, namely ${}^7\text{F}_0 \rightarrow {}^5\text{H}_5$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{G}_2$, ${}^7\text{F}_0 \rightarrow {}^5\text{G}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, ${}^7\text{F}_1 \rightarrow {}^5\text{L}_6$, ${}^7\text{F}_1 \rightarrow {}^5\text{D}_3$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$, ${}^7\text{F}_1 \rightarrow {}^5\text{D}_1$, and ${}^7\text{F}_1 \rightarrow {}^5\text{D}_0$. Moreover, the emission spectra (500–775 nm) reveal several specific

emission peaks located at 538, 582, 593, 614, 649, 674 and 752 nm, attributed to distinct $4f$ level transitions of Eu^{3+} ions, namely $^5D_0 \rightarrow ^7F_1$ (538 nm), $^5D_0 \rightarrow ^7F_0$ (582 nm), $^5D_0 \rightarrow ^7F_1$ (593 nm), $^5D_0 \rightarrow ^7F_2$ (614 nm), $^5D_0 \rightarrow ^7F_3$ (649 nm), $^5D_0 \rightarrow ^7F_4$ (674 nm) and $^5D_0 \rightarrow ^7F_5$ (752 nm).[109] The samples, subjected to annealing at various temperatures, were analysed within the wavelength range of 500 nm to 775 nm, with excitation occurring at the most prominent peak at 393 nm, corresponding to the $^7F_0 \rightarrow ^5L_6$ transition. Results demonstrate a noticeable increase in PL intensities at 614 nm with rising annealing temperatures within the constraints of the glass substrate temperature limits.[109] Both excitation and emission are illustrated in Figure 2-23. Chen et al. investigated the effect of annealing temperature on the PL intensity of Eu-doped TiO_2 films.[110] Their study revealed that the emission intensity increased with rising annealing temperatures, reaching a maximum at 700°C for 1 hour. Beyond this temperature, the intensity gradually declined. The results indicate that the annealing temperature primarily affects the excitation and emission intensities. However, at temperatures exceeding 900°C, there is a risk of Eu^{3+} ion segregation within the phosphor matrix and the formation of impurity phases such as rutile TiO_2 and $\text{Eu}_2\text{Ti}_2\text{O}_7$, which can lead to a significant reduction in Eu^{3+} emission.[110]

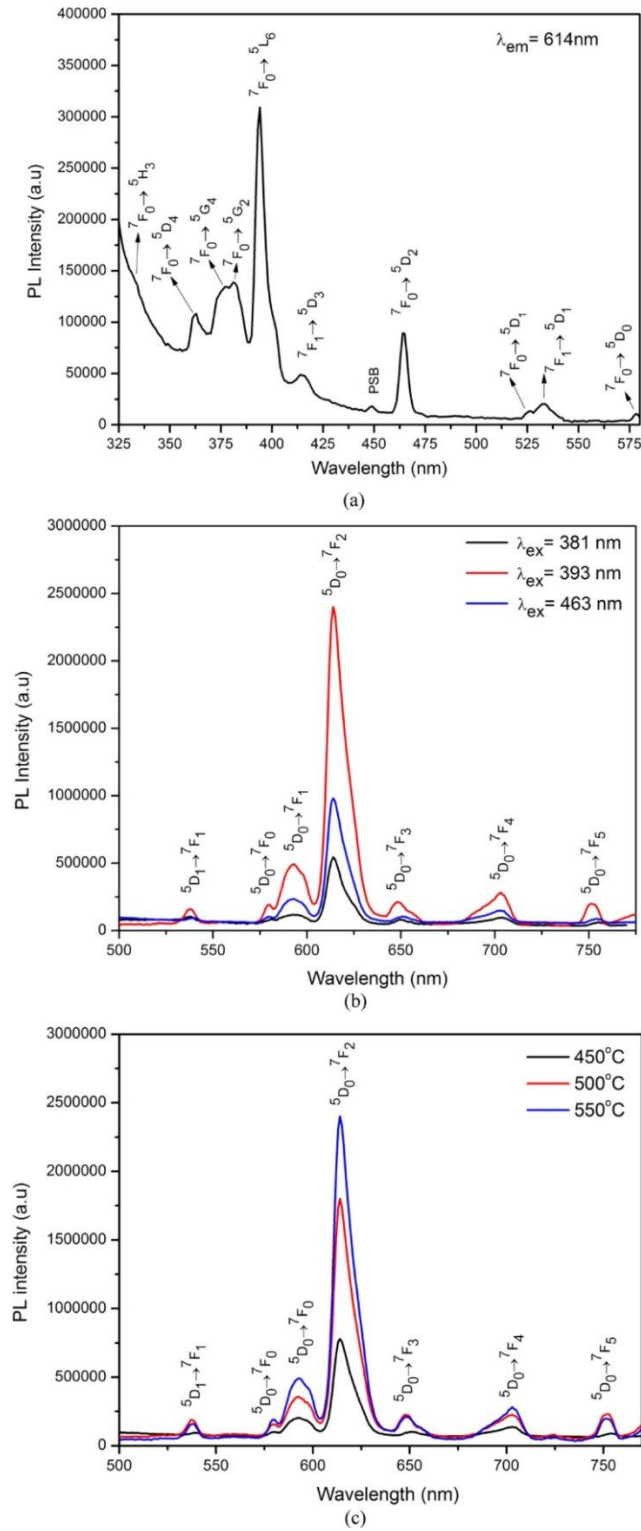


Figure 2-23 (a) the photoluminescence excitation spectra of the $\text{TiO}_2:0.07\text{Eu}^{3+}$ thin film annealed at 550°C , (b) the photoluminescence emission spectra of the $\text{TiO}_2:0.07\text{Eu}^{3+}$ film annealed at 550°C excited at wavelengths of 381 nm, 393 nm, and 463 nm, and (c) the photoluminescence emission spectra of the $\text{TiO}_2:0.07\text{Eu}^{3+}$ thin films annealed at various temperatures. [109]

Table 2-2 Selected lanthanide-doped down-conversion materials applied for PV applications.

Down-conversion									
Dopant ion	Host materials	Manufacturing process	Excitation (nm)	Emission (nm)	Concentration	Crystalline phase	Maximum quantum efficiency (%)	Application	Ref.
Ce ³⁺	Y ₃ Al ₅ O ₁₂	Vacuum sintering method	470	530	3 at% (Ce ³⁺)		90.80%	Cu(In,Ga)Se ₂ solar cell	[111]
Ce ³⁺	TiO ₂	One-pot hydrothermal method	330	450	Ce _(0.05) -TiO ₂	110, 101, 211, 112, 220, 310, 224, 314	24.6%	Perovskite solar cell	[71]
Ce ³⁺ , Yb ³⁺	Yttrium aluminium garnet (YAG)	Magnetron sputtering	330/455	560/1030	9.5 at% (Yb) and 0.22 at.% (Ce), 8.9 at.% (Yb) and 0.288 at.% (Ce)			Silicon-based solar cell	[112]
Pr ³⁺	Ga-Ge-Sb-Se	Magnetron co-sputtering	1550	2500, 4500	1300, 2700, 4100, 6700, and 10000 ppmw			Single crystalline silicon substrates	[113]
Pr ³⁺ , Yb ³⁺	ZnO	RF magnetron co-sputtering	325	630	0.3% and 0.9% (Pr), 0.8% (Pr) and 0.4% (Yb)	002		Silicon solar cell	[114]
Eu ³⁺	ZnO	RF magnetron sputtering	244	372, 536	97% (ZnO), 3% (Eu)	100	1.33% (11.1% enhancement)	Dye sensitized solar cells	[115]
Eu ³⁺	ZnO	Pulsed laser deposition	379	616	3 mol% (Eu)	002		Silicon-based solar cell	[116]
Eu(TTA) ₃ phen	ZnO	Spin-coating and thermally annealed	200-400	612	2×10 ⁻³ mol/L, 5×10 ⁻³ mol/L, 8×10 ⁻³ mol/L		9.22%	Polymer solar cell	[102]
Gd ₂ O ₃	ZnO	Sputtering deposition	221 (5.61 eV) (Gd ₂ O ₃)	380 (Gd ₂ O ₃)	70-30, 60-40, 55-45, 100-0 and 0–100 of ZnO-Gd ₂ O ₃	100, 222			[117]

Tb ³⁺	SiO ₂ and Si ₃ N ₄	Magnetron co-sputtering	380	490/545/590/624	0.73 at.% (Tb), 13 at.%--17 at.% (O), 29 at.%--36 at.% (Si), 24.4 at.%, 17.9 at.%, 14.9 at.%, 14.7 at.%, 9.4 at.% (N)			PV cells	[118]
Tb ³⁺	ZnO	RF magnetron sputtering	244	492, 543, 563, 595, 624,	97% (ZnO), 3% (Tb)	100, 002, 110, 202	1.36% (17% enhancement)	Organic solar cell	[72]
Tb ³⁺ , Yb ³⁺	SiO ₂ and Si ₃ N ₄	Magnetron co-sputtering	239/488	545, 590, 624, 976, 1026	32.98 (Si) 46.00 (N) 20.28 (O) 0.74 (Tb) 0 (Yb), 31.53 (Si) 34.11 (N) 32.54 (O) 1.34 (Tb) 0.48 (Yb), 30.45 (Si) 38.28 (N) 27.46 (O) 1.84 (Tb) 1.97 (Yb), 28.89 (Si) 26.06 (N) 39.68 (O) 1.86 (Tb) 3.51 (Yb), (at.%)		197%	Silicon-based solar cell	[119]
Tb ³⁺ , Yb ³⁺	ZnO	Spray pyrolysis technique, Drop casting	355	710	ZnO: 5% Yb ³⁺ -1% Tb ³⁺ and ZnO: 5% Yb ³⁺ -3% Tb ³⁺	100, 002, 101, 102, 112, 103		PV cells	[120]
Er ³⁺	ZnO	RF magnetron sputtering	532	1160/1540	0.6 at.% (Er ₂ O ₃)	100, 002, 101, 122, -242			[70]
Er ³⁺	Ta ₂ O ₅	RF magnetron sputtering	325	550/670	0.46 mol%, 0.63 mol%, 0.96 mol%, 1.32 mol%, 2.08 mol%	001, 200, 201		Skypointer	[10]

Er ³⁺	Ga-Ge-Sb-S	RF magnetron sputtering, pulsed laser deposition	808	1550	0.5 wt.% (Er)		Glass substrates	[121]	
Er ³⁺ , Ce ³⁺	Ta ₂ O ₅	RF magnetron co-sputtering	350	550/670	1.6 mol% (Er), 3.4 mol% (Ce)	001, 200, 201	High-efficiency silicon solar cells	[122]	
Yb ³⁺	Zinc tin oxide (ZTO)	RF magnetron co-sputtering	355/710	975/1010	0.09, 0.12, 0.17, 0.18, 0.25 at.% (Yb)	002, 103	10.3%	Cu(In,Ga)Se ₂ solar cell	[103]
Yb ³⁺	ZnO	RF magnetron sputtering	325	980	0.2, 0.3, 0.5, 0.8, 1.3, 3.3 at.% (Yb)	100, 110, 101, 102, 002, 112, 203	Solar cell	[123]	
Yb ³⁺	ZnO	Magnetron co-sputtering	325	980	0, 0.1, 0.2, 0.4, 0.5, 0.65, 0.85, 1.07, 1.35 at.%	002, 3-30, -1-19, 220, 222, 102, -129	Crystalline silicon wafer	[80]	
Cr ³⁺ , Yb ³⁺	Oxyfluoride silicate glasses	Conventional melt quenching method	430	1010	0, 0.5 mol% (Yb ₂ O ₃), 0, 0.025, 0.05, 0.075, 0.1 mol% (Cr ₂ O ₃)	133.50%	Crystalline silicon (c-Si) solar cell	[104]	

2.6 Manufacturing Process of lanthanides-doped thin films

The selection of materials for luminescent thin films holds significant importance, as each material serves a distinct role and possesses unique fluorescent properties tailored for various applications. Dopant materials like Yb^{3+} and Eu^{3+} , alongside host materials such as ZnO and TiO_2 , play crucial roles in enhancing the PCE of solar cells. However, the performance of thin films is also substantially influenced by their configuration and manufacturing processes. Various specific manufacturing techniques, including drop casting and evaporation spray coating can be applied to fabricate luminescent thin films, each contributing to the optimisation of thin film performance.[124,125] Each manufacturing process possesses distinct features and advantages. However, the primary objective of fabrication remains consistent: to achieve a continuous, homogeneous luminescent thin film with precise control over thickness and coating dimensions.[126]

2.6.1 Physical vapour deposition (PVD)

Various manufacturing processes, including single target sputtering and combinatorial sputtering, are employed to fabricate high-quality luminescence thin films. Among these, radio-frequency (RF) magnetron sputtering and direct-current (DC) magnetron sputtering are commonly utilised techniques.[26,127]

RF and DC magnetron sputtering are widely recognised as effective methods for producing high-quality thin films.[127] Parameters such as working pressure, substrate temperature, Ar sputtering atmosphere, sputtering power, and sputtering time must be meticulously adjusted during the fabrication process.[128,129] RF magnetron sputtering, renowned for its simplicity, low substrate temperature, and ability to produce high-quality films, is particularly favoured in thin film fabrication.[130] DC reactive magnetron sputtering is a method utilised to deposit high-quality TiO_2 coatings on extensive surfaces at reduced temperatures. The process involves directing plasma-derived gaseous ions towards a target composed of the desired deposition material. Zhang et al. demonstrated the feasibility of employing DC reactive magnetron sputtering to produce doped TiO_2 coatings.[131] From an industrial perspective, DC sputtering is preferable to RF sputtering for large-area coating due to its simplicity and higher deposition rate.[127] Comparison of sputtering rates across

various materials underscores the notable contrast in deposition speeds. While highly conductive materials like silver can be effectively sputtered using DC methods, typical insulators like silicon dioxide necessitate RF techniques for efficient deposition.[26]

The parameters of deposition processes vary depending on the materials and configurations of thin films. Additionally, within the same deposition technology, various equipment options exist, including different devices for RF and DC magnetron sputtering. Commonly used host materials for lanthanide-doped thin film deposition include ZnO and TiO₂. Furthermore, dopants such as Er, Eu, and Yb are deposited in luminescent thin films using RF and DC magnetron sputtering techniques.

In a study conducted by Francis et al. in 2020, thin film deposition was performed using a ZnO (97%): Eu (3%) (99.99% purity) target with a diameter of 76 mm and a thickness of 6 mm. The researchers utilised an RF magnetron sputtering system and employed P-type (001) Si and quartz substrates for optical measurements, while FTO-coated glass substrates were utilised for device fabrication. The thin film deposited on the Si substrate underwent testing using SEM, RBS, GXRD, and PL techniques. UV-Vis spectroscopy was employed to analyse the thin film deposited on the Quartz substrate, while J-V characterisation was performed on the thin film deposited on the FTO substrate.[115]

Jorge et al. (2016) employed DC magnetron sputtering in their study, providing a comprehensive description of the experimental setup and procedure for fabricating Eu:ZnO thin films. The ZnO matrix was deposited utilising a zinc target with a 50 mm diameter, powered by a pulsed DC power supply (AE Pinnacle Plus+) operating at 150 W (frequency 120 kHz, reversal time 2.5 μ s). During the deposition process, the gas mixture is 20 sccm consisting of 50% Ar and 50% O₂. By adjusting the deposition rates of Eu (effusion cell) and Zn (magnetron sputtering) sources, precise control over the Eu content in the films was achieved. The PL spectra of the synthesised films, featuring Eu to Zn ratios ranging from 0.5 to 5.3 at%, exhibited the characteristic PL spectra of Eu³⁺-doped oxides, with intensity varying linearly with europium content. The normalised PL spectra of selected Eu:ZnO thin films containing increasing concentrations of europium revealed emission spectra akin to those of Eu³⁺ integrated into ZnO films and other matrix oxide films. The prominent emission band at 615 nm corresponded to the decay from the excited ⁵D₀ to the final ⁷F₂ state.[8]

In a study conducted by Pansila et al. (2012), reactive DC sputtering was employed to deposit TiO₂ thin films onto Si wafer (100) substrates and glass slides. Ti metal served as the target material. The reactive sputtering process was conducted in an atmosphere comprising Ar and O₂ gases at a total pressure of 3.75 mTorr. The vacuum chamber, measuring 310 mm in diameter and 370 mm in height, accommodated the deposition process. A 99.97% pure Ti disc with a diameter of 54 mm served as the sputter target. Deposition occurred on unheated substrates, with a distance of 120 mm between the substrate holder and the Ti target, and a substrate radius location of 40 mm. Mass flow controllers regulated the flow rates of Ar and O₂ at 99.99%. The sputtering chamber maintained a base pressure of 3.75×10^{-2} mTorr and a total pressure of 3.75 mTorr. Three different oxygen partial pressures were set at 1.65 mTorr, 2.7 mTorr, and 3.0 mTorr, respectively. A DC power of 210 watts was applied during the deposition process.[132]

As reported by Francis et al. the Xrump code simulation yielded a layer thickness of 357 nm, corroborated by surface profilometer measurements showing 356.6 nm. The thin film exhibited an excitation wavelength of 244 nm, with the primary emission peak observed at 613 nm.[115], Conversely, Jorge et al. employed DC magnetron sputtering to achieve deposition rates ranging from 2 to 10 nm/min.[8] Following deposition, the samples underwent vacuum heating at 250°C for 1 hour to eliminate any residual precursor contamination. The excitation wavelength of the thin film was measured at 280 nm, with its highest emission peak observed at 615 nm.[8]

A versatile fabrication technique known as combinatorial magnetron sputtering enables the rapid production of complex and diverse materials with distinct characteristics.[133] Gaines et al. (2017) employed combinatorial magnetron sputtering to investigate composition-structure-property relationships in complex materials. The primary objective of combinatorial research is to analyse large datasets, encompassing over 5,000 samples per wafer, to identify property trends for detailed characterisation swiftly. Effective sample generation methods must be coupled with high-throughput characterisation techniques like X-ray diffraction and X-ray fluorescence to screen numerous compounds efficiently within a short timeframe. The researchers utilised an advanced synchrotron-based characterisation method, enabling combined X-ray diffraction and X-ray fluorescence measurements every 18 seconds, facilitating the characterisation of approximately 5,000 samples daily.

Collaborating with Cal Tech, KJLC adapted a sputtering equipment manufactured by the Kurt J. Lesker Company, as depicted in Figure 2-24. Variations in source voltage, gas pressure, reactive gases, and deposition geometry were manipulated to tailor the characteristics of thin films deposited via sputtering. Leveraging this enhanced capability, Cal Tech researchers synthesised ternary libraries encompassing compositions ranging from 8% to 82% of each element on a single 100 mm wafer.[26]

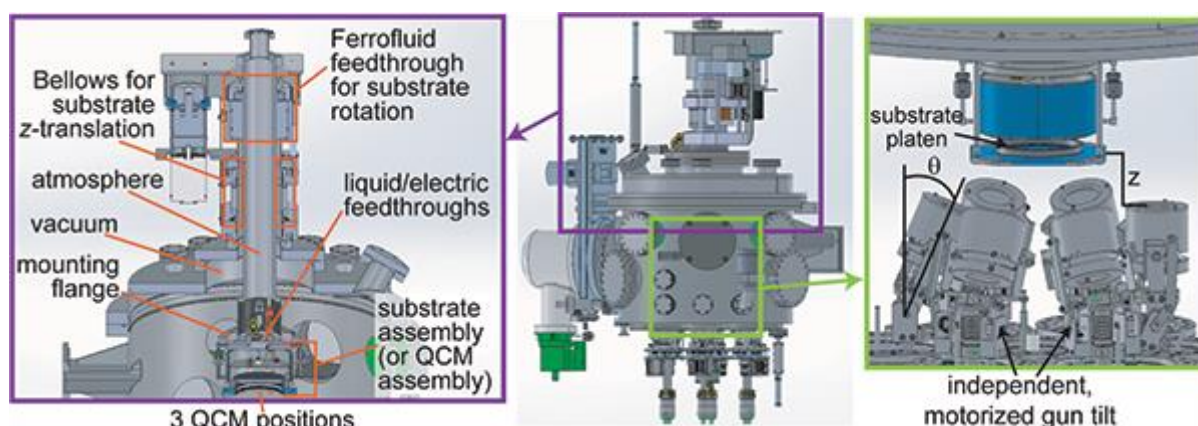


Figure 2-24 Schematic the internal structure of the Kurt J. Lesker CMS-24 combinatorial magnetron sputtering device.[26]

2.6.2 Combinatoric co-sputtering

Kube et al. (2019) employed combinatorial sputtering followed by high-throughput energy-dispersive EDX and synchrotron XRD to determine the elemental composition and structure of each alloy patch, as illustrated in Figure 2-25.[12] Each of the 14 compositional libraries was divided into 177 alloy patches, resulting in 2478 unique alloys. To represent all combinations of a maximum of three independent sources mathematically on a planar substrate, quinary high-entropy alloy (HEA) thin films were manufactured using three sputtering sources instead of five. Two binary element targets were utilised to deposit quinary systems, with the two elements deposited in a specified ratio.[134] In the realm of sputtering, similar elements are typically amalgamated into a single target for convenience. The tetrahedral disposition of the sputtering source relative to the substrate induces compositional diversity. Patches in close proximity to a particular source exhibit a heightened concentration of the corresponding components. For instance, in Figure 2-25, a notable accumulation of element E is observed near the red source. Given that the molar fraction ratio of two paired elements remains relatively constant across a library, the quinary composition range can be likened to a quasi-ternary system within a Gibbs triangle. This approach

enables the simultaneous fabrication of numerous samples with varying concentrations, thereby streamlining manufacturing processes and saving time. Moreover, employing elements deposited in a continuously varying ratio facilitates performance comparison. Ultimately, employing high-throughput synchrotron XRD, an X-ray diffractogram is obtained for each patch, aiding in structural characterisation.[26] When employing a 2D detector, diffractograms are less susceptible to texturing effects. These 2D diffraction images are subsequently transformed into 1D diffractograms for phase identification purposes. By integrating compositional and structural data, composition-structure phase diagrams are constructed, providing valuable insights into the relationship between material composition and structure.[12]

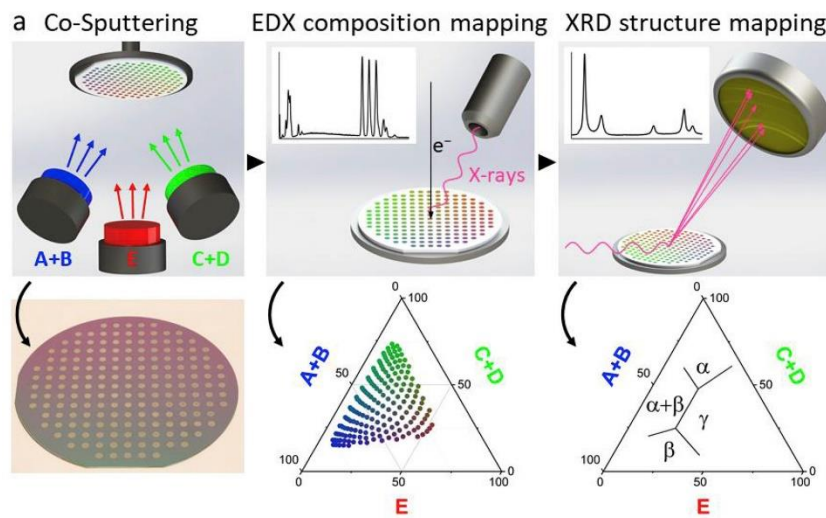


Figure 2-25 Manufacturing processes: (a)Co-sputtering, (b)EDX composition mapping, (c)XRD structure mapping. (closing to the red will have a higher concentration of element E).[12]

Through the study of Physical Vapour deposition, we know the manufacturing processes and mechanism of this method. Either RF or DC magnetron sputtering can fabricate excellent thin film and the more precise thickness of the thin film can be controlled when adjusting the manufacturing parameters, such as working pressure, substrate temperature, sputtering atmosphere, sputtering power, sputtering time and target substrate distance. In addition, combinatorial sputtering is one of the PVD processes which can fabricate large-scale samples at the same time to reduce the manufacturing time and the elements deposited in a continuous variation ratio will be better for performance comparison. PVD is a suitable method for lanthanide-doped luminescent thin film fabrication in the future. However, the PVD method for lanthanide-doped luminescent thin films is still in the development process, most of

them have just been validated in the lab. From a commercial viewpoint, the large-scale fabrication costs need to be considered for this approach of manufacturing.

2.6.3 Other methods: sol-gel and melt-quench

The enhancement of power conversion efficiencies in PV devices relies on three distinct spectral matching mechanisms. Each mechanism, including down-shifting, down-conversion, and up-conversion, entails the application of different luminescent thin films tailored to specific solar cell configurations. The efficacy of each luminescent thin film is contingent upon the chosen materials and fabrication techniques.[135] To cater to the requirements of individual solar cells, a precise selection of materials and structures is imperative throughout the manufacturing process.[136] Key characteristics such as broad spectrum absorption, emission of photons within the desired radiation spectrum, high PLQYs, and prevention of self-reabsorption of emitted photons are crucial for the development of luminescence thin films. These attributes must be carefully addressed to ensure optimal performance of the thin films.[137,138]

To achieve maximum efficiency and prevent self-reabsorption of emitted photons, luminescent NCs must surpass unity PLQYs and Stokes shifts. Notably, $\text{Yb}^{3+}:\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$, a down-shifting thin film, has demonstrated nearly 200% PLQYs. Through meticulous measurement and analysis in a liquid phase environment, the negligible reabsorption of $\text{Yb}^{3+}:\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$ has been confirmed in one-dimensional studies. These findings serve as foundational data for the fabrication of luminescent solar concentrators (LSCs) using nanocrystal luminescent thin films. Specifically, employing $\text{Yb}^{3+}:\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)_3$ as the top layer in a novel monolithic bilayer thin film, alongside a narrower-gap LSC serving as the bottom layer, enables the establishment of a unified waveguide structure within a single PV device. This innovative configuration facilitates efficient photoelectrical conversion by harnessing the complementary properties of both layers.[139]

The deposition of Yb^{3+} -doped CsPbCl_3 NCs thin films involves the incorporation of approximately 6% Yb^{3+} ions, strategically chosen to enhance the emission wavelength to align with the solar cell spectrum while elevating the PLQYs. Notably, the PLQYs are susceptible to the excitation power, with saturation effects observed at low excitation powers. Remarkably, Yb^{3+} -doped CsPbCl_3 NCs thin films demonstrate a

significant enhancement in PLQYs, surpassing 170%, representing a more than 60% increase compared to undoped CsPbCl₃ NCs. This achievement marks the attainment of the maximum PLQY value for colloidal NCs, nearing the theoretical peak of 200% for visible-to-NIR quantum cutting facilitated by Yb³⁺. Furthermore, the emission wavelength of Yb³⁺-doped CsPbCl₃ NCs is measured at 990nm under a 380nm excitation wavelength.[58]

In alternative configurations, the utilisation of lanthanides and ZnO for fabricating Yb³⁺-doped ZnO luminescent thin films has emerged as a more efficient and cost-effective approach. A dual-target magnetron co-sputtering apparatus is employed for the deposition of Yb³⁺-doped ZnO films onto n-type single-c-Si wafers. The first target contains a mixture of ZnO and Yb₂O₃ powders, with purity levels of 99.999% and 99.99%, respectively, combined at a weight ratio of 9:1. Meanwhile, the second target exclusively comprises 99.999% pure ZnO. The deposition process is conducted under a vacuum pressure of 6.7×10^{-5} Pa. The flow rate ratio of Ar gas to O₂ gas is set at 25.0 sccm and 5.0 sccm, respectively, at a gas pressure of 0.33 Pa. In Figure 2-26, the SEM images depict the surface morphology of the thin films following annealing at 1000 °C for 30 min in N₂, illustrating variations in film characteristics corresponding to different Yb concentrations. The depicted Yb concentrations range from 0 at.% to 1.35 at.%, represented by designations 'a' through 'i' in Figure 2-26. The excitation wavelength of the film is 380 nm, while the emission wavelength, dependent on Yb³⁺ ions, is measured at 980 nm.[80]

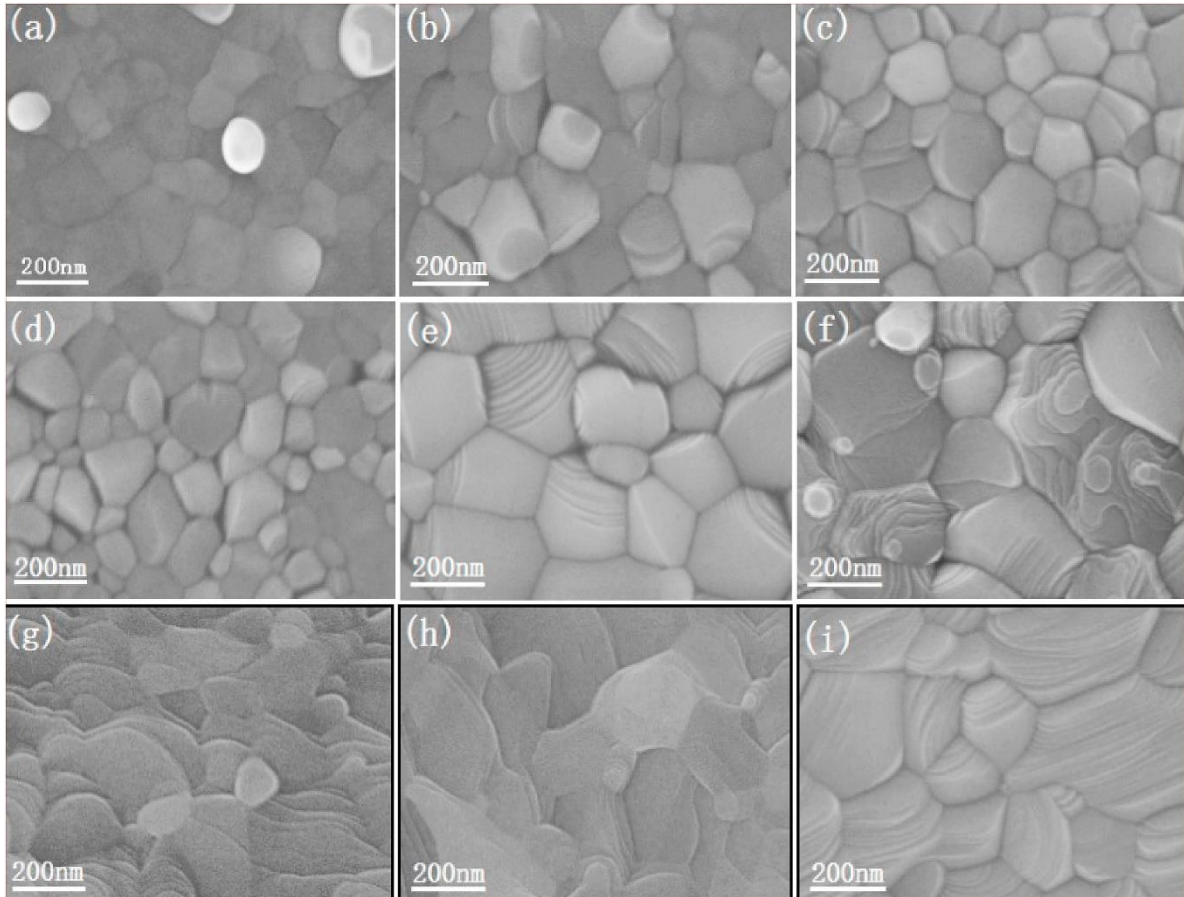


Figure 2-26 Surface of various concentrations of Yb-doped in ZnO under 1000°C annealing in SEM. Yb dopant concentration of (a) 0 at.%, (b) 0.1 at.%, (c) 0.2 at.%, (d) 0.4 at.%, (e) 0.5 at.%, (f) 0.65 at.%, (g) 0.85 at.%, (h) 1.07 at.%, and (i) 1.35 at.%.[80]

As-deposited, the amorphous TiO_2 matrix serves as both an effective host for well-dispersed Eu^{3+} ions and a sensitizer facilitating the transfer of absorbed energy to the Eu^{3+} ions.[140] The surface morphology of TiO_2 pellets, as observed using the VEGA3 TESCAN SEM, reveals uniformly distributed nanosized spherical particles with no signs of aggregation. The topography images obtained by Atomic force microscopy (AFM) XE-100 further confirm the uniform distribution of these spherical particles. TiO_2 thin films are typically amorphous when deposited at temperatures $\leq 350^\circ\text{C}$, lacking a strict crystallographic structure, often containing voids and having relatively low density. Upon annealing at temperatures above 350°C , anatase phase formation occurs, while the most stable rutile phase emerges at temperatures exceeding 800°C . [141] The as-deposited TiO_2 initially exhibits an amorphous structure, which transitions into the anatase phase upon annealing above 350°C and further transforms into the rutile phase at temperatures exceeding 900°C . TiO_2 nanoparticles annealed

at 450°C exhibit small grain sizes, but with further increases in annealing temperature to 900°C, particle agglomeration occurs, leading to larger particle sizes.[142] As the annealing temperature increased from 350°C to 900°C, the intensities of the anatase (101) peaks in the XRD pattern showed a corresponding increase, indicating an enhancement in the crystalline structure and a growth in crystallite size. The increase in size is attributed to densification effects induced by the elevated annealing temperatures.[143] The crystallite sizes of both anatase and rutile phases grew correspondingly when the annealing temperature was increased from 350°C to 800°C. This trend indicates that crystallite size progressively increases with higher annealing temperatures.[144] The phonon lifetime is correlated with the Raman line-width, showing an increasing trend as the annealing temperature rises. This is attributed to the formation of larger crystallites at higher temperatures, which contribute to an enhanced phonon distribution, thereby extending the phonon lifetime.[109]

2.7 Conclusions

The primary obstacle to achieving optimal energy PCE in PV devices lies in the disparity between the solar radiation spectrum and the spectral response of PV cells. An Extensive review of over 100 papers encompassing the state-of-the-art advancements in solar cells, luminescent materials, and thin film manufacturing processes up to 2024. This comprehensive analysis identified the materials associated with the highest PCE in solar cells, as well as the most effective luminescent mechanisms and expedient manufacturing processes.

The c-Si solar cell stands out as a widely adopted solution for energy conversion due to its cost-effectiveness and the most mature technology. With a band-gap energy of 1.12 eV, c-Si exhibits a spectral response with a peak at 1000 nm. However, the peak energy of sunlight resides around 500 nm. Consequently, the PCE of c-Si is theoretically capped at 33% by the Shockley-Queisser limit, considering only radiative recombination.[50] Consequently, the development of multi-junction solar cells with varying bandgaps capable of harnessing diverse solar spectra offers a promising way to overcome these challenges and circumvent the constraints of the Shockley-Queisser limit.[36]

To enhance the PCE of PV with additional PL thin film and mitigate PV fundamental losses, various mechanisms such as up-conversion, down-conversion, or down-

shifting are employed to minimise thermalisation and sub-bandgap losses of solar cells. Notably, the down-conversion mechanism has demonstrated the capability to achieve a PLQY exceeding 100%, thereby compensating for optical losses and theoretically reaching values between 170% and 200%.[58,139] Yb^{3+} ions serve as effective dopants for converting UV-Vis light into the NIR spectrum, emitting photons at approximately 980 nm when excited at 450 nm wavelengths.[83] The Eu^{3+} ion stands out as an exemplary pure red-emitter in the characteristic ${}^5D_0 \rightarrow {}^7F_2$ (614 nm) transition under UV radiation.[108] Within the literature, lanthanide ions have emerged as pivotal components facilitating both down-conversion and up-conversion processes in PV applications. However, a gap in current understanding persists regarding whether thin films necessitate crystallinity to exhibit PL, or if amorphous structures are adequate for this purpose. Additionally, the potential influence of thin film microstructure on PL remains uncertain and requires further investigation.

The thin films are fabricated by PVD combinatorial sputtering with RF and DC magnetron sputtering which are commonly employed in the manufacturing of luminescent thin films due to their cost-effectiveness and efficiency, particularly at low temperatures.[127] Concurrently, combinatorial sputtering is able to produce homogeneous thin films with enhanced control over thickness.[87] Combinatorial sputtering systems, by virtue of accommodating two or more independent source targets, offer the capability to swiftly generate diverse concentration gradients on the substrate concurrently. This method can unravel the intricate composition-structure-property interdependencies within complex material systems.

The lifetime of luminescence thin films has not been thoroughly examined in existing literature. Moreover, the impact of both material composition and microstructure on the degradation properties of these thin films remains unexplored and warrants further investigation. Moreover, the anticipated contributions to knowledge lie in the utilisation of combinatorial PVD techniques to expedite the discovery of materials.

3 Methodology

3.1 Introduction to the methodology (Meaning of research and strategies)

Several methodologies exist for enhancing the efficiency of photovoltaic cells. In this research, the synthesis of photoluminescence thin films involves the utilisation of various materials and manufacturing processes. Specifically, PVD of ceramic targets and Liquid Chemical Drop-casting with polymer sample fabrication methods are employed. Diverse characterisations of PL thin films are conducted and juxtaposed to discern the performance of the samples. The degradation characteristics of PL samples are determined through a comparative analysis of their performance and exposure to UV radiation experiments.

3.2 Materials

Different materials are used in the process to fabricate the photoluminescence thin films for the PVD method and Liquid Chemical Drop-casting method. Different materials have various properties, such as excitation wavelength, emission wavelength, emission intensity, transmittance and degradation properties.

During combinatorial synthesis, two deposition targets are used in the PVD instrument at the same time, lanthanide-oxide (Eu_2O_3) target (purity:99.9%) (Supplied by K-tech supplies) and metallic-oxide (TiO_2) target (purity:99.9%) (Supplied by K-tech supplies) or (ZnO) target (purity:99.99%) (Supplied by PI-KEM), as demonstrated in Table 3-1. The Eu^{3+} is doped into the TiO_2 or ZnO host materials during the deposition process. All sputtering targets used in this research are 76.2 mm (3 inches) diameter $\times$ 3.18 mm thick with 76.2 mm (3 inches) diameter $\times$ 3 mm thick copper backing plate. Quartz and Si wafers are used as sample substrates, and Quartz has high transmittance in wavelengths between 200 nm and 1500 nm.

Table 3-1 Selected sputtering targets used to synthesis the luminescence thin films in PVD.

Material	Size	Purity	Supplier	Description
Eu ₂ O ₃	76.2mm (3 inches) diameter × 3.18mm thick	99.9%	K-tech supplies	Sputtering target
TiO ₂	76.2mm (3 inches) diameter × 3.18mm thick	99.9%	K-tech supplies	Sputtering target
ZnO	76.2mm (3 inches) diameter × 3.18mm thick	99.99%	PI-KEM	Sputtering target

In drop-casting, two transparent polymer matrices are PVA (Polyvinyl acetate) and PMMA (Poly (methyl methacrylate)). DCM(Dichloromethane) is used as a solvent, and the quantum dots (CuInS₂/ZnS) and Eu(dbm)₃ are used as luminescence centres, as demonstrated in Table 3-2. Both polymer matrices and luminescence centres powder will mix with solvent, and either PVA or PMMA will combine with quantum dots (CuInS₂/ZnS) or Eu(dbm)₃ to be ink solution for the sample fabrication. Low Iron Glasses are used as sample substrates and have high transmittance in wavelength between 200 nm and 1500 nm.

Table 3-2 Selected materials and solvents used to synthesis the luminescence thin films in drop-casting.

Materials	Supplier	Description
PVA (Poly(vinyl acetate))	ALDRICH	Beads, 99.99%
PMMA (Poly(methyl methacrylate))	Alfa Aesar	Powder, 99.8%
DCM (Dichloromethane)	SIGMA-ALDRICH	Solvent (Anhydrous), ≥99.8%
Copper Indium Disulfide/Zinc Sulfide Quantum Dots (CuInS ₂ /ZnS)	Strem Chemicals	Powder, 99.9%
Tris(dibenzoylmethane)mono(phenanthroli ne)Europium(III) (Eu(dbm) ₃ phen)	Alfa Aesar	Powder, 99.4%

3.3 Sample fabrication

3.3.1 Physical Vapour Deposition (PVD) – Ceramic samples

DC and RF magnetron sputtering are PVD methods utilised in this project, frequently used in fabricating homogeneous luminescence thin films. PVD offers advantageous film properties which include, thermostabilisation, mechanical stability, homogeneous and good adhesion. Lanthanide-oxide (Eu_2O_3) and metallic-oxide (TiO_2 , ZnO) targets will be fixed into magnetrons of the equipment before the deposition. The properties of thin films depend on sputtering parameters: gas flow rate, pressure, substrate temperature during deposition and total power, the setup of the PVD system is exhibited in Figure 3-1. The samples need annealing at 450°C and 600°C for an hour after deposition to form a crystalline structure.

Eu_2O_3 target with RF power and the metallic-oxide (TiO_2 or ZnO) with DC power for co-sputtering. Experimental results demonstrate that Eu_2O_3 targets with RF power and metallic-oxide targets with DC power exhibit high deposition rates. Oxide targets provide better control over the oxygen composition in thin films, enabling more precise adjustment of film stoichiometry to meet desired specifications. The vacuum chamber underwent an evacuation process employing a rotary roughing pump, achieving a base pressure of 1.5×10^{-1} Torr. Subsequently, additional pump-down procedures were executed utilising a turbomolecular pump, reducing the pressure further to 2.0×10^{-6} Torr. The target-substrate distance is set at 80mm, the targets are placed above the substrates with Eu_2O_3 magnetron angled 15 degrees towards the centre of the substrate table.

There are three different types of substrates: 25×25 mm quartz, 25×25 mm Si wafer (100) and 200mm (8 inches) Si wafer (100). For each sputtering run, four pieces of 25×25 mm quartz or 25×25 mm Si wafer (a diamond cutter was used to cut the 100 mm diameter Si wafer) are arranged in a linear configuration with one substrate positioned vertically aligned under the metallic-oxide target, while another substrate will be vertically aligned under the Eu_2O_3 target. The remaining two substrates are positioned equidistant between these two targets. Moreover, the 200mm (8 inches) Si wafer will be placed in the centre between two targets. Before sputtering the surface of substrates must be cleaned following the cleaning procedures, which are ultrasonic baths in acetone and ultrasonic baths in IPA for 10 minutes respectively. Furthermore,

50 W power oxygen plasma should be applied for 3 minutes cleaning to increase the surface energy of substrates for better coating. During the sputtering, the mixed gases with 20% oxygen / 80% Argon gas and 100% Argon gas are applied into the chamber through the gas flow controller at a gas flow rate of 5.0 sccm and 15 sccm respectively, and the working pressure is 1×10^{-2} Torr. The RF power supply is 70W connected to the Eu_2O_3 , and the DC power supply is 100W connected to the metallic-oxide (TiO_2 or ZnO). All samples fabricated by PVD combinatorial co-sputtering are annealed in a furnace (Carbolite Furnace 1100°C ELF11/14), and the annealing temperature is 450°C and 600°C in air for 1 hour respectively.



Figure 3-1 Physical Vapour Deposition instrument for the fabrication of the ceramic samples with DC and RF power supply.

3.3.2 Liquid Chemical Drop-casting – polymer samples

The liquid phase drop-casting chemical process is a simple and economically efficient approach to apply a coating on a surface. This process is a room-temperature method of preparing transparent organic thin films. The quality, durability and performance of the thin film samples from drop-casting are compared with the samples prepared by PVD.

The luminescence centre powder and solvent are mixed to make a stock solution. 0.005 g quantum-dots ($\text{CuInS}_2/\text{ZnS}$) mix with 2.5 g DCM to be 2 mg/g $\text{CuInS}_2/\text{ZnS}$ stock solutions, and 0.005 g $\text{Eu}(\text{dbm})_3$ mix with 2.5 g DCM to be 2 mg/g $\text{Eu}(\text{dbm})_3$ stock solutions. The two stock solutions were combined and subjected to ultrasonic mixing for 10 minutes to ensure thorough homogenisation. In addition, 1 g PVA polymer mixed with 5 g DCM and 0.1 g PMMA polymers mixed with 8.9 g DCM to be polymer solutions. 0.66g $\text{CuInS}_2/\text{ZnS}$ stock solution and 0.66 g $\text{Eu}(\text{dbm})_3$ stock solution are mixed with 6 g PVA solution to produce ink solution, respectively. 1 g $\text{CuInS}_2/\text{ZnS}$ stock solution and 1g $\text{Eu}(\text{dbm})_3$ stock solution are mixed with 9 g PMMA solution to produce ink solution, respectively. The concentrations of ink solutions are 0.2 mg/g and 0.2 mg/g for quantum-dots ($\text{CuInS}_2/\text{ZnS}$) and $\text{Eu}(\text{dbm})_3$. All ink solutions were mixed and subjected to ultrasonic treatment for 30 minutes to ensure thorough homogenisation. Low-iron glasses are cut to 26 × 26 mm as substrates for these samples. They must be cleaned on the surface following the cleaning procedures, which are ultrasonic baths in acetone and ultrasonic baths in IPA for 10 minutes respectively. Drop-casting is used to fabricate the samples after substrate cleaning, and the ink solutions are dropped on top of the glass slide and cured the samples on the hot plate at 80°C in air for 30 minutes.

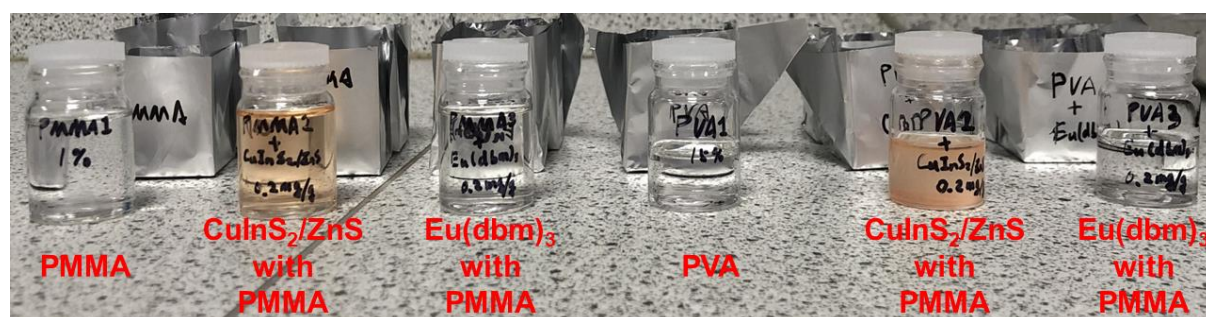


Figure 3-2 Ink solution preparation for the polymer samples, which are pure PMMA and PVA, $\text{CuInS}_2/\text{ZnS}$ and $\text{Eu}(\text{dbm})_3$ with PMMA and PVA solutions.

3.4 Characterisation

3.4.1 Visual inspection under UV light

All luminescence thin films are colourless and transparent under visible light after being fabricated by both combinatorial PVD and liquid chemical drop-casting, even after UV exposure degradation tests. A red colour will be emitted by the samples when they are exposed under certain wavelengths of UV light. Visual inspection is under 365nm UV light with 5W power from in a dark room. The pictures of the samples are taken by a digital single-lens mirrorless camera SNOY α6400 with a 3.2" shutter speed, F18 aperture and ISO 100. Each sample will take a photograph as-deposited and after every UV exposure degradation test.

3.4.2 SEM and EDX (Morphological)

The cross-section morphologies and thickness of the luminescence thin films are observed by TESCAN S8000 SEM. ETO thin films coated on top of 25 × 25 mm Si wafers (100) are placed on cleanroom paper and the thin films are faced down. The samples are cut in half on the back by the diamond cutter, and the samples are split. The morphologies of the cross-section of the thin films as-deposited are measured by the microscope. After that, the samples are annealed in the furnace and the morphologies are measured. Various thicknesses of the films depend on the sputtering parameters and the position of the substrates that have been placed. Oxford Instruments EDX system is used to study the corresponding doping rate and concentrations of lanthanide-oxide and metallic-oxide in atomic percentage. The 10k eV acceleration voltage and 40k magnification are used for imaging. The 20k eV acceleration voltage and 40k magnification are used for corresponding doping rates and concentrations.

3.4.3 XRD

The crystallised structures of the luminescence thin films are conducted by powder XRD at Cranfield University and thin film XRD at University of Manchester in 2θ mode, which can investigate the crystallinity of lanthanide-doped thin films as-deposited, annealed at 450°C and 600°C. The XRD data are obtained with SIEMENS D5005 (powder XRD) using 40 kV, 40 mA and wavelength 0.154 nm Cu Kα radiation source with Ni-filter. The scanning range of 2θ is from 10° to 90°, with 4001 seconds

(0.02°/second), step size: 0.02 2 θ /s, spot width: 17.5 mm, spot length: 5.2—25.5 mm, slit: 2. And Thin film XRD using 40 kV, 45 mA and wavelength 0.154 nm Cu K α radiation source, and the scanning range of 2 θ is from 10° to 120°, with 4001 seconds (0.02°/second)

3.4.4 Raman

The vibrational characterisation of luminescence thin films shown in Raman spectra is detected by a confocal microscope RAMAN (ISA-DILOR JOBIN YVON SPEX-Group HORIBA) with an excitation wavelength of 632.81 nm, Filter 100%, Hole 400 μ m, Slit 100 μ m and Spectrometer 2823.75 cm⁻¹. The ranges of the Raman shift are 100—1000 cm⁻¹ and 100--2000 cm⁻¹ for the spectrums at room temperature.

3.4.5 UV-Vis

The optical characteristic of the thin film samples is measured at room temperature by a spectrophotometer, which is JASCO V-670 UV-Vis-NIR. This UV-Vis spectroscopy measurement is for transmittance tests with the spectrophotometer in the wavelength range from 200 nm to 1500 nm. The data interval is 0.5 nm with 400 nm/min scan speed in the measurement, and the light source is D2/WI.

3.4.6 Photoluminescence spectroscopy

The PL spectrum of the solid-state luminescence thin films is measured by photoluminescence spectroscopy (HORIBA Scientific, Jobin-Yvon SAS, Fluoromax+ Spectrofluorometer) at room temperature. PL measurements are carried out using a 150 W Xenon lamp as the excitation light source, and the Photomultiplier Tube (PMT) from HAMAMATSU (NIR PMT Module H10330B Series). The excitation spectra are measured from 320 to 500 nm with an increment of 1 nm, a slit of 1 nm and 0.1 s dwell time, and the emission spectra are measured from 550 to 710 nm with an increment of 1 nm, a slit of 1 nm and 0.1 s dwell time. An excitation wavelength from the light source will be absorbed by the samples, and a lower energy wavelength emitted to the spectrophotometer will be detected. The fluorescence will be measured for samples as-deposited, after annealing and after each UV exposure degradation test with a solid-state film sample holder. The sample holder is set 60° toward the excitation monochromator and 30° toward the emission monochromator. Moreover, every test needs to be repeated three times for validity and reliability.

3.4.7 Solar simulator

The solar simulator used in this project is a class ABB small area Oriel LCS-100 solar simulator, which was applied for PV performance detection. Class ABB includes spectral match (0.75–1.25), irradiance spatial (5%) and temporal instability (5%), which will affect the result in a fluctuation range by the beam or sample position. The filter of this solar simulator sets the sunlight at AM1.5G (sunlight intensity is 1000.4W/m²). Reference solar meter, TC-K connector, integral Type K thermocouple and reference PV cell are included in the reference solar cell system. Keithley 2400 SMU system is used for data collection and the temperature is controlled between 23—25 °C. In the measurement, thin film samples should face down to the solar cell when the samples are placed in the system.

During the operational process of the solar cell current and voltage are generated. The formula for calculating the output power (P_{out}) involves multiplying the current (I) by the voltage (V), as demonstrated in the following equation.

$$P_{out} = I \times V \quad (3-1)$$

The fundamental parameters used for characterising solar cells include Short Circuit Current (I_{sc}), Open Circuit Voltage (V_{oc}), Maximum Current (I_{max}), Maximum Voltage (V_{max}), and Maximum Power (P_{max}). Typically, the Maximum Power point is determined by measuring the Maximum Current and Maximum Voltage, as depicted in the following equation:

$$P_{max} = I_{max} \times V_{max} \quad (3-2)$$

Power Conversion Efficiency (PCE) represents the ratio of Maximum Output Power (P_{max}) to Sunlight Power Intensity ($P_{Sunlight}$). This relationship can be expressed in equation form as follows:

$$PCE = \frac{P_{max}}{P_{Sunlight}} = \frac{I_{max} \times V_{max}}{P_{Sunlight}} \quad (3-3)$$

The Fill Factor (FF) in a solar cell is defined as the ratio of Maximum Output Power (P_{max}) to the product of Short Circuit Current (I_{sc}) and Open Circuit Voltage (V_{oc}). The Fill Factor serves as a representation of the actual characteristics of the I-V curve and is indicative of the quality of the solar cell. The equation for the Fill Factor is as follows:

$$FF = \frac{P_{max}}{I_{sc} \times V_{oc}} = \frac{I_{max} \times V_{max}}{I_{sc} \times V_{oc}} \quad (3-4)$$

3.5 Degradation measurements

Degradation measurements are used to test the lifetime of the luminescence thin films under controlled conditions. In order to accelerate the simulation of real use, the accelerated lifetime method is used in this research. All degradation measurements are performed in the LEEC-SFC3C-CRH Salt Solution Humidity cabinets with 45% relative humidity and 25°C. Industry standards IEC60068 2-78 / 2-30, and IEC61345 7500Wh/m² are followed. During the testing, A UV LED (LZ1-10UV0R VIOLET LED365nm) is used as a light source for irradiating the samples. For studying the photostability of all samples are placed at a distance of 50mm from the light source on a sample holder. A radiation energy meter (UV 513AB light meter) is used to measure the average power of the UV LED power which is equal to $P = 75 \text{ W/m}^2$, and this intensity is used in all experiments.

Four different ceramic samples are placed together in the same degradation measurements with 5, 10, 20 and 40 hours respectively. On the other hand, four different polymer samples are placed together in the same degradation measurements with 1, 2, 3, 4, 5, 10, 15 and 20 hours respectively. The degradation measurements of polymer samples are shorter than those of ceramic samples because the photobleaching of the polymer samples is shorter than the ceramic samples. The transmittance properties of the samples are measured before and after degradation measurement. Furthermore, the PL properties are measured after every UV exposure degradation test.

4 Microstructure of ETO synthesised by Combinatorial Sputtering

4.1 Introduction

Rare earth elements doped luminescent materials have attracted considerable interest in the advancement of nanoparticle-based technologies. XRD is often utilised alongside luminescence analysis to study the structural properties of TiO_2 . [145] Europium-titanium oxides typically crystallize in a pyrochlore structure, represented by the formula $\text{Eu}_2\text{Ti}_2\text{O}_7$. Additionally, the europium-titanium compound Eu_2TiO_5 is characterized by its orthorhombic crystal structure. [146]

TiO_2 , often called titania, is a transition metal oxide semiconductor known for its exceptional properties, such as high chemical stability, insolubility in water, robust oxidative capability, strong photosensitivity, and resistance to corrosion. Additionally, it is non-toxic and environmentally friendly. [109,127] TiO_2 can exist in both amorphous and crystalline states. It naturally occurs in three polymorphic forms, which can be categorised into two primary crystalline structures. These structures differ based on the symmetry of the oxygen anions (O^{2-}) bonded to titanium cations (Ti^{4+}). The tetragonal structure is characteristic of the rutile and anatase phases, while the orthorhombic structure is specific to the brookite phase. [147] Anatase and rutile are the only two phases attainable through synthesis methods conducted at atmospheric pressure and within the temperature spectrum of 0 to 1200 °C. [148–150]

Physical vapour deposition (PVD) is an advanced thin film deposition technique widely employed in various industries and research applications. [24] Combinatorial sputtering involves the simultaneous sputtering of multiple materials onto a substrate, thereby establishing compositional gradients throughout the deposited film. [25] This technique facilitates the expeditious exploration of various material combinations and their ensuing properties, all achieved within a singular deposition process. Wojcieszak et al. employed the 'high energy' magnetron sputtering technique for the production of TiO_2 thin films, incorporating a 0.2 at.% Eu doping, followed by annealing at 800 °C. [151]

The physical properties of these materials are largely influenced by the specific rare earth elements integrated into their crystal lattice. [152] However, a comprehensive understanding of the stability of TiO_2 in relation to the behaviour of Eu ions requires

more than just luminescence and XRD analysis. The incorporation of both quantitative and qualitative Raman spectroscopy, in conjunction with these techniques, is essential to gain deeper insights into the material's stability.[145] The microstructure and crystalline structural of europium-doped titanium dioxide was detected using SEM-EDXS, XRD and Raman.[140,153,154]

This research study centres on the utilisation of the combinatorial sputtering method for synthesising luminescent thin films of ETO. This manufacturing method can produce thin film samples with a seamless variation in Europium ratios, ranging from 0 at% to 100 at% in Eu/(Eu+Ti), and various concentration ratios of ETO luminescence thin films. During the research process, endeavours to scrutinise the crystallisation behaviour and the reaction mechanism dictating the formation of nanocrystalline ETO thin films via co-sputtering. The morphology and structural characteristics of the generated nanocrystals are intricately associated with the temperature applied during the thermal treatment.

4.2 Results

The characteristics of the ETO thin films are measured. Through the characterisation measurement, the morphologies, crystalline structures, optical performances and fluorescence properties of ETO thin films as-deposited, annealed at 450°C and 600°C with different Europium concentrations are obtained and analysed.

4.2.1 Visual inspection

Three different substrates are used during this study, which are 25 × 25 mm quartz, 25 × 25 mm Si wafer (100) and 200mm (8 inches) Si wafer (100). The samples with both 25 × 25 mm quartz and Si wafers are used for characterisation measurement and further experiments. ETO thin film coating on the 200mm (8 inches) Si wafer, which makes it easier to understand and observe the distribution of the compositions and luminescence properties. The experimental procedure of the combinatorial sputtering applied in this research is shown in Figure 4-1 (a). The magnetron with Eu₂O₃ is tilted 15 degrees from its normal position towards the TiO₂ magnetron. Various Eu concentrations ranging between 0 at% to 100 at% Eu/(Eu+Ti) luminescence thin films are fabricated.

The experimental procedure of spatially resolved luminescence thin films by SEM, EDS, PL and XRD is illustrated in Figure 4-1 (a). Figure 4-1 (b) shows the luminescence from the thin film on a 200mm (8 inches) Si wafer positioned between the two magnetrons, which is under both visible light and UV LED (LZ1-10UV0R VIOLET LED 365nm). In Figure 4-1 (b), the visible fringes on the Si wafer occur due to variations in coating thickness and Eu dopant concentration. The left fringe is the position under the TiO₂ target and the right fringe is the position under the Eu₂O₃ target, with the middle fringe being the position where there would be a mixed Eu and TiO₂ flux. When illuminated with UV light, the area fluorescence in red has measured Eu ratios between 1 to 50 at% Eu/(Eu+Ti), over a distance of 5 to 90 mm. Figure 4-1 (c) plots the Eu dopant concentration as a function of position along the Si wafer. A logistic function is used to model the Eu dopant concentration across the Si wafer. In the logistic regression equation, y is % Eu/(Eu+Ti) (at%), x is sputtering position (mm), x_0 is the centre sputtering position, A_1 is initial value (0%), A_2 is final value (100%), p is power, is exhibited as follows:

$$y = A_2 + \frac{A_1 - A_2}{1 + (\frac{x}{x_0})^p} \quad (4-1)$$

The Eu concentrations are from 0 at% to 100 at% Eu/(Eu+Ti), obtained from the EDS data. The total sputtering width is 180 mm, the 0 mm position is under the TiO₂ target centre, and the 180 mm position is under the Eu₂O₃ target centre during the combinatorial sputtering. The resulting fit to the data shows a low probability of Eu in the region under the TiO₂ target, which increases along the wafer reaching a maximum where the wafer is under the Eu₂O₃ target.

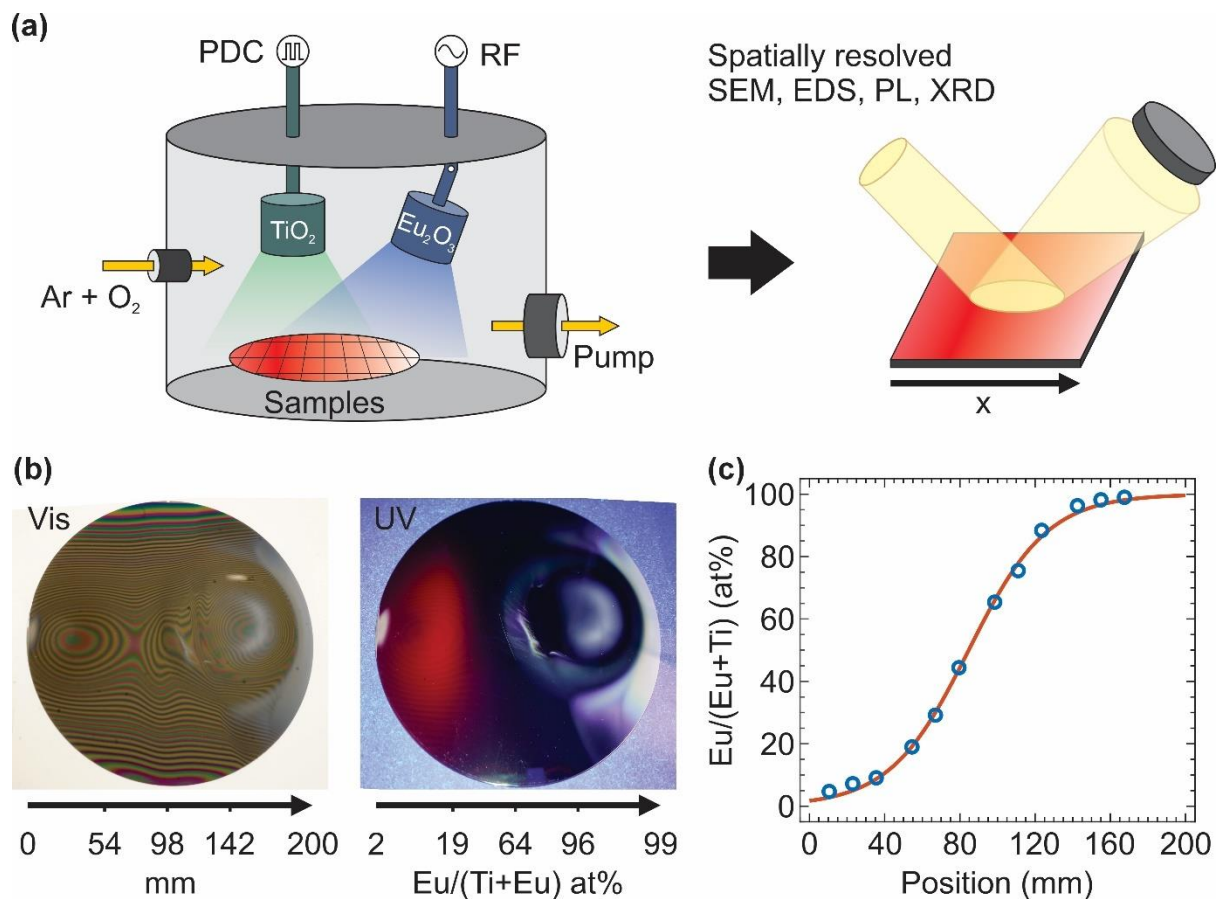


Figure 4-1 (a) Sputtering process in PVD instrument with TiO_2 and Eu_2O_3 targets connected to pulse DC and RF power supply respectively, samples are placed under the targets during the sputtering with Ar and O_2 gas; Luminescence thin films as-deposited and after annealing at 600°C are spatially resolved by SEM, EDS, PL and XRD for different concentration. (b) Visual inspection of luminescence thin film with various sputtering positions and europium ratios on a 200mm (8 inches) silicon wafer as-deposited under visible and 365nm UV lights. (c) The relationship between the composition of ETO luminescence thin films and the sputtering position matches with the logistic regression.

4.2.2 Film morphology and elemental composition

All ETO samples have changed in the fluorescence spectrum before and after annealing, and their microstructure also changed at the same time. Figure 4-2 shows the SEM secondary electron images of the cross-sections for the half of cut samples as-deposited in different sputtering positions, (a) 10.5, (b) 23, (c) 35.5, (d) 54.5, (e) 67, (f) 79.5, (g) 98.5, (h) 111, (i) 123.5, (j) 142.5, (k) 155, (l) 167.5 mm. Each thin film has a homogenous surface after co-sputtering, as shown in the images, which have a magnification of 40k and 10k eV acceleration voltage. SEM images show that the

cross-section of as-deposited thin films consists of the vertically oriented columnar microstructure with closer positions (Figure 4-2 (a), (b), (c), (d), (e) and (f)), and the average size of the columnar is about 100nm wide. This morphology is consistent with that typically observed for ETO or pure TiO_2 at the sputtering position from 0 to 90 mm. Furthermore, the films with columnar microstructure have fluorescence to glow red when the films are as-deposited. Moreover, the cross-sections of farther samples are shown in Figure 4-2 (g), (h), (i), (j), (k) and (l), which indicate these films have a fine-grained structure and are agglomerated by europium grains, except Figure 4-2 (g) exhibited vague columns of thin film at 98.5 mm sputtering position. The thicknesses of those as-deposited thin films with 23, 67, 111 and 155 mm sputtering positions are roughly 3.50 μm , 3.25 μm , 3.31 μm and 4.03 μm respectively.

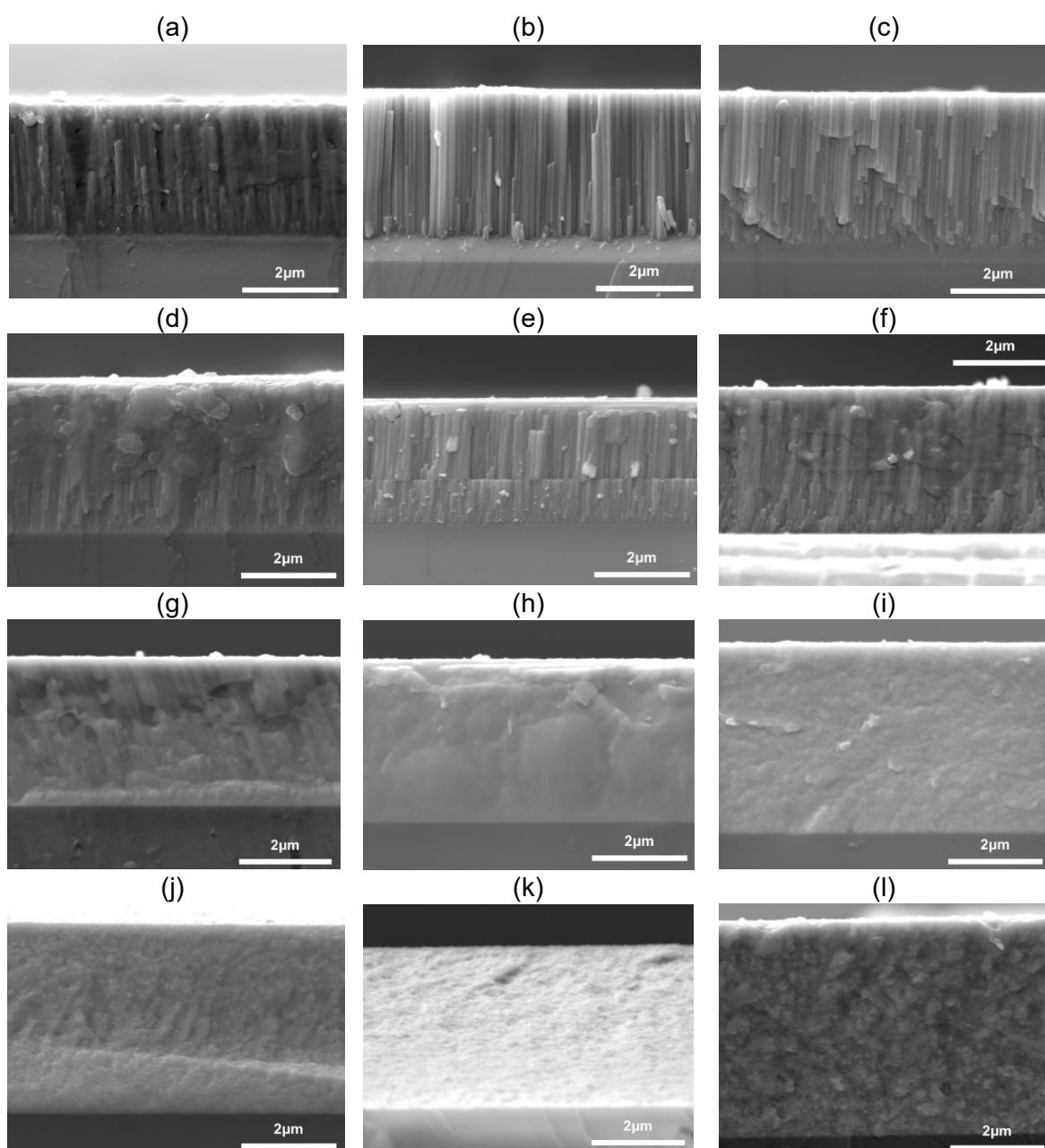


Figure 4-2 SEM images for cross-section of the ETO as-deposited in different sputtering positions, (a) 10.5, (b) 23, (c) 35.5, (d) 54.5, (e) 67, (f) 79.5, (g) 98.5, (h) 111, (i) 123.5, (j) 142.5, (k) 155, (l) 167.5 mm.

Various microstructures are observed in the cross-section of ETO thin films before annealing, as depicted in previous SEM images. Additionally, the surface microstructure of the as-deposited ETO thin films is captured in top view by SEM, as shown in Figure 4-3. These SEM images, acquired with magnifications of 500x and 10kx and an acceleration voltage of 10 keV, reveal that the thin films possess a continuous and homogeneous surface. However, minute dense protrusions are evident on the surface of thin films deposited with closer sputtering positions,

attributable to the columnar structure observed in the cross-section images. Conversely, thin films deposited at further sputtering positions exhibit a smoother surface at this scale, albeit with irregular small pits appearing on the surface of films deposited at sputtering positions exceeding 140 mm. Figure 4-3 specifically showcases thin films deposited at sputtering positions of 10.5, 35.5, 79.5, and 167.5 mm, while the surface microstructure of ETO thin films at other sputtering positions is detailed in Appendix A -- SEM images for surface of ETO thin films.

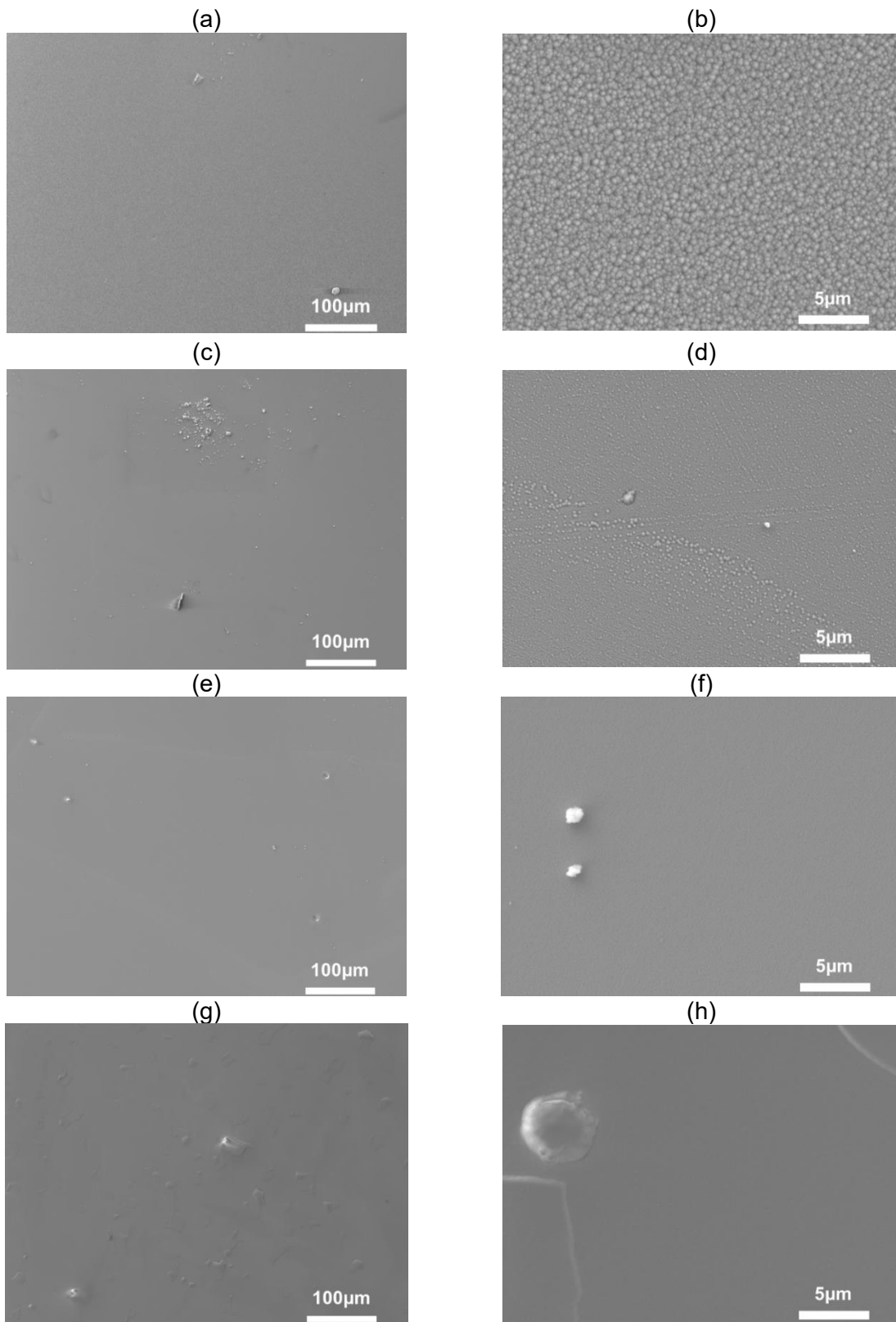


Figure 4-3 SEM images with 500 and 10k magnification for surface of the ETO as-deposited in different sputtering positions, (a) & (b) 10.5, (c) & (d) 35.5, (e) & (f) 79.5, (g) & (h) 167.5 mm.

These ETO thin films on Si wafers cut in half have similar and few variations in microstructure after annealing at 600°C when compared to these thin films as-deposited at various sputtering positions, as shown in Figure 4-4, (a) 10.5, (b) 23, (c) 35.5, (d) 54.5, (e) 67, (f) 79.5, (g) 98.5, (h) 111, (i) 123.5, (j) 142.5, (k) 155, (l) 167.5 mm. SEM imaging shows that the after 600°C annealing thin films consist of the vertically oriented columnar microstructure with the closer sputtering position (0—90 mm) in Figure 4-4 (a), (b), (c), (d), (e) and (f). The average size of the columnar is about 50nm width, it is narrower and sharper. On the other way, the microstructures of the samples with further sputtering position (90—180 mm) have changed obviously as shown in Figure 4-4 (g), (h), (i), (j), (k) and (l). The disordered line textures are formed in the thin film sample after annealing at 600°C shown in Figure 4-4 (g), (h) and (i). In the cross-section of the thin film sample agglomerate grains are shown in Figure 4-4 (j), (k) and (l). The thicknesses of those thin films after annealing at 600°C are roughly 3.48 μm , 3.01 μm , 3.12 μm and 3.95 μm relative to 23 mm, 67 mm, 111 mm and 155 mm sputtering positions respectively.

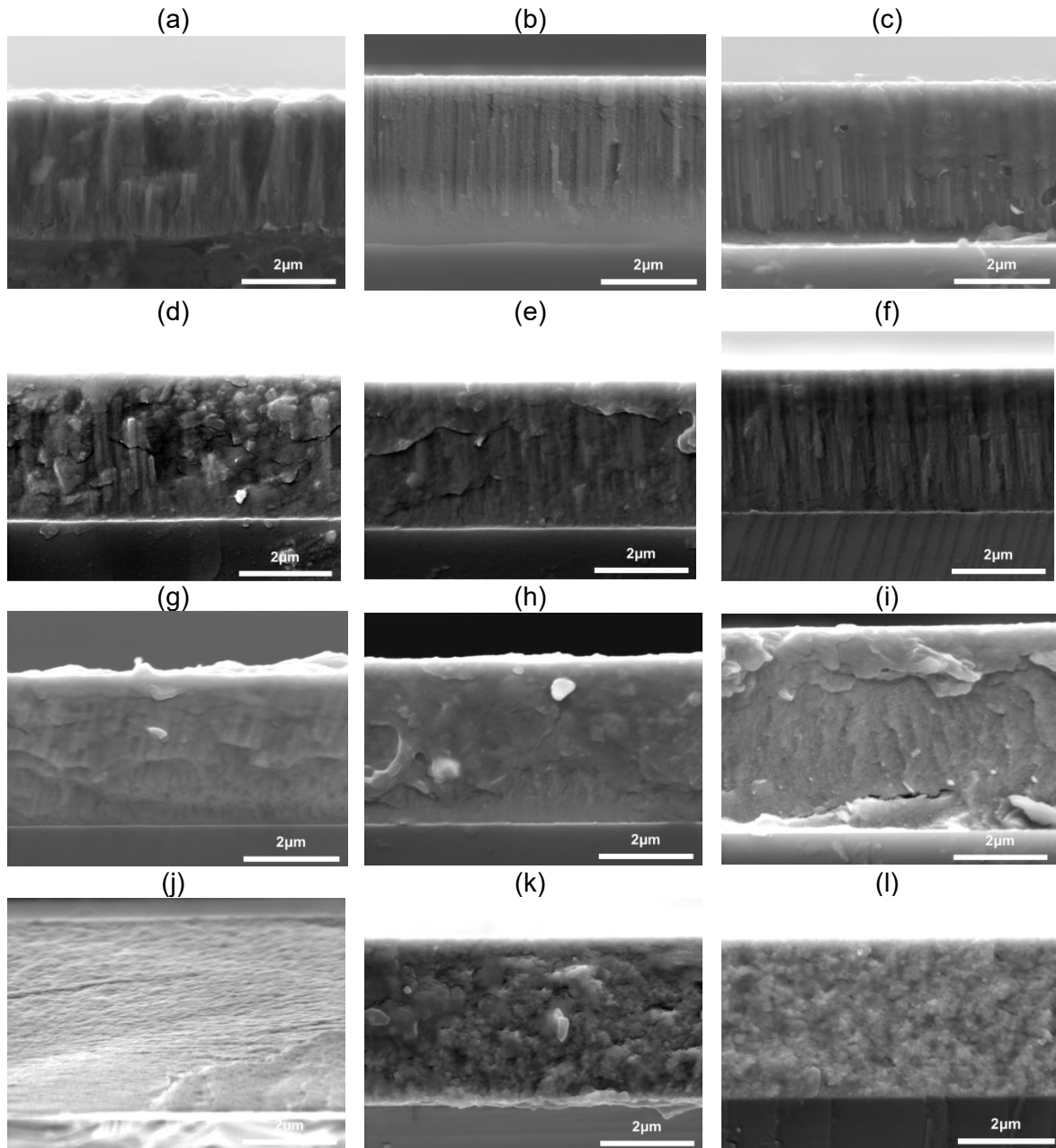


Figure 4-4 SEM images for cross-section of the ETO after annealing at 600°C in different sputtering positions, (a) 10.5, (b) 23, (c) 35.5, (d) 54.5, (e) 67, (f) 79.5, (g) 98.5, (h) 111, (i) 123.5, (j) 142.5, (k) 155, (l) 167.5 mm.

The surface microstructure of the ETO thin films after annealing at 600°C was examined in top view using SEM, as depicted in Figure 4-5. Across all samples, a homogenous surface was maintained following annealing at 600°C, as evidenced in the images captured at magnifications of 500x and 10kx with a 10k eV acceleration voltage. However, subtle dense protrusions were observed on the surfaces of thin films deposited at closer sputtering positions, attributed to the columnar structure observed in the cross-sectional images. Additionally, these protrusions became more

pronounced after annealing at 600°C. Furthermore, irregular small pits persisted on the surfaces of films deposited at sputtering positions exceeding 140 mm. Notably, numerous cracks appeared on several thin film samples after annealing. Annealing facilitates the release of internal stresses in coatings, which may have developed during the deposition process, thereby enhancing the crystalline structure of the film. This improvement in crystal structure can lead to an optimised bandgap in the coated film. However, it is possible that the brittleness of the substrate during annealing leads to the formation of microscopic defects, such as cracks within the coating. These defects may contribute to the film's reduced adhesion and its subsequent detachment when subjected to adhesion tape testing.[144] Figure 4-5 specifically presents thin films deposited at sputtering positions of 10.5, 35.5, 79.5, and 167.5 mm, while the surface microstructure of ETO thin films at other sputtering positions is elaborated in Appendix A -- SEM images for surface of ETO thin films.

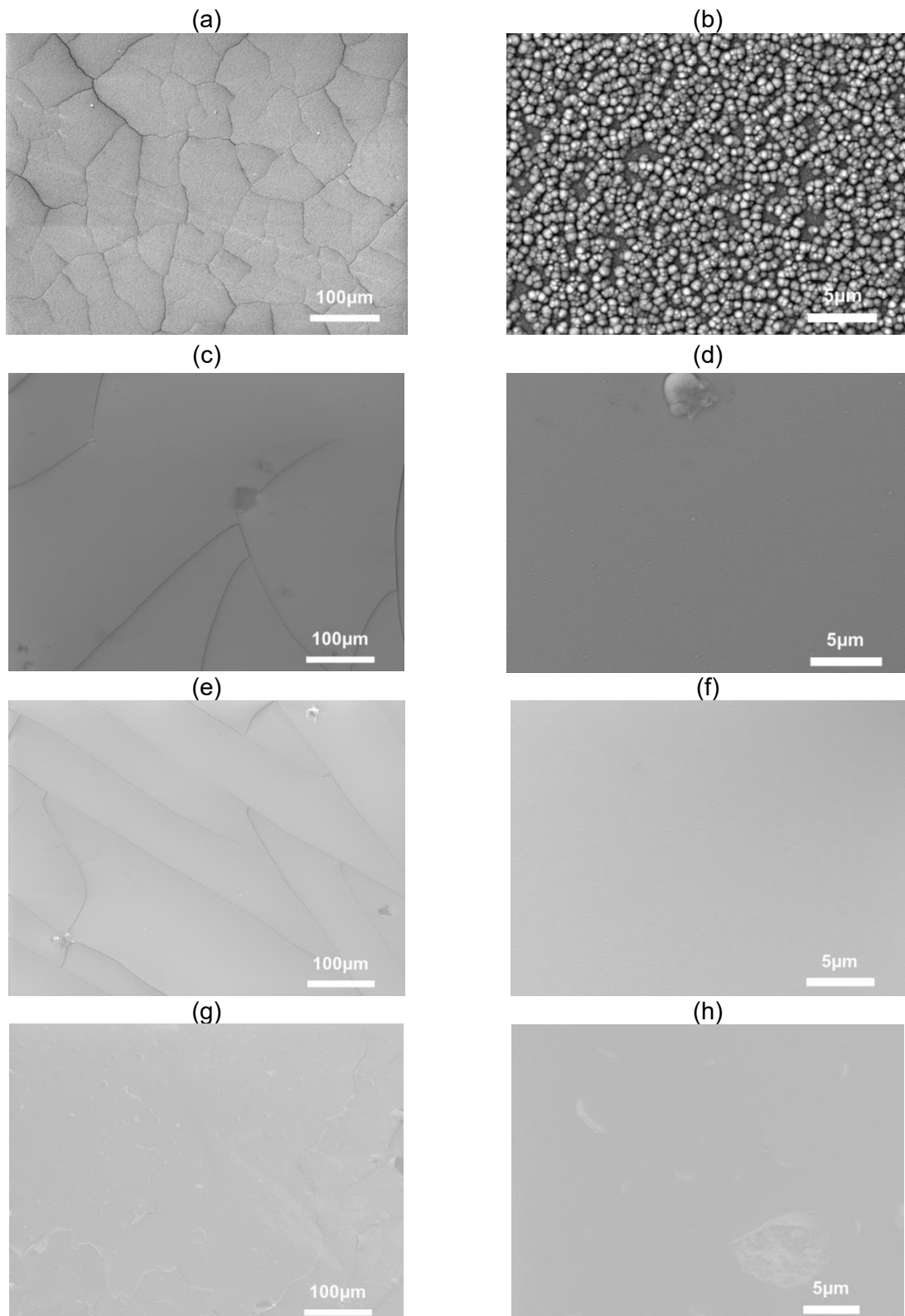


Figure 4-5 SEM images with 500 and 10k magnification for surface of the ETO after annealing at 600°C in different sputtering positions, (a) & (b) 10.5, (c) & (d) 35.5, (e) & (f) 79.5, (g) & (h) 167.5 mm.

The cross-sectional and surface morphology of the thin films, both before and after annealing, is examined through SEM scanning, providing clear insights into the microstructure of the films. Furthermore, a more comprehensive analysis of the chemical composition of these thin films, including elemental mapping before and after annealing, is conducted using EDX analysis, as depicted in the accompanying Figure 4-6 and Figure 4-7. These figures illustrate thin films featuring different europium ratios at 4.7 at%, 9.1 at%, 44.4 at% and 99 at% Eu/(Eu+Ti) corresponding to 23, 67, 111 and 155 mm sputtering positions respectively. Additionally, it is noteworthy that the areas mapped by EDX correspond to the same regions observed in SEM imaging. Furthermore, the EDX mappings for the other compositions of the ETO thin films are listed in the Appendix B -- EDX mappings of ETO thin films.

The elemental analysis conducted via EDX mapping reveals that Eu, Ti, and O atoms maintain an even distribution within the films both before and after the annealing at 600°C. The oxygen content is not uniform when the ETO thin films as-deposited. There are more oxygen interstitials on the surface of the thin films as-deposited because of the amorphous structure of the thin films. Moreover, The thin films are crystallised and more stoichiometric after annealing at 600°C, and the oxygen contents of thin films are more uniform. However, the positions of sputtering exhibit a notable influence on the concentrations of europium and titanium. Thin films with lower percentages of Eu/(Eu+Ti), associated with sputtering positions closer to the TiO₂ target, display denser Ti and sparser Eu. Conversely, thin films with higher percentages of Eu/(Eu+Ti), linked with sputtering positions nearer to the Eu₂O₃ target, exhibit denser Eu and sparser Ti.

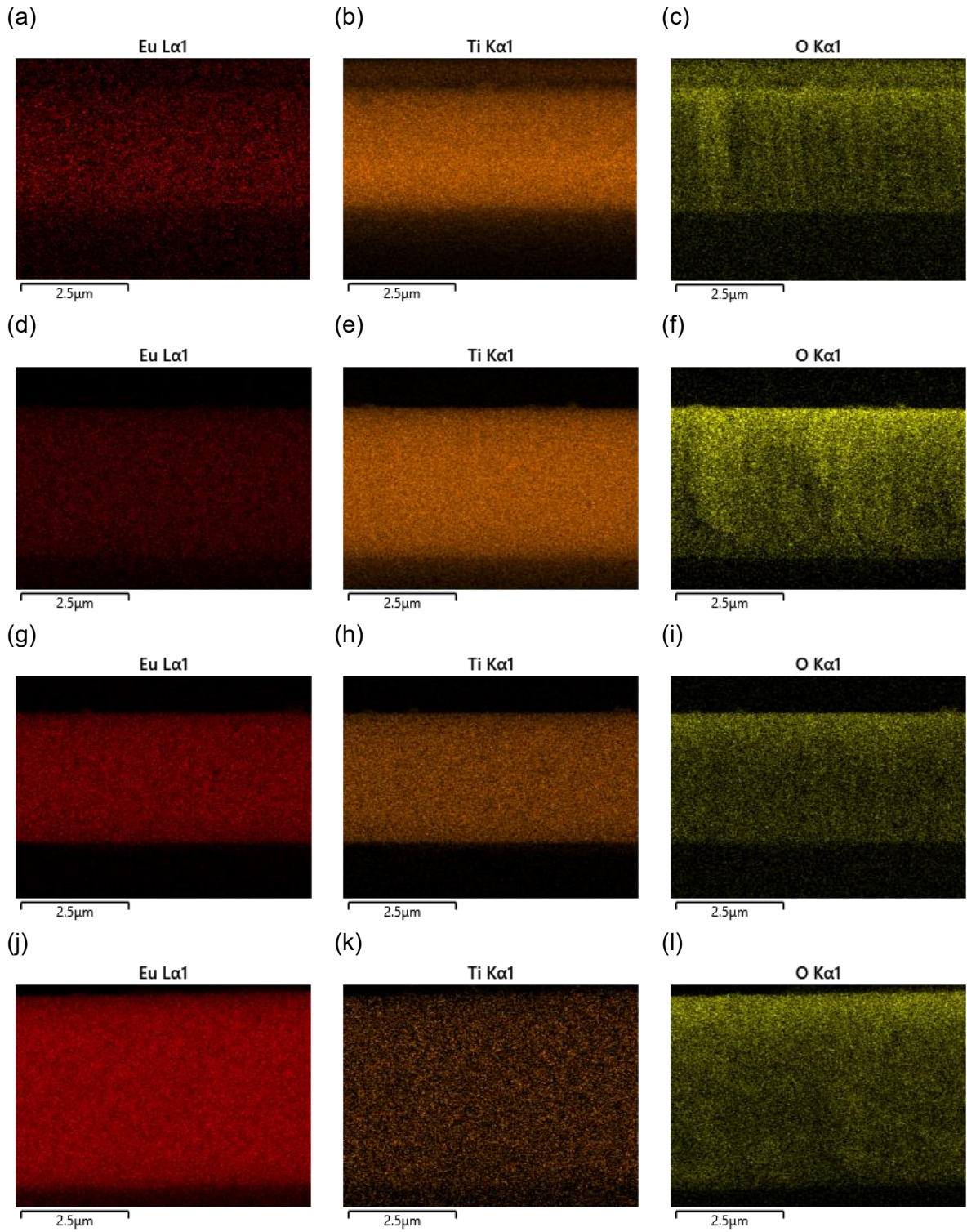


Figure 4-6 EDX mapping for the samples As-deposited with Eu, Ti and O composition in thin films at different concentration, (a) (b) (c) 4.7 at% Eu/(Eu+Ti), (d) (e) (f) 9.1 at% Eu/(Eu+Ti), (g) (h) (i) 44.4 at% Eu/(Eu+Ti), (j) (k) (l) 99 at% Eu/(Eu+Ti).

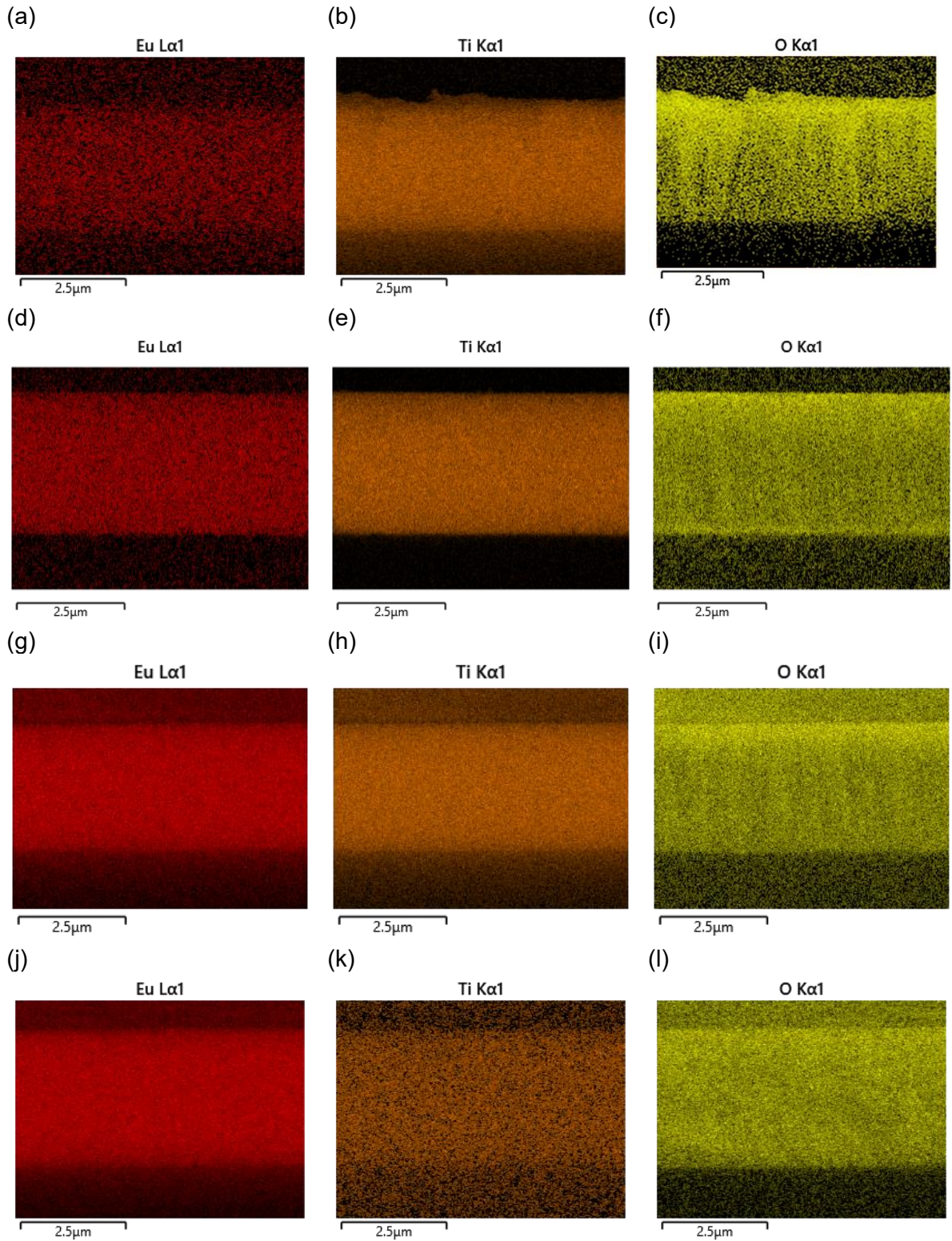


Figure 4-7 EDX mapping for the samples after annealing at 600°C with Eu, Ti and O composition in thin films at different concentration, (a) (b) (c) 4.7 at% Eu/(Eu+Ti), (d) (e) (f) 9.1 at% Eu/(Eu+Ti), (g) (h) (i) 44.4 at% Eu/(Eu+Ti), (j) (k) (l) 99 at% Eu/(Eu+Ti).

4.2.3 Crystalline phase and crystal orientation

The XRD pattern about these luminescence thin films which have various molar ratios of x at% Eu/(Eu+Ti) ($x = 0-100$) and the quartz substrate are achieved. The crystallised structural properties of these thin films as-deposited and after annealed at 600°C are analysed by the XRD results shown in Figure 4-8 and Figure 4-9 respectively, these pattern are measured by powder XRD. The thin film samples are synthesised of different europium ratios of 0 at%, 7.2 at%, 29.2 at%, 75.5 at%, 98.2 at%, 100 at% Eu/(Eu+Ti) and the quartz substrate are illustrated in the XRD patterns.

The Debye-Scherrer equation is applied to determine the average grain size of crystals.

$$D = \frac{k\lambda}{\beta \cos\theta}$$

D is the crystallite size in nm, k is the shape constant (0.9), λ is the X-ray wavelength of Cu- α radiation in nm, θ is the Bragg's angle in degrees, and β is the observed peak width at half-maximum peak height in rad.[142] The synthesis of TiO₂ at temperatures below 600°C typically results in the formation of the anatase phase. In contrast, the rutile phase is generally obtained at temperatures exceeding 800°C. Thus, the annealing temperature required to produce the anatase phase is significantly lower than that needed for the rutile phase transformation.[143] Anatase TiO₂ possesses a wider bandgap compared to its rutile counterpart, resulting in superior absorption properties in the UV region. Moreover, under UV excitation, anatase exhibits higher PL intensity than rutile.[155,156]

In Figure 4-8, most samples exhibit broad and inconspicuous peaks when the samples are as-deposited, whereas in Figure 4-9, sharper and more prominent peaks emerge after annealing at 600°C. Both Figure 4-8 and Figure 4-9 XRD patterns reveal that the 0 at% Eu/(Eu+Ti) (100 at% TiO₂) thin film sample, whether as-deposited or annealed at 600°C, demonstrates an anatase phase lattice (*anatase*-TiO₂) (ICSD 202242).[157,158] The patterns display two distinctive diffraction peaks at $2\theta = 25.32^\circ$ and 47.98° corresponding to the (101) and (200) anatase crystal phases, with the (101) plane exhibiting the most intense reflection. Anatase crystallised lattice size is $a=0.3805$ nm, $c=0.942$ nm and the grain size of nanocrystallites is 22.7 nm as-deposited, crystallised lattice size is $a=0.3789$ nm, $c=0.943$ nm and the grain size of nanocrystallites are 58.4 nm after 600°C annealing. The 100 at% Eu/(Eu+Ti) (100 at% Eu₂O₃) thin film sample is a monoclinic phase lattice (*m*-Eu₂O₃) (ICSD 631461).[159]

The as-deposited thin film composed entirely of Eu_2O_3 is found to be amorphous, as demonstrated in Figure 4-8, with no discernible strong peaks evident. The 100 at% Eu_2O_3 monoclinic illustrated in Figure 4-9 patterns display distinctive diffraction peaks at 27.97° (111), 29.35° (401), 30.93° (003), 31.44° (310), 32.19° (11-2), 38.89° (600), 40.85° (51-1), 42.14° (601), 47.20° (313), 50.61° (020), 51.81° (80-1), 53.66° (404), 55.16° (022) and 59.94° (42-2). The monoclinic lattice constant is $a=1.4108$ nm, $b=0.3604$ nm, $c=0.8806$ nm and the grain size of nanocrystallites is 61 nm after 600°C annealing. Upon annealing at 600°C , crystallisation becomes apparent within the film, only the 0 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ thin film has crystalline structure as-deposition.

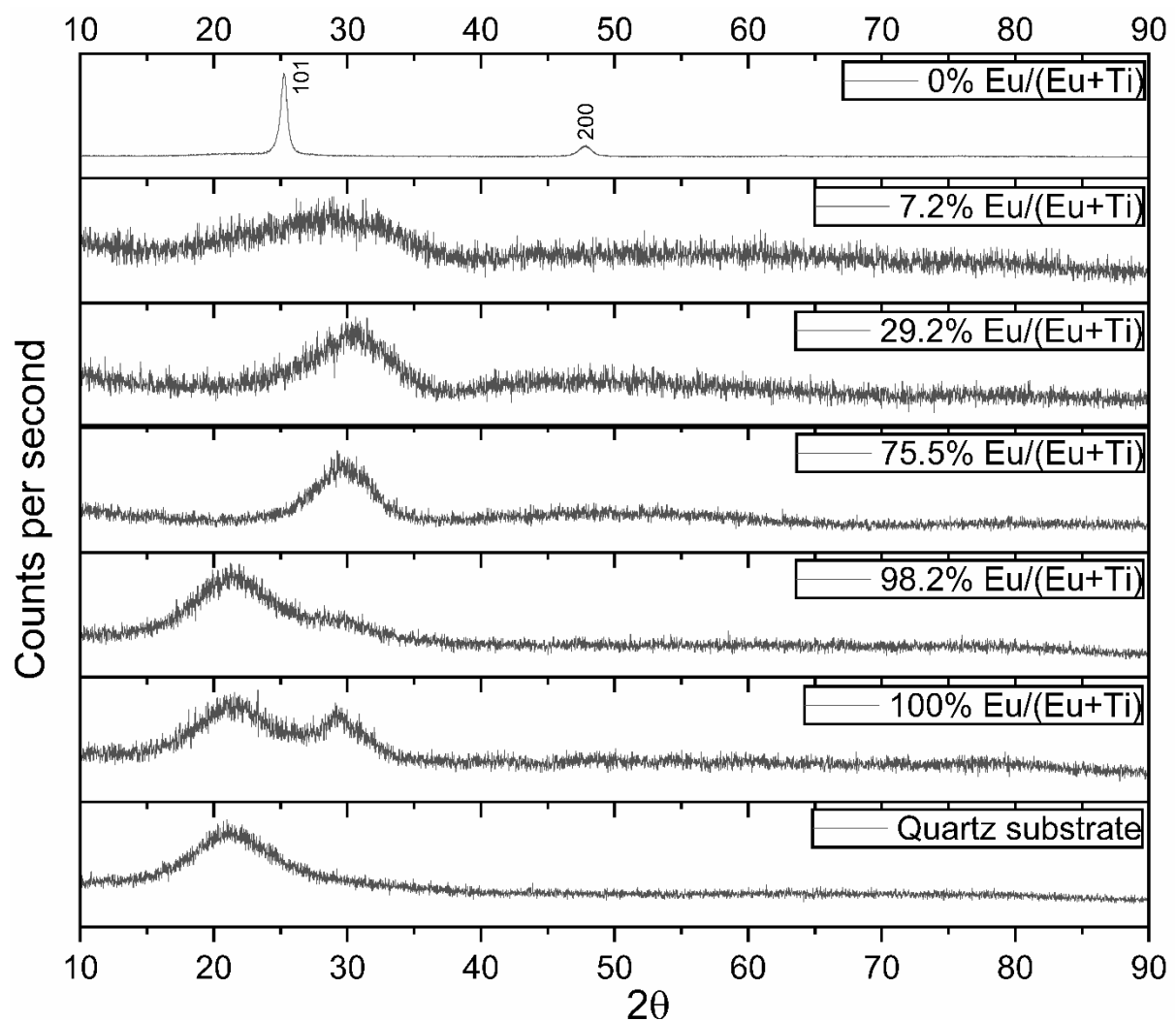


Figure 4-8 XRD patterns for the samples of the as-deposited with the europium ratios of 0 at%, 7.2 at%, 29.2 at%, 75.5 at%, 98.2 at%, 100 at% $\text{Eu}/(\text{Eu}+\text{Ti})$, and the Quartz substrate from Powder XRD.

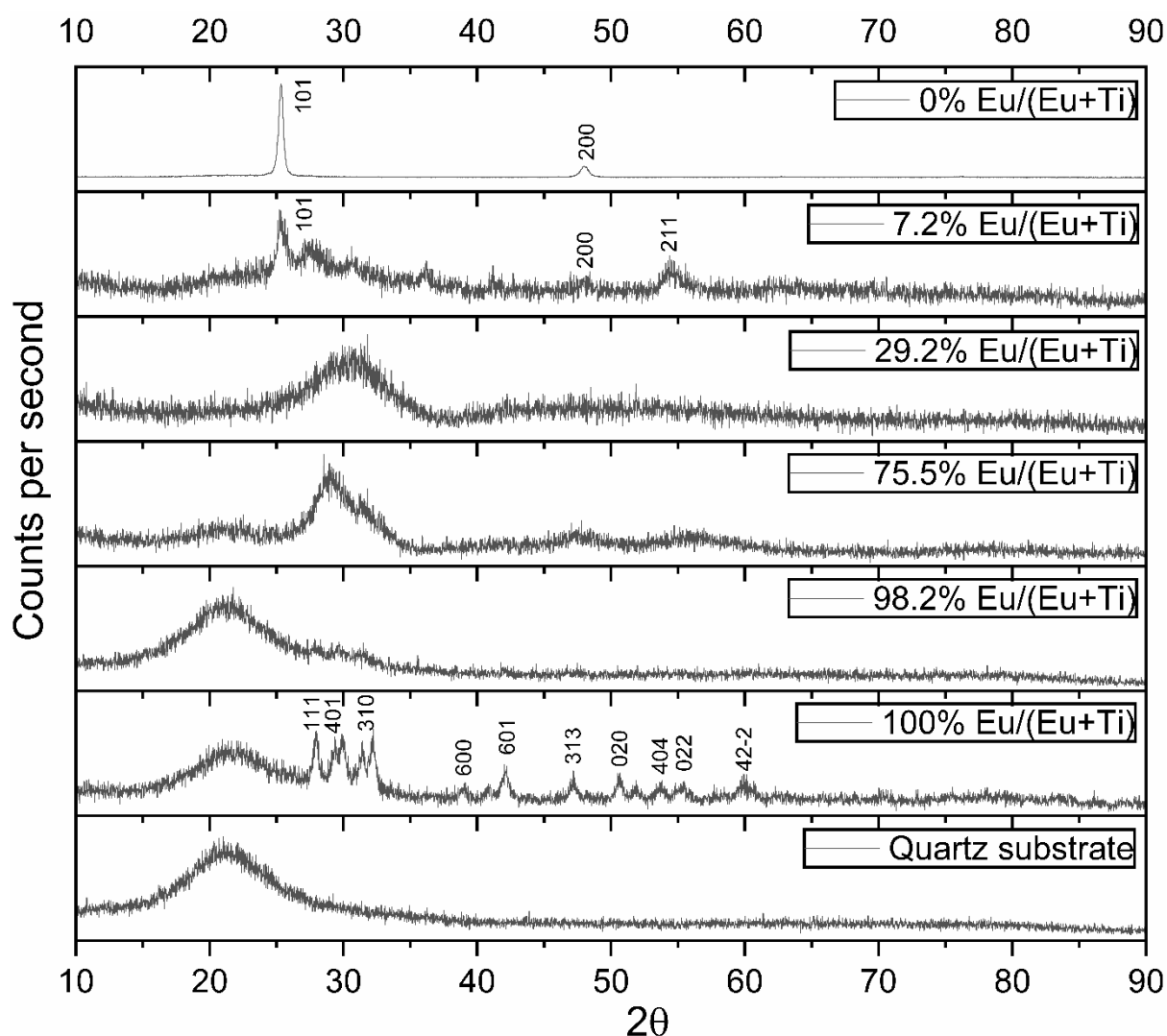


Figure 4-9 XRD patterns for the samples annealed at 600°C with the europium ratios of 0 at%, 7.2 at%, 29.2 at%, 75.5 at%, 98.2 at%, 100 at% Eu/(Eu+Ti) and Quartz substrate from Powder XRD.

To verify the XRD results, thin film XRD analysis was conducted on the ETO thin films, and the resulting patterns are presented in Figure 4-10 and Figure 4-11. A comparison between the powder and thin film XRD results reveals that the patterns obtained from thin film XRD exhibit reduced noise and smoother profiles than those from powder XRD. Moreover, the powder and thin film XRD patterns remain similar for the same ETO thin films both before and after annealing at 600°C. However, it is noteworthy that the patterns obtained from thin film XRD analysis of thin films with a composition of 98.2 at% Eu/(Eu+Ti) before annealing closely resemble those from powder XRD analysis of 100 at% Eu/(Eu+Ti) before annealing. This discrepancy may be attributed to the inherent limitations of powder XRD in accurately detecting thin films. In contrast,

thin film XRD offers more precise measurements of thin films. Additionally, thin films with compositions exceeding 90 at% Eu/(Eu+Ti), which are amorphous before annealing and exhibit a fine-grained structure based on SEM images, pose challenges for powder XRD analysis, leading to the appearance of substrate signals in the XRD patterns.

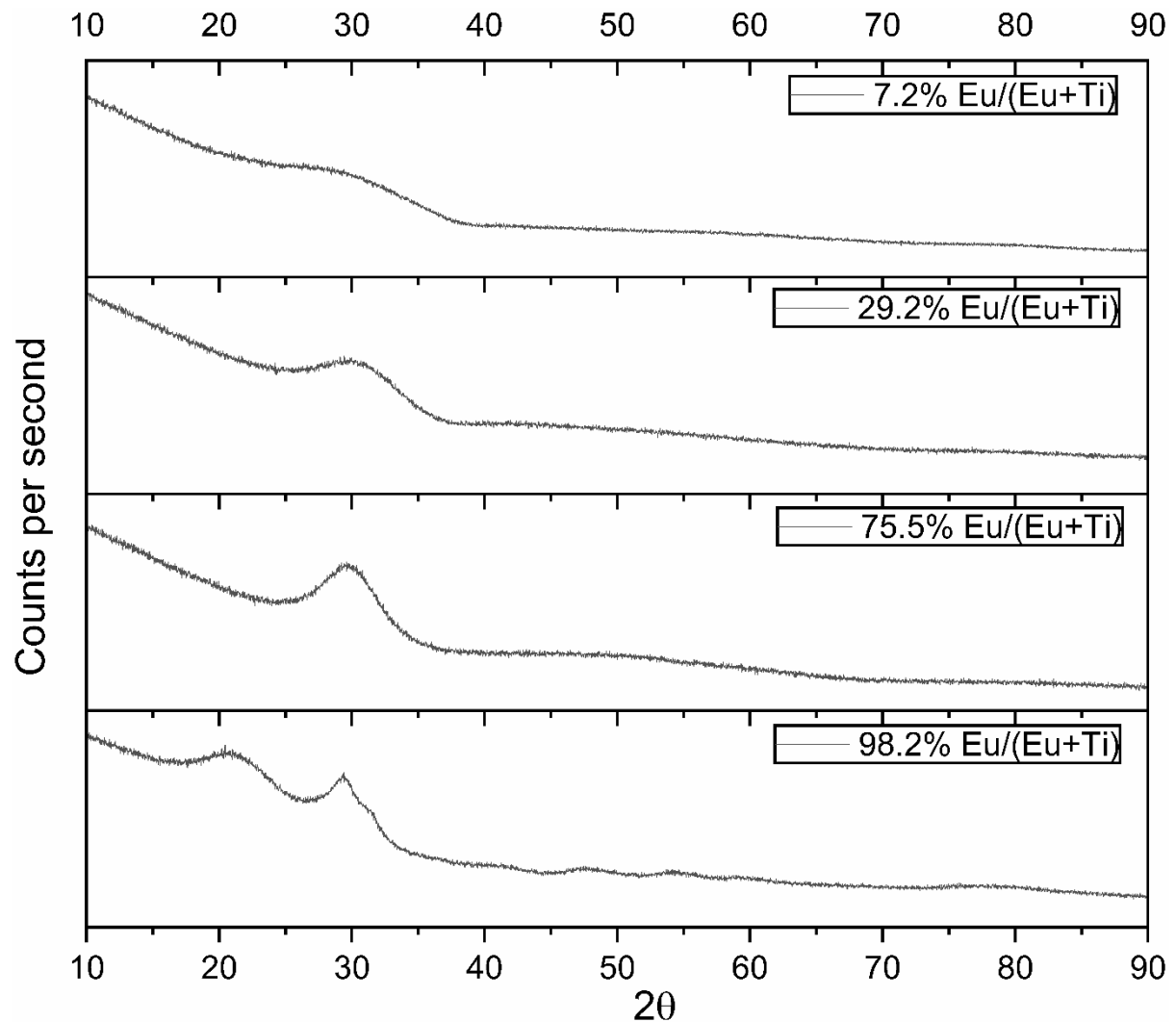


Figure 4-10 XRD patterns for the samples as-deposited with the europium ratios of 0 at%, 7.2 at%, 29.2 at%, 75.5 at%, 98.2 at%, 100 at% Eu/(Eu+Ti) and Quartz substrate from Thin Film XRD.

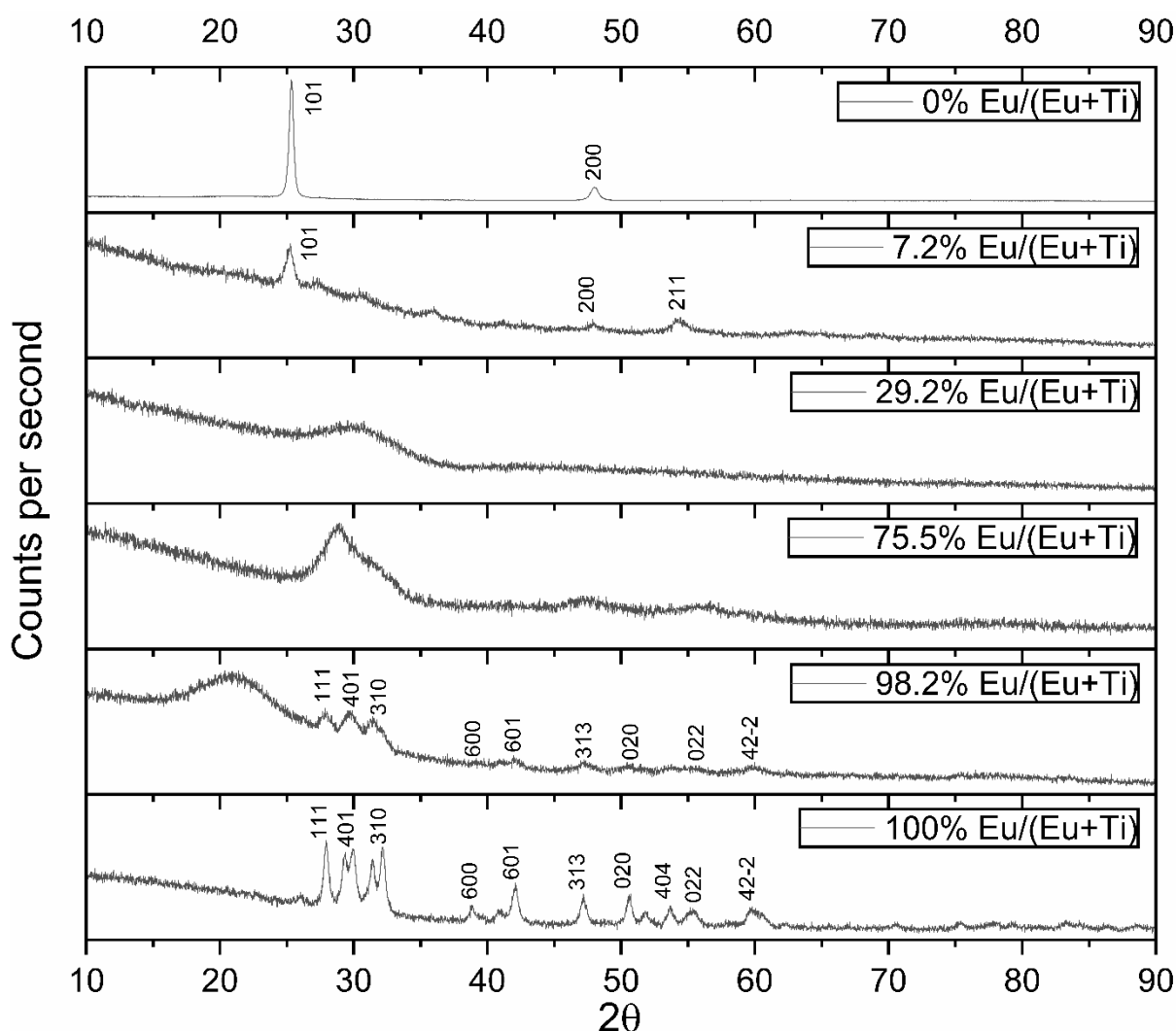


Figure 4-11 XRD patterns for the samples annealed at 600°C with the europium ratios of 0 at%, 7.2 at%, 29.2 at%, 75.5 at%, 98.2 at%, 100 at% Eu/(Eu+Ti) and Quartz substrate from Thin Film XRD.

4.2.4 Raman (Before and after annealed)

Vibration modes of molecules in the luminescence thin films are investigated by Raman spectroscopy. The Raman spectra of these luminescence thin films are observed and shown in Figure 4-12 & Figure 4-13. Various peaks illustrated in the Raman spectra of pure TiO_2 simulate with 7.2 at% Eu/(Eu+Ti) after annealed at 600°C (Figure 4-13) are 144(E_g), 401(B_{1g}), 521($A_{1g}+B_{1g}$) and 637 cm^{-1} (E_g) correspond to the Raman active mode. The specific large intensity peak at Raman shift 144 cm^{-1} indicates the anatase phase of TiO_2 . [160,161] The pure TiO_2 sample is the least complex compound analysed, which exhibits a strong resemblance between XRD (Figure 4-8 & Figure 4-9) and Raman (Figure 4-12 & Figure 4-13) analyses. The as-

deposited thin film consisting entirely of Eu_2O_3 is confirmed to be amorphous, as shown in Figure 4-12, which displays broad peaks in the Raman spectra and XRD patterns. After annealing, the 100 at% Eu_2O_3 thin film exhibits several distinct peaks, as illustrated in Figure 4-13. These peaks are characteristic of the monoclinic structure of Eu_2O_3 , indicating a transition from the amorphous to a more crystalline phase following the annealing process. Various peaks illustrated in the Raman spectra are $111(\text{B}_g)$, $175(\text{A}_g)$, $243(\text{A}_g)$, $282(\text{B}_g)$, $424(\text{B}_g)$ and $583\text{ cm}^{-1} (\text{E}_g)$ correspond to the Raman active mode.[162]

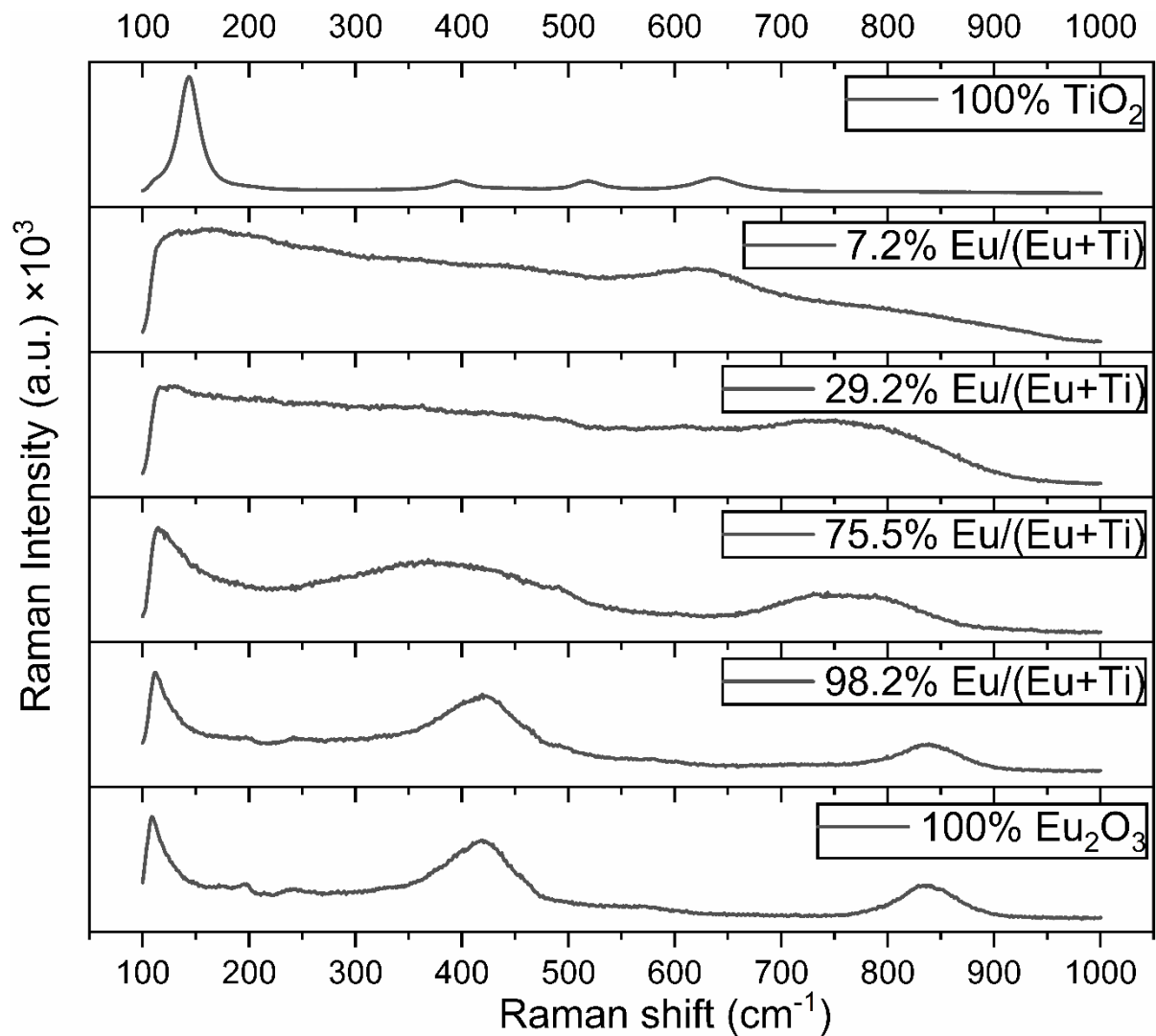


Figure 4-12 Raman spectra of ETO, pure TiO_2 and pure Eu_2O_3 thin films as-deposited.

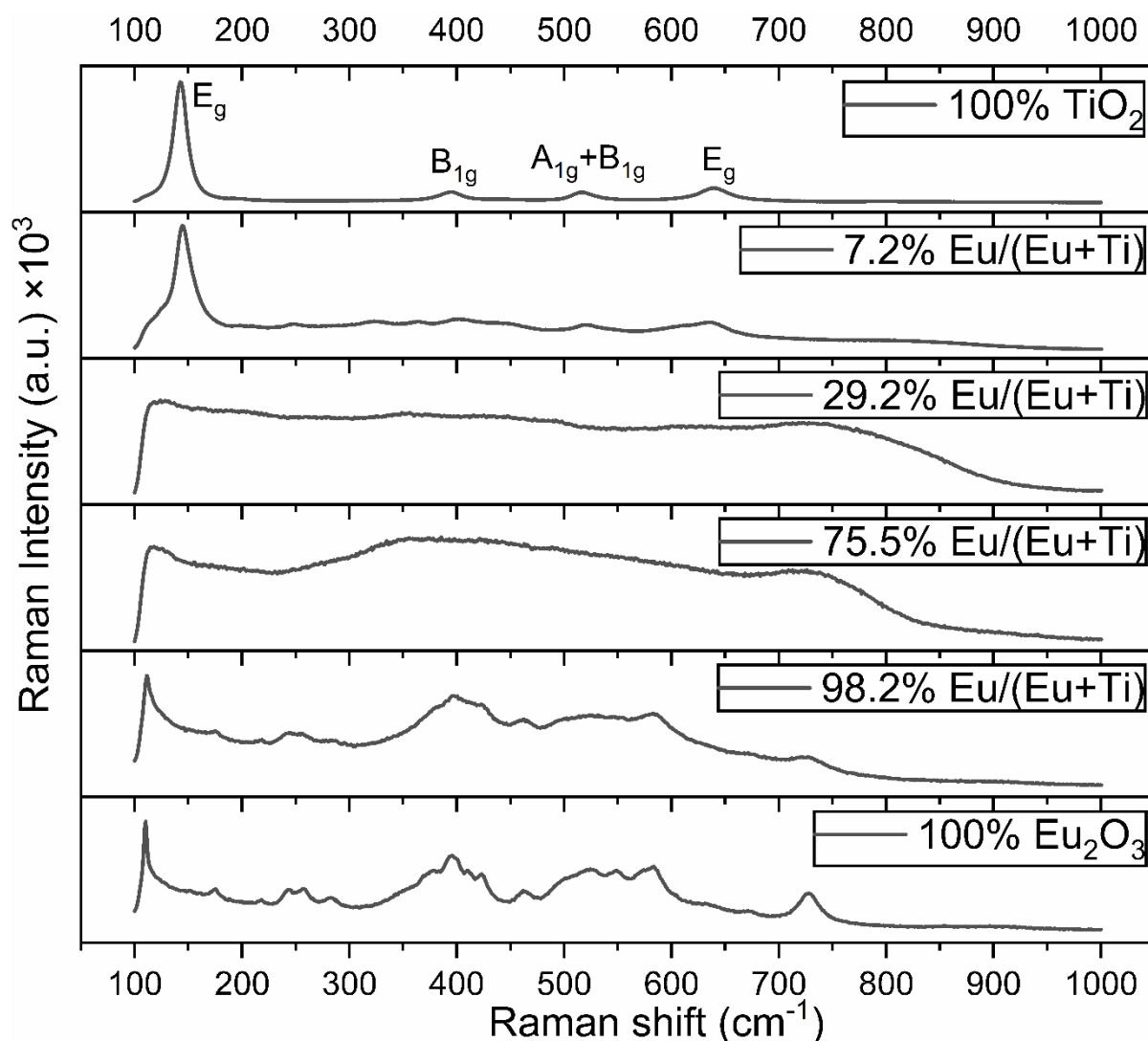


Figure 4-13 Raman spectra of ETO, pure TiO_2 and pure Eu_2O_3 thin films after annealing at 600°C .

4.3 Discussion

Correlation emerges between red light emission and sputtering position is intuitively illustrated in Figure 4-1. Brighter red areas typically correspond to a Europium ratio lower than 50 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ and sputtering positions below 90 mm. Moreover, thin films within this region exhibit a columnar microstructure, as evidenced by cross-sectional morphology images obtained via SEM. Nevertheless, the thin films featuring a europium ratio exceeding 50 at% $\text{Eu}/(\text{Eu}+\text{Ti})$, characterised by small grains as observed in SEM images, do not demonstrate red light emission. Unfortunately, the size of these grains is insufficient for the precise identification of disordered line textures and agglomerated grains. The microstructure is distinguished in four zones

demonstrated in Figure 4-14, zone 1 and 2 illustrate the thin films with lower than 50 at% Eu/(Eu+Ti), and zone 3 and 4 illustrate the thin films with higher than 50 at% Eu/(Eu+Ti). Consequently, this microstructure contributes to the absence of fluorescence in thin films as-deposited with a high europium ratio (more than 50 at% Eu/(Eu+Ti)). Conversely, films characterised by a columnar microstructure exhibit significantly brighter red fluorescence. The "Thornton Diagram" represents the nanostructural evolution of thin films synthesised through sputtering under varying deposition gas pressures and substrate temperatures. The diagram highlights how these parameters influence the microstructure of the thin films, with the substrate temperature, T_s , and the melting point of material, T_M , serving as a key reference point in the process.

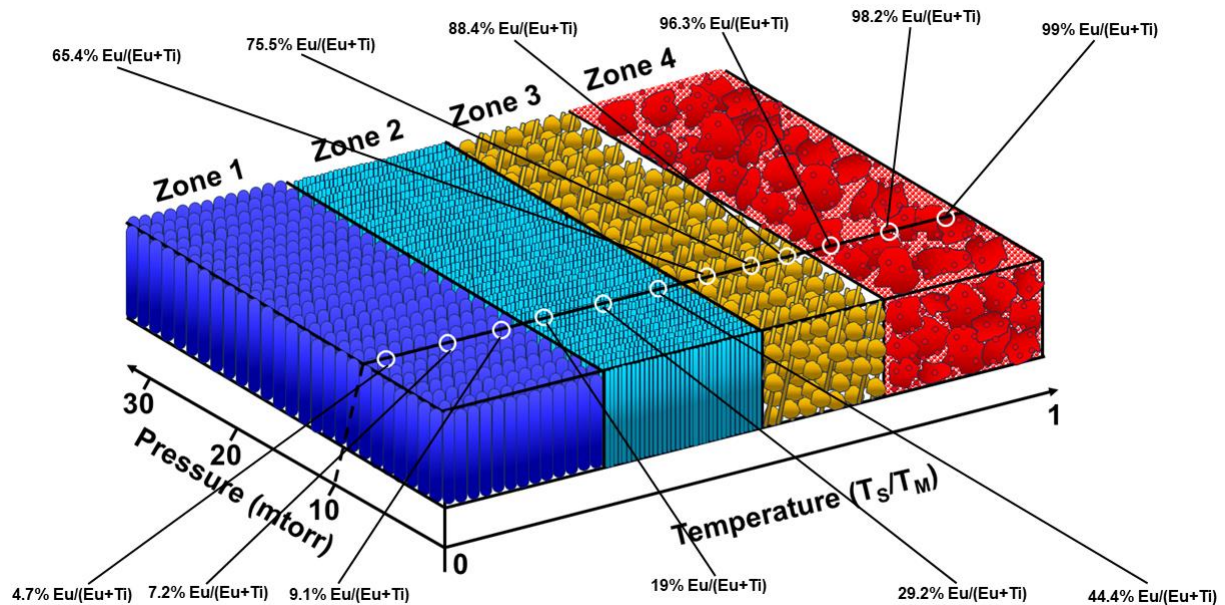


Figure 4-14 Thornton diagram of ETO thin films fabricated by combinatorial sputtering at different sputtering positions.

The presence of Eu and Ti is uniformly distributed within the luminescence thin films exhibited in the EDX mapping, although the atom concentrations within various percentage ranges are situated at different sputtering positions. However, O seems to be a higher concentration on the surface than near the substrate, which can be compared with the EDX line scan for the Oxygen element (illustrated in Appendix C -- EDX Oxygen element Line scan for the cross-section of the ETO thin films). There are more oxygen vacancies on the surface of the thin films as-deposited because the amorphous structures of the thin films have a higher susceptibility of the thin film

surface to oxidation. Films characterised by lower percentages of $\text{Eu}/(\text{Eu}+\text{Ti})$ are typically associated with sputtering positions situated closer to the TiO_2 target (lower than 90 mm in sputtering positions). Conversely, films featuring higher percentages of $\text{Eu}/(\text{Eu}+\text{Ti})$ are often linked with sputtering positions nearer to the Eu_2O_3 target (higher than 90 mm in sputtering positions).

Our finding shows that the co-sputtering of TiO_2 and Eu_2O_3 in combinatorial configuration results in a variation in $\text{Eu}/(\text{Eu}+\text{Ti})$ ratio as a function of sample positioning that can be approximated by a logistic regression. The profile of such logistic regression (Figure 4-1 c) is influenced by the deposition parameters such as the positioning of the samples relative to each target, the distance between the targets, and the power density of each sputtering target. In this study, we demonstrated that the positioning of the samples plays a significant role in the variation of film compositions, where samples closer to the TiO_2 target have lower $\text{Eu}/(\text{Eu}+\text{Ti})$ while those nearer to the Eu_2O_3 target have higher $\text{Eu}/(\text{Eu}+\text{Ti})$. As the distance between the samples and the targets also affects the deposition rate and deposition area, a larger distance between the targets and/or a lower power density of the sputtering targets may lead to a logistic regression profile with a gentler transition. Conversely, a smaller distance between the targets and/or higher power density leads to a logistic regression curve characterised by a narrower range and a steeper slope. Moreover, the results of the elemental analysis indicate a large variation of the Eu ratio from 19 at% to 75.5 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ in just a span of 55 mm takes place somewhere between the two magnetrons. While this is not explored in this study, we believe the logistic profile can be further tuned by varying the placement of the magnetrons and the power setting of each magnetron, thus opening a pathway to tailor film composition for rapid investigation or discovery of complex materials systems beyond our Eu_2O_3 - TiO_2 model systems.

Unlike the XRD pattern of as-deposited TiO_2 thin films that strongly shows the anatase phase of TiO_2 , the XRD patterns of as-deposited ETO thin films with Eu ratio higher than 1 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ exhibit broad peaks, which indicate that these films are dominated by an amorphous matrix with anatase TiO_2 nanocrystallites are either absent or present in minimal amounts with diameters of <2 nm.[163] This strongly suggests that the incorporation of a small amount of Eu^{3+} is sufficient to suppress the formation of anatase TiO_2 crystallites. This is in contrast to the previously reported

studies that reported the formation of rutile TiO_2 by magnetron sputtering or the presence of cubic phases of Eu_2O_3 without annealing.[164] The presence of such microstructures can be confirmed by transmission electron microscopy, which should be performed in future study. Our PL and XRD data indicate that the ETO films with 4.7 at% -- 44.4 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ are mildly luminescent despite being amorphous. At 7.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$, nearly all Eu^{3+} ions reside within the amorphous TiO_2 matrix.[165]

Most the thin film samples are identified as nanocrystals as-deposited by the XRD patterns, which illustrate broad peaks, except the pure TiO_2 thin film as-deposited has sharp peaks. The smaller size of particles has more peak broadening exhibited in the XRD patterns.[163] The XRD pattern of pure TiO_2 reveals crystalline features, with notable peaks at $2\theta = 25.32^\circ$ and 47.98° . These peaks correspond to the $\langle 101 \rangle$ and $\langle 200 \rangle$ planes of the anatase phase of TiO_2 (space group: $I4_1/amd$), respectively. The lattice parameters of the anatase structure are measured as $a = 0.3789$ nm and $c = 0.943$ nm, with a crystallite size of 58.4 nm.[147] In the XRD pattern of thin film with 7.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$, the discovery of characteristic peaks at an annealing temperature of 600°C suggests the formation of crystalline clusters, corresponding to the anatase phase of TiO_2 and nano-sized rutile TiO_2 clusters, the composition ratio between the anatase and rutile phases is determined to be 68:32. Both thin films with a europium ratio higher than 90 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ and pure Eu_2O_3 are amorphous before annealing illustrated the background quartz substrate in the XRD patterns, no apparent peaks do suggest fully amorphous or nanocrystallites. In the XRD pattern of pure Eu_2O_3 film, the discovery of characteristic peaks at an annealing temperature of 600°C indicates the formation of crystalline clusters, which can be associated with the monoclinic phase lattice ($m\text{-Eu}_2\text{O}_3$) (space group: $C2/m$, 12). The monoclinic lattice constants are determined to be $a = 1.4108$ nm, $b = 0.3604$ nm, and $c = 0.8806$ nm, with a corresponding crystallite size of 61 nm. Both the XRD and Raman findings reveal that the thin films with 0 at%--10 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ thin films exhibit the anatase phase. In the absence of other bands, it is challenging to determine the presence of an ordered rutile phase and suggest the rutile phase was not detected.

4.4 Conclusion

In this study, various europium ratios with ETO luminescence thin films are synthesised by combinatorial sputtering for comparison. This production technique can synthesise thin film samples with a seamless variation in Europium ratios, ranging from 0 at% to 100 at% in Eu/(Eu+Ti). The thin film specimens generated through this fabrication approach are utilised for testing to ensure a more comprehensive and comparable assessment. The characteristics of the thin films are detected by SEM, EDX, XRD and Raman before and after annealing. The range of europium ratio (at%Eu/(Eu+Ti)) is from 0 at% to 100 at%, and the annealing temperature is 25 °C, 450 °C and 600 °C, which are able to influence the structural properties and optical properties of the thin films. The vertically oriented columnar microstructure is found in the thin film samples with low europium ratios by SEM, and the average size of the columnar has become narrower and sharper after 600 °C annealing. However, the samples with high europium ratios have disordered line textures and the agglomerated grains illustrated after 600 °C annealing. Crystallised structures of the thin films before and after annealing are investigated by XRD spectroscopy. There are more phases and crystallised structures are generated by annealing. The strongest intensity vibration at 144(E_g) in Raman spectra is increased after 600 °C annealing with low europium ratios.

5 Optical and fluorescence properties of ETO synthesised by Combinatorial Sputtering

5.1 Introduction

Lanthanide materials have been extensively researched in the last decade due to their distinct properties, particularly their unique luminescent characteristics.[6] Titania is recognised as a commendable optoelectronic material, finding applications in the fields of photocatalysis, photochromic technologies, and solar cells.[166]

TiO₂ anatase and rutile are the only two attainable through synthesis methods conducted at atmospheric pressure and within the temperature spectrum of 0 to 1200 °C.[148–150] TiO₂ is characterised by its wide optical bandgaps, which are 3.0 eV for the rutile phase, 3.2 eV for anatase, and 3.3 eV for the brookite phase. Additionally, TiO₂ exhibits high refractive indices, with values of 2.609 for rutile, 2.488 for anatase, and 2.583 for brookite. These properties contribute to its utility in various optical and electronic applications.[147] These outstanding properties position TiO₂ as an ideal material for photocatalytic applications.[109]

Recent research has increasingly concentrated on the development of titania-based nanophosphors doped with various RE ions, owing to their exceptional luminescent properties. These materials are particularly valued for their sharp emission peaks, which arise from characteristic intra *f-f* electronic transitions, as well as their large Stokes shift and extended decay times, making them promising candidates for advanced luminescence applications.[109] The incorporation of lanthanide ions as luminescence centres into various host lattices has significantly enhanced the performance of luminescent materials.[146] However, the emission intensity of these ions can differ depending on the host matrix, which is closely linked to the local crystallographic environment surrounding the lanthanides. This relationship provides insight into the structural characteristics of TiO₂ and how they influence the varying emission intensities of lanthanide transitions, effectively allowing the material to serve as a structural probe.[145] Within the array of RE elements, the Eu³⁺ ion stands out as an exemplary pure red-emitter. Its distinctive and confined red emission, observed in the characteristic $^5D_0 \rightarrow ^7F_2$ transition under UV radiation, makes it an ideal choice.

Additionally, the PL emission from Eu^{3+} ions is remarkably responsive to their environment within the host matrix.[105,106]

ETO thin films to the additional annealing process, notable changes were observed, including an augmentation in crystallite size, a reduction in defect states, and the formation of voids in the film microstructure. These alterations significantly influenced the PL efficiency.[151] The investigation of transmittance in ETO is conducted through UV-Vis spectroscopy, and the calculation of the bandgap of samples is derived from this data.[167] The PL properties of ETO thin films are measured by fluorescence spectroscopy. Upon excitation with visible light, the $\text{Eu}:\text{TiO}_2$ samples exhibit distinctive photoluminescence, corresponding to the $^5\text{D}_0 / ^7\text{F}_i$ ($i = 0, 1, 2, 3, 4$) transitions of Eu^{3+} ions within the visible spectral range.[108] In the context of solar cell applications, the efficiency is assessed using a solar simulator.[168]

This research study centres on the luminescence properties that are explicated in correlation with the structural attributes of the formed nanocrystals and the temperature of the thermal treatment. The findings presented herein contribute essential insights into the intricate interplay between the structure, morphology, and luminescence properties of the developed nanocrystals.

5.2 Results

5.2.1 Visual inspection

Sizes of substrates are 25×25 mm quartz during this study, and samples on the quartz are used for characterisation measurement and further experiments. ETO luminescence thin films will glow red when exposed to UV light from 350 nm to 460nm in some areas. The fluorescence phenomenon is shown on the samples with 25×25 mm quartz as-deposited in Figure 5-1. The fluorescence position and intensity are changed after annealing at 450°C and 600°C shown in Figure 5-1, the x-axis shows the Europium ratio of samples, and the y-axis shows the heat treatment states of samples. Each sample has fluorescence after annealing at 600°C even the samples with the Europium rates higher than 50 at% have fluorescence to glow red. Furthermore, the red fluorescence of the samples between 0 and 50 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ annealed at 600°C is much brighter than that of samples annealed after 450°C and as-deposited, as shown in Figure 5-1. The microstructure and fluorescence of the

luminescence thin film will be affected by the element ratio and the annealing temperature.

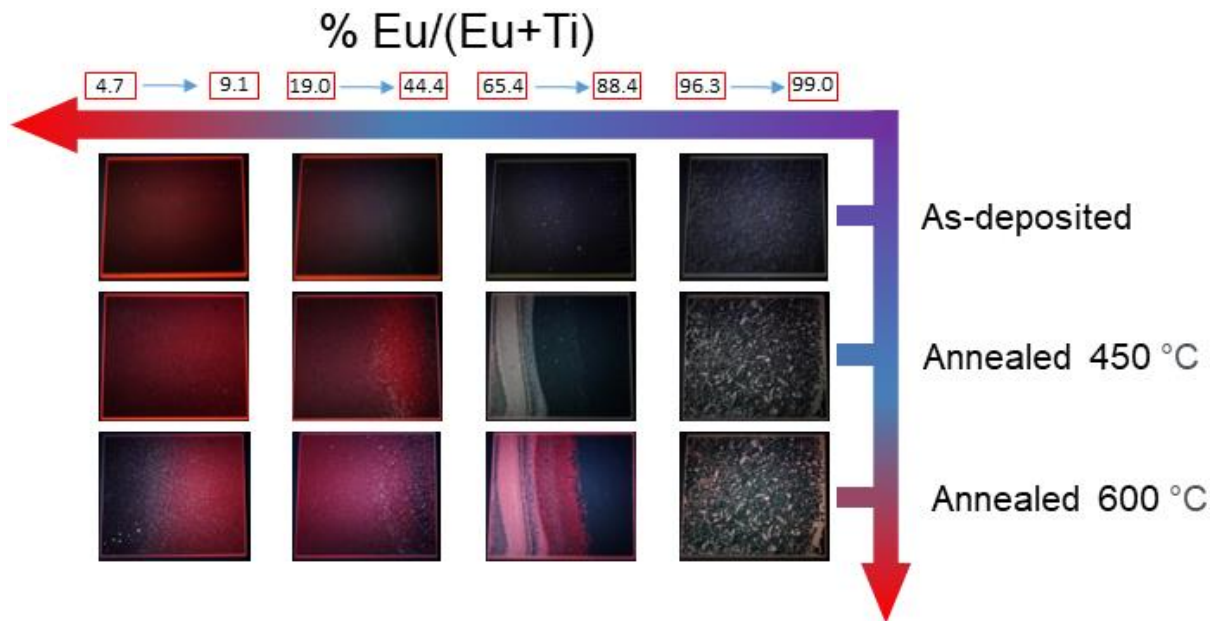


Figure 5-1 Visual inspection of Luminescence thin films on quartz as-deposited, annealed at 450°C and annealed at 600°C under 365nm UV light.

5.2.2 Fluorescence of different rates of Europium

The fluorescence distribution and intensity of ETO thin film will be affected by the europium ratio and annealing temperature. Figure 5-1 shows the visual inspection of the luminescence thin films on Quartz before and after annealing, which can distinguish the films by the red-light reflection brightness. Furthermore, the comparison for the maximum emission intensity of the films with various europium ratios as-deposited, after annealing at 450°C and 600°C, which is able to analyse and compare the fluorescence variation intuitively in Figure 5-2. In Figure 5-2, it is obvious that annealing temperature has a significant impact on fluorescence intensity. The fluorescence intensity of most of the samples after annealing at 600°C has increased, especially the samples with a europium ratio from 5 at% to 40 at% Eu/(Eu+Ti). The maximum emission intensity of the sample is shown when the film is 9.1 at% Eu/(Eu+Ti) sample after annealing at 600°C. Only the sample with 44.4 at% Eu/(Eu+Ti) has emission intensity after 450°C annealed higher than that after 600°C annealed. Even when there is a high proportion of Eu, there will be a relatively strong emission intensity. All the measurements are repeated three times for reliability and validation. However,

the thin film with 72 at% to 88.4 at% Eu/(Eu+Ti) is delaminated after annealing, causing poor adhesion between the thin film and substrate.

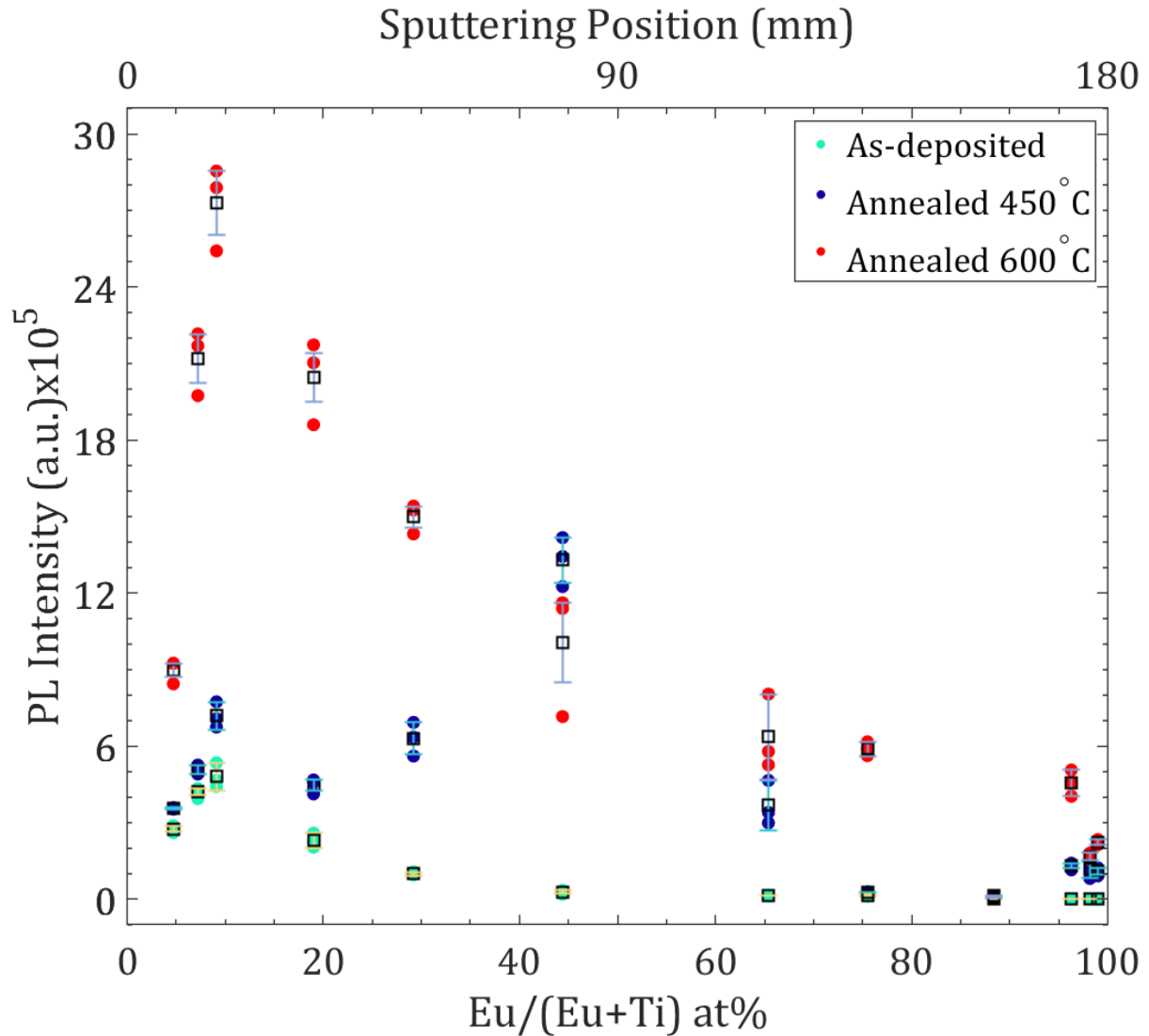


Figure 5-2 Maximum emission intensity of 0—100 at% Eu/(Eu+Ti) samples from 0 to 180 mm sputtering positions with excitation wavelength at 394nm as-deposition, after annealed at 450°C and after annealed at 600°C.

5.2.3 Fluorescence of samples As-deposited and after 450°C and 600°C annealed

Microstructure, crystalline structure and vibration modes of these ETO luminescence thin films with various europium ratios are achieved and approved. Based on these results, it can be verified the fluorescence of the films is generated by ETO. The excitations of Eu^{3+} are associated with electronic transitions from the ground state $^7\text{F}_0$ to energy levels above $^5\text{D}_0$. Energy from states higher than $^5\text{D}_0$ undergoes non-

radiative transitions, relaxing to the $^5D_0$ state. The visible emissions of Eu^{3+} ions result from radiative transitions from the lowest $^5D_0$ excited states to ^7F_J ($J = 0-4$) states.[169]

Excitation and Emission spectra are used to analyse the photoluminescence properties of these Eu^{3+} films. The annealing temperature changed and various europium ratios will influence the PL spectra. Figure 5-3 presents the PL spectra of the samples that are synthesised by 7.2 at% $Eu/(Eu+Ti)$ when it is as-deposited, after annealing at 450°C and 600°C. For the excitation spectra (Figure 5-3 (a)) with a fixed typical emission wavelength at 613 nm, and the emission spectra (Figure 5-3 (b)) with a fixed typical excitation wavelength at 394 nm. The electronic structure and subsequent luminescent characteristics of Eu^{3+} ions offer several advantages for evaluating luminescence spectra and identifying the local site symmetry of Eu^{3+} ions within the host matrix.[169] The ground state $^7F_0$ and the primary emitting level $^5D_0$ are non-degenerate. Several specific excitation peaks exhibited in the excitation spectra (320—500 nm) are located at 362, 376, 382, 394, 414 and 464 nm which are attributed to the specific $f-f$ transition of Eu^{3+} ions corresponding to $^7F_0 \rightarrow ^5D_4$ (362 nm), $^7F_0 \rightarrow ^5G_4$ (376 nm), $^7F_0 \rightarrow ^5G_2$ (382 nm), $^7F_0 \rightarrow ^5L_6$ (394 nm), $^7F_1 \rightarrow ^5D_3$ (414 nm) and $^7F_0 \rightarrow ^5D_2$ (464 nm). Comparing all those transitions in the excitation spectrum, both $^7F_0 \rightarrow ^5L_6$ (394 nm) and $^7F_0 \rightarrow ^5D_2$ (464 nm) have strong intensity shown in the spectra of 7.2 at% $Eu/(Eu+Ti)$. $^7F_0 \rightarrow ^5L_6$ (394 nm) transition always shows one of the highest intensities, which will be used as a fixed typical excitation wavelength for the emission spectra recording. Eu^{3+} ions are excited to the $^5L_6$ level under the excitation wavelength 394 nm, but the emission spectra show all the transitions starting from the $^5D_0$ level. The intensity of excitation is increased as the annealing temperature rises from 25°C to 600°C. There is about 5 times improvement of the intensity when the samples were annealed after 600°C compared with that of the as-deposited at 394 nm. However, the intensity of excitation has slightly changed after 450°C compared with as-deposited. Variations in annealing temperatures induce alterations in microstructure and crystalline arrangement, leading to modifications in fluorescence intensity.

Emission spectra of the 7.2 at% $Eu/(Eu+Ti)$ thin film sample as-deposited, after annealing at 450°C and 600°C are shown in Figure 5-3 (b), and the emission wavelength range is from 550 to 710 nm. $^7F_0 \rightarrow ^5L_6$ transition will be the typical excitation wavelength corresponding to 394 nm for the emission spectra investigation.

Several specific emission peaks exhibited in the emission spectra (550—710 nm) located at 579, 592, 613, 625 and 700 nm which are attributed to the specific $4f$ level of Eu^{3+} ions corresponding to $^5D_0 \rightarrow ^7F_0$ (579 nm), $^5D_0 \rightarrow ^7F_1$ (592 nm), $^5D_0 \rightarrow ^7F_2$ (613 nm), $^5D_0 \rightarrow ^7F_3$ (625 nm) and $^5D_0 \rightarrow ^7F_4$ (700 nm). Comparing all those transitions in the emission spectra, the most intense and well-defined red emission peak at 613 nm is associated with the electric-dipole (ED) allowed transition $^5D_0 \rightarrow ^7F_2$ (613 nm) transition of 7.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ shown in the spectra, commonly referred as the "hypersensitive" transition,[170] which will be used as a fixed typical emission wavelength for the excitation spectra recording. This designation implies that its intensity is highly responsive to the local environment of Eu^{3+} . The intensity of the peak at 592 nm, associated with the magnetic-dipole (MD) allowed $^5D_0 \rightarrow ^7F_1$ (592 nm) transition, exhibits minimal variation with respect to the crystal field strength surrounding Eu^{3+} ions,[170]. The R/O ratio, also referred to as the asymmetric ratio, is employed to calculate the distortion resulting from the lack of inversion symmetry in the local environment surrounding the Eu^{3+} ions within the TiO_2 host matrix. The manifestation of this transition arises from the violation of selection rules, as the Judd-Ofelt (J-O) rules prohibit the 0-0 transition. The J-O intensity parameters, extracted from emission spectra, serve as a valuable tool for comprehending the symmetry and coordination environment of Eu^{3+} ions within the TiO_2 matrix,[171]. Both excitation and emission have similar intensity; the PL intensity compared with the sample as-deposited is raised slightly after 450°C annealing and has 5 times improvement when the samples annealed after 600°C.

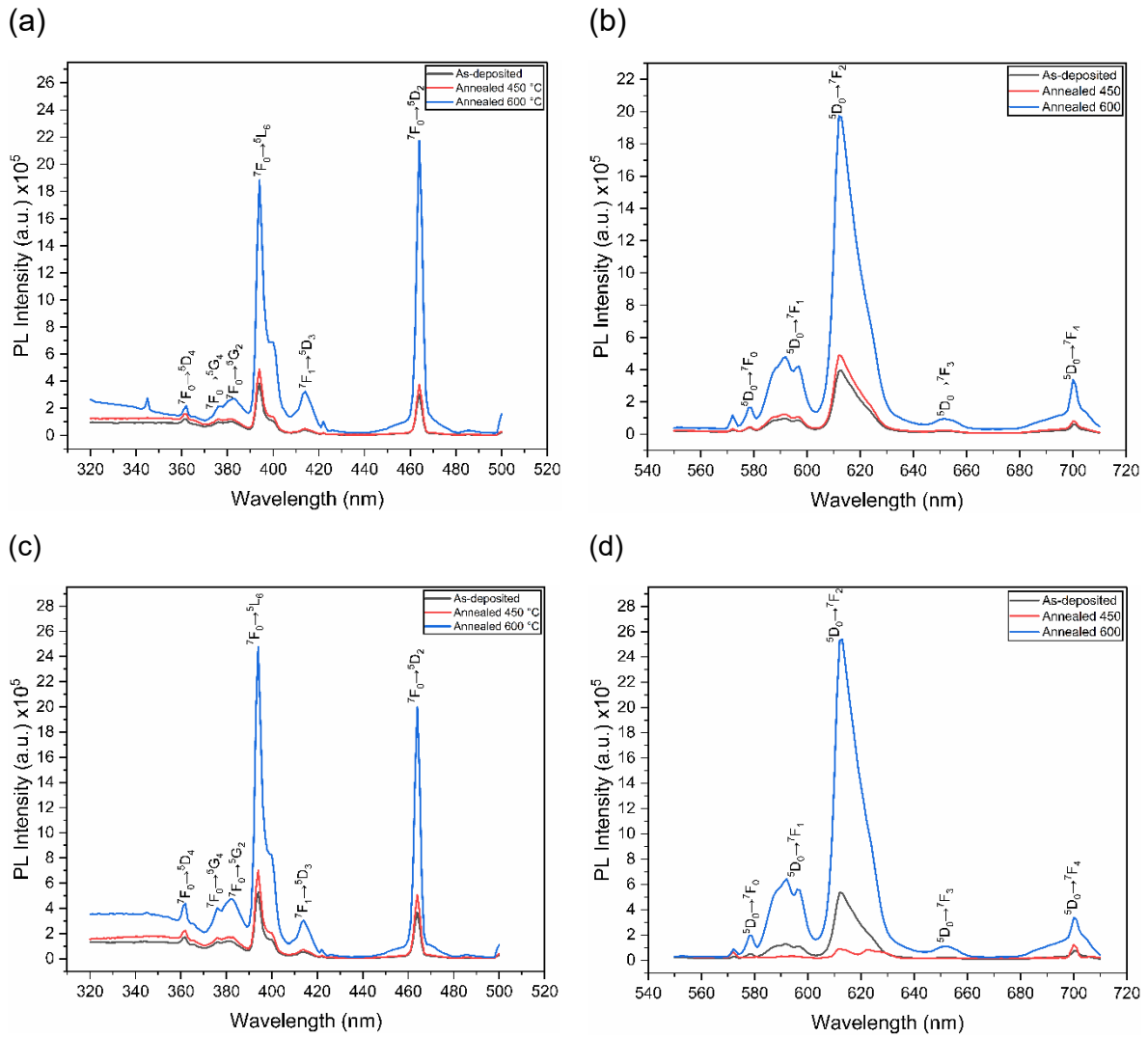


Figure 5-3 (a) Excitation and (b) emission spectra of 7.2 at% Eu/(Eu+Ti), and (c) Excitation and (d) emission of 9.1 at% Eu/(Eu+Ti) samples as-deposition, after annealed at 450 °C and annealed at 600 °C.

The annealing temperature markedly influences the excitation and emission spectra intensity of the luminescence thin film samples illustrated in Figure 5-3, but in this emission spectra only analyse the typical excitation wavelength corresponding to ${}^7F_0 \rightarrow {}^5L_6$ (394 nm) transition. A fixed typical emission wavelength at 613 nm is used to measure the excitation spectra of 7.2 at% Eu/(Eu+Ti) (Figure 5-4 (a)) and of 9.1 at% Eu/(Eu+Ti) samples (Figure 5-4 (c)). The various transitions ${}^7F_0 \rightarrow {}^5D_4$ (362 nm), ${}^7F_0 \rightarrow {}^5G_2$ (382 nm), ${}^7F_0 \rightarrow {}^5L_6$ (394 nm) and ${}^7F_0 \rightarrow {}^5D_2$ (464 nm) as excitation wavelengths for the emission spectra measurement are shown in the Figure 5-4 (b) & (d). In these emission spectra, the sample has the same transitions and peaks with various excitation wavelengths. The peaks are attributed to the specific 4f level of Eu^{3+} ions

corresponding to $^5D_0 \rightarrow ^7F_0$ (579 nm), $^5D_0 \rightarrow ^7F_1$ (592 nm), $^5D_0 \rightarrow ^7F_2$ (613 nm), $^5D_0 \rightarrow ^7F_3$ (625 nm) and $^5D_0 \rightarrow ^7F_4$ (700 nm). Nevertheless, some artefact peaks are observed in the emission spectra of the photoluminescence (PL) spectroscopy when using excitation wavelengths of 362 nm and 382 nm. This occurrence is attributed to the low emission intensity, insufficient to mask the artefact noise. The maximum emission intensity of each spectrum is shown at $^5D_0 \rightarrow ^7F_2$ (613 nm), its excitation wavelength intensity in its excitation spectrum is similar to the maximum emission intensity. It can be understood that the intensity of the excitation wavelength significantly affects the emission intensity.

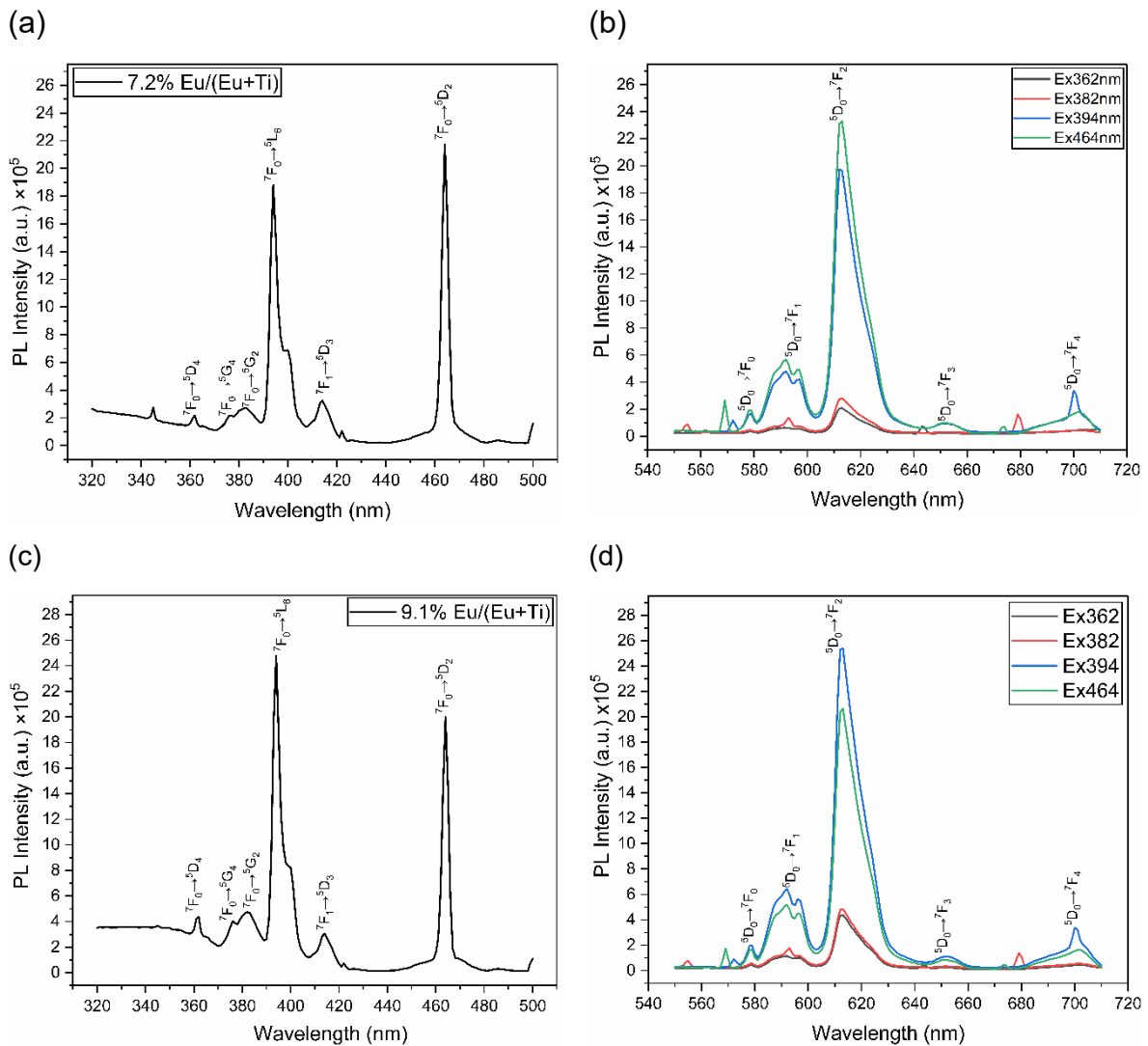


Figure 5-4 (a) Excitation and (b) emission of 7.2 at% Eu/(Eu+Ti), and (c) Excitation and (d) emission of 9.1 at% Eu/(Eu+Ti) samples after annealing at 600°C, the emission spectrum based on different excitation wavelengths.

Various europium ratios of the luminescence thin films are synthesised by the combinatorial sputtering. Several representative samples with different europium ratios are selected to have the fluorescence testing for the comparison, which are 4.7 at%, 7.2 at%, 9.1 at%, 19 at%, 29.2 at%, 75.5 at% and 98.2 at% Eu/(Eu+Ti) respectively. Both the excitation and emission spectra of these luminescence thin film samples are presented in Figure 5-5. A fixed typical emission wavelength at 613 nm is used to measure the excitation spectra of 4.7 at%, 7.2 at%, 9.1 at%, 19 at%, 29.2 at%, 75.5 at% and 98.2 at% Eu/(Eu+Ti) samples (Figure 5-5 (a)). The various transitions ${}^7F_0 \rightarrow {}^5D_4$ (362 nm), ${}^7F_0 \rightarrow {}^5G_2$ (382 nm), ${}^7F_0 \rightarrow {}^5L_6$ (394 nm) and ${}^7F_0 \rightarrow {}^5D_2$ (464 nm) as excitation wavelengths. The emission spectra measurements are shown in Figure 5-5 (b), the samples have the same transitions and peaks with various excitation wavelengths. The peaks are attributed to the specific 4f level of Eu^{3+} ions corresponding to ${}^5D_0 \rightarrow {}^7F_0$ (579 nm), ${}^5D_0 \rightarrow {}^7F_1$ (592 nm), ${}^5D_0 \rightarrow {}^7F_2$ (613 nm), ${}^5D_0 \rightarrow {}^7F_3$ (625 nm) and ${}^5D_0 \rightarrow {}^7F_4$ (700 nm). All these ETO thin films have the same transitions in excitation and emission spectra with different europium ratios. However, the maximum intensity of excitation and emission spectra is affected by the europium ratios of the thin films, and the thin film with 9.1 at% Eu/(Eu+Ti) has the highest excitation (at 394 nm) and emission (at 613 nm) intensity. ETO luminescence thin films with lower europium ratios will generate higher fluorescence intensity when comparing the excitation and emission spectra in Figure 5-5.

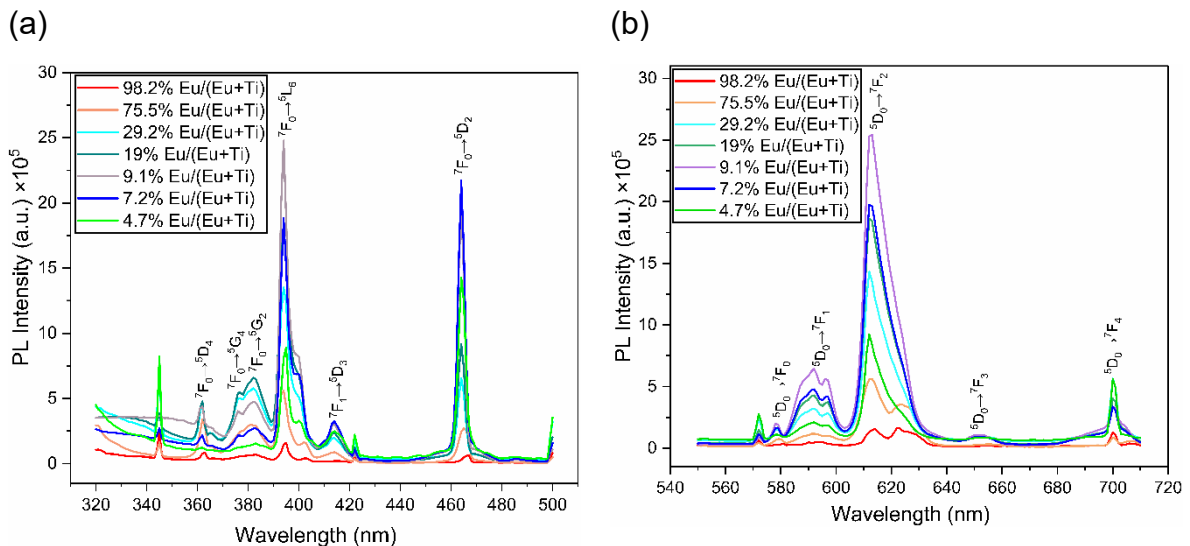


Figure 5-5 (a) Excitation and (b) emission of 4.7 at%, 7.2 at%, 9.1 at%, 19 at%, 29.2 at%, 75.5 at% and 98.2 at% Eu/(Eu+Ti) samples after annealing at 600°C, the emission spectrum based on 394 nm excitation wavelengths.

5.2.4 Transmittance and Bandgap of samples As-deposited and after 450°C and 600°C annealed

Transmittance spectra of the ETO are measured by the JASCO V-670 UV-Vis-NIR from 200 to 1500 nm. In addition, the Bandgaps of the samples are achieved in the Tauc plot calculated from transmittance spectra. The Tauc plot equation is exhibited as following:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (5-1)$$

$$(\alpha h\nu)^2 \text{ vs } h\nu \quad (5-2)$$

In the context of this thesis, the symbol α represents the absorption coefficient, which is dependent on wavelength and expressed as $\alpha(\lambda)$. Other variables include h , representing Planck's constant; E_g , denoting the optical band gap of a semiconductor; ν , signifying frequency; A , representing a proportionality constant; and n , representing the Tauc exponent. The Tauc plot will be drawn by (5-1). Several representative samples with different europium ratios are selected to have the UV-Vis testing for the comparison, which are 7.2 at%, 29.2 at%, 75.5 at% and 98.2 at% Eu/(Eu+Ti) respectively. Transmittance spectra and Tauc plots of the samples as-deposited, after annealing at 450°C and 600°C are shown in Figure 5-6. The samples have high transmittance (T%) from 450 to 1500 nm when the europium ratios of the samples increase, 7.2 at%, 29.2 at%, 75.5 at% and 98.2 at% Eu/(Eu+Ti) samples have about 75T%, 78 T%, 82 T% and 90 T% respectively. And all the samples have sharp absorption edges from 300 to 400 nm and those are able to absorb the photons in the UV region. Meanwhile, the bandgap of the sample is higher when the europium ratio of the sample increases, The bandgaps of 7.2 at%, 29.2 at%, 75.5 at% and 98.2 at% Eu/(Eu+Ti) samples are 3.33, 3.61, 3.95, and 5.32 eV respectively after 600 °C annealing. Transmittance spectra and bandgaps of each sample have similar results as-deposited, after annealing at 450°C and 600°C. The oscillations observed in the transmittance spectra result from interference in ETO films, arising from multiple reflections at the air-film and film-substrate interfaces.[160,170]

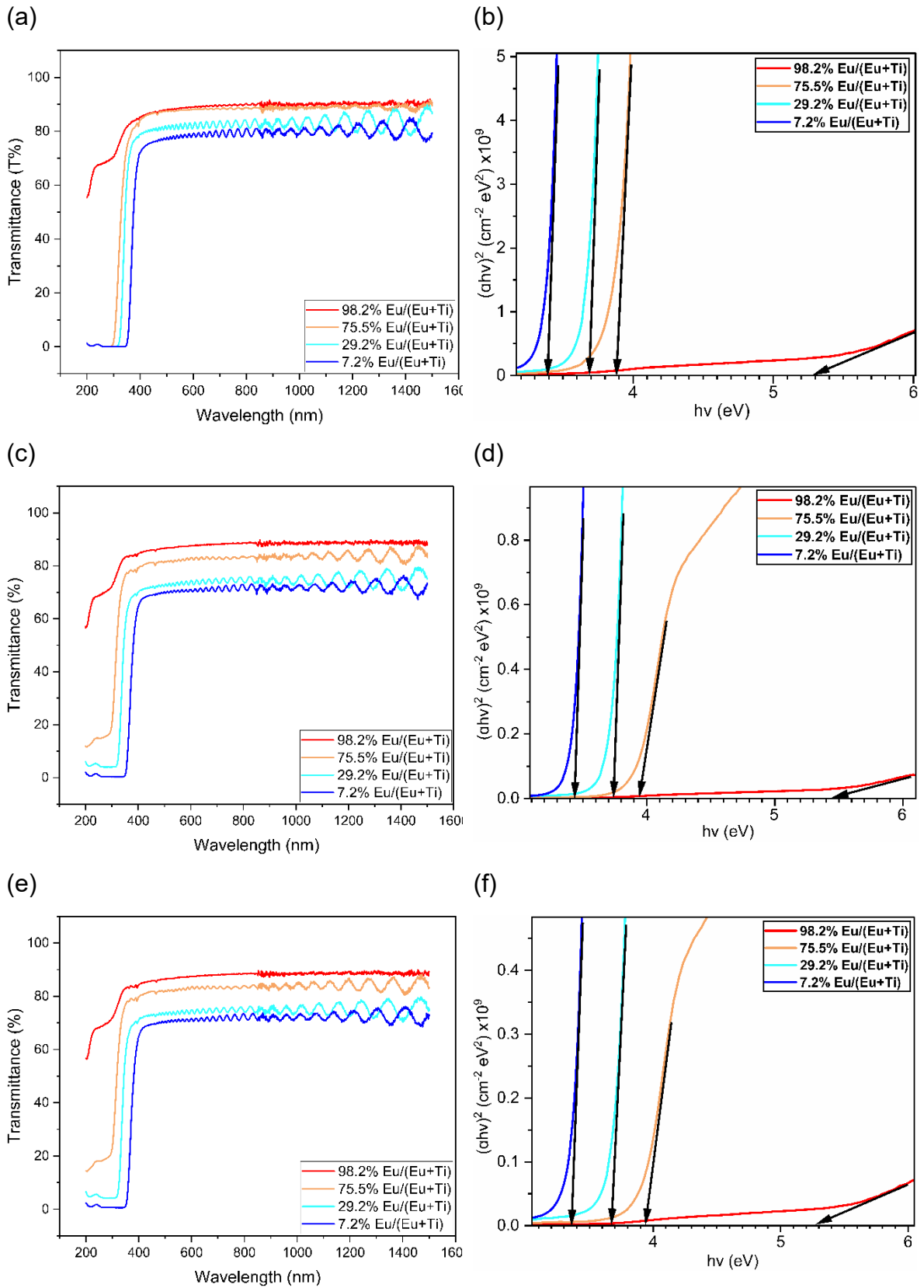


Figure 5-6 Transmittance and Bandgap of 7.2 at%, 29.2 at%, 75.5 at% and 98.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ samples (a) & (b) as-deposited, after annealing at (c) & (d) 450°C and (e) & (f) 600°C.

For the comparison, pure Eu_2O_3 and pure TiO_2 thin films are synthesised by PVD and transmittance spectra are measured by UV-Vis. The transmittance spectra and tauc plot of the pure Eu_2O_3 and pure TiO_2 thin films after annealing at 600°C are shown in Figure 5-7. These two samples have higher transmittance from 450 to 1500 nm about 75 T%, but the pure TiO_2 sample has strong oscillations observed in this region. The pure Eu_2O_3 sample has sharp absorption edges around 300 nm, and the pure TiO_2 sample has sharp absorption edges around 400 nm, which can absorb the photons in the UV region. The bandgap of the pure Eu_2O_3 and pure TiO_2 thin films are 3.28 and 3.83 eV respectively.

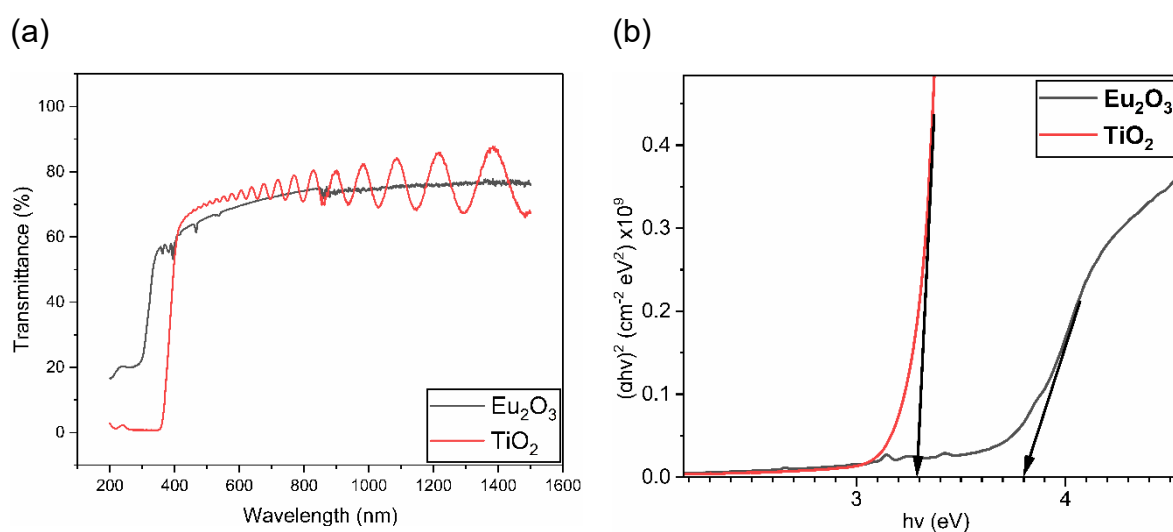


Figure 5-7 Transmittance and Bandgap of (a) pure Eu_2O_3 and (b) pure TiO_2 thin films after annealing at 600°C .

5.2.5 Power conversion efficiency of solar cell with lanthanide-doped luminescence thin films

ETO samples are down-conversion thin films which are able to be used on top of the solar cell to improve the power conversion efficiency (PCE).[172] The Oriel LCS-100 solar simulator is applied for PV performance assessment, and the area of the reference solar cell is 20×20 mm, 400 mm^2 . Several representative samples with different europium ratios are selected to have the power conversion efficiency testing for the comparison, which are Pure TiO_2 (0 at% $\text{Eu}/(\text{Eu}+\text{Ti})$) and Pure Eu_2O_3 (100 at% $\text{Eu}/(\text{Eu}+\text{Ti})$) samples, 7.2 at%, 29.2 at%, 75.5 at% and 98.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ samples respectively, and the results of the samples after annealing at 600°C are presented in the I-V plot in Figure 5-8.

After calculation by the equation (3-1) and (3-2), each sample has a different output power shown in the I-V plot, which is 43.08, 46.016, 50.072 and 55.39 mW for 7.2 at%, 29.2 at%, 75.5 at% and 98.2 at% Eu/(Eu+Ti) samples respectively. In addition, the maximum output power of Pure TiO₂ and Pure Eu₂O₃ samples are 43.58 and 48.82 mW.

The PCE calculated by the equation (3-3) result in 7.2 at%, 29.2 at%, 75.5 at% and 98.2 at% Eu/(Eu+Ti) samples are 10.770%, 11.504%, 12.518%, and 13.848% respectively. The PCE of Pure TiO₂ and Pure Eu₂O₃ samples are 10.895% and 12.205%. From these findings, it becomes evident that samples with a reduced europium ratio in ETO exhibit lower PCE.

After the calculation by the equation (3-4), the results of FF are 72.418%, 72.929%, 73.062% and 73.366% for the 7.2 at%, 29.2 at%, 75.5 at% and 98.2 at% Eu/(Eu+Ti) samples. And the FF of Pure TiO₂ and Pure Eu₂O₃ samples are 72.7% and 72.8%. Each sample has high and similar FF results, and the difference is within 1%, which means these samples have similar quality.

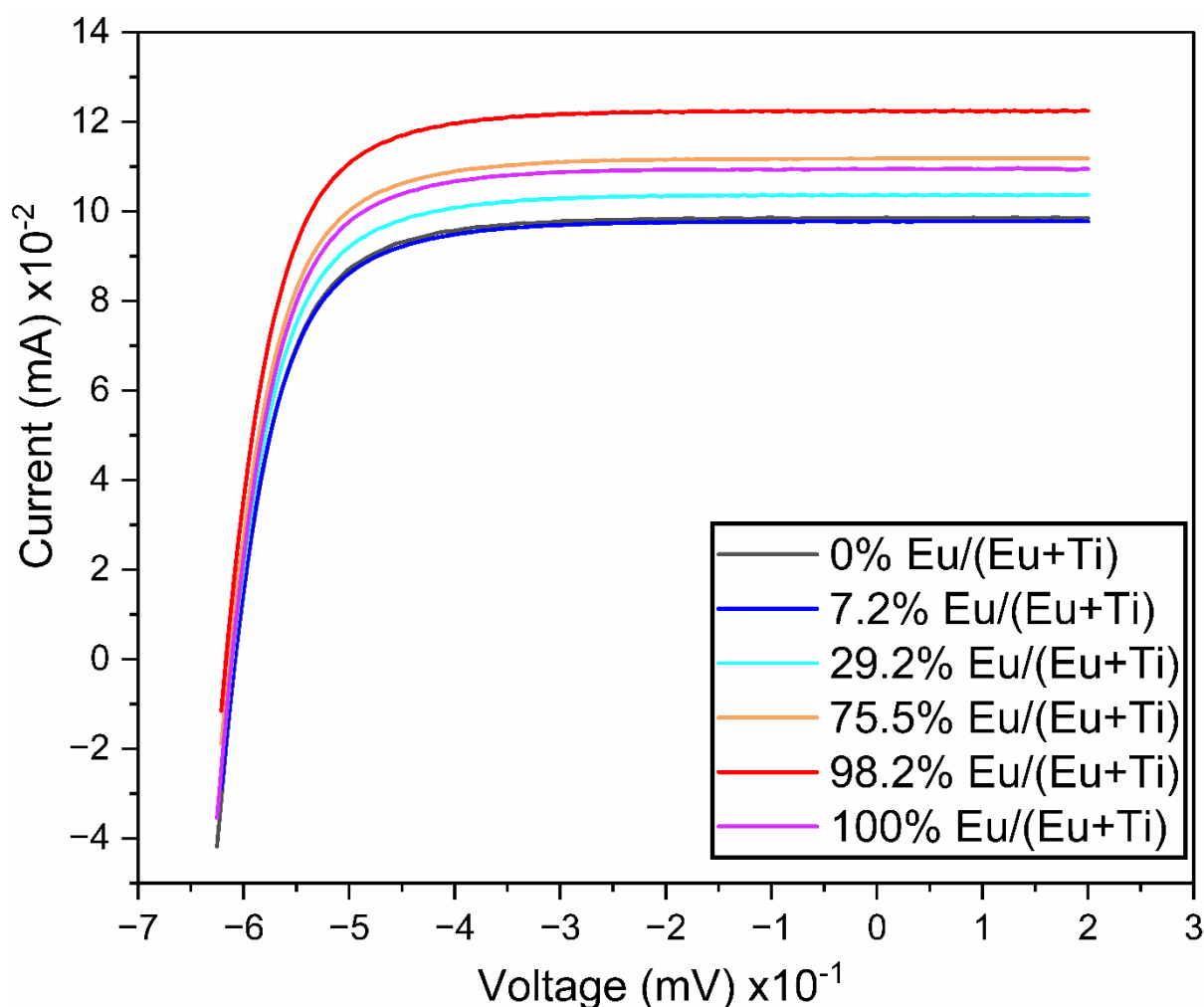


Figure 5-8 Power conversion efficiency of 0 at%, 7.2 at%, 29.2 at%, 75.5 at%, 98.2 at% and 100 at% Eu/(Eu+Ti) samples after annealing at 600 °C.

5.3 Discussion

Europium-doped thin films stand out for their remarkable properties, making them highly attractive for diverse applications. These nano crystallites possess exceptional chemical and thermal stabilities, alongside minimal toxicity, rendering them safe and versatile for numerous applications. Their luminescence properties are particularly noteworthy, characterised by narrow emission bands resulting from $f-f$ electron transitions. ETO thin films exhibit a range of remarkable properties, particularly in the domain of photoluminescence. Among rare-earth (RE) elements, the Eu^{3+} ion stands out as a prominent pure red-emitter, showcasing its distinctive $^5D_0 \rightarrow ^7F_2$ transition. This transition results in a discernible and confined red emission under UV radiation.[173,174]

Integrating fluorescence observations with the microstructural morphology of the cross-section of luminescence thin films, samples as-deposited with a columnar structure exhibit fluorescence under UV irradiation, particularly within the europium ratio range of 4 at% to 50 at% Eu/(Eu+Ti). Additionally, XRD pattern analysis confirms the amorphous or nano crystallites nature of the thin films as-deposited with fluorescence properties. Komaraiah et al. presented the ETO has tetragonal structure with 101, 004, 200, 105, 211 and 204 crystallography planes.[109] This discovery underscores the capability of luminescence thin films with specific compositions to exhibit fluorescence without the need for annealing, but the fluorescence intensity is influenced by annealing temperature. In the amorphous TiO₂ host, anatase TiO₂ clusters are either absent or present in minimal amounts, with nearly all Eu³⁺ ions residing within the amorphous matrix. These Eu³⁺ ions are excited through the charge transfer band (CTB) of O²⁻ → Eu³⁺ (280 nm) or the ⁷F₀ → ⁵L₆ transition (394 nm) of Eu³⁺ itself, albeit with very low excitation efficiency. Following annealing, anatase TiO₂ clusters form within the amorphous TiO₂, increasing in grain size. A portion of the Eu³⁺ ions diffuse into these anatase clusters, where they exhibit significantly higher excitation efficiency due to energy transfer from the crystalline TiO₂ hosts, which effectively absorb UV photons across their bandgap.[165]

There are reports that the 394 nm excitation can induce a charge transfer process from the O 2p states to the Eu 4f states.[175] This process involves the absorption of photons by the O atoms, promoting electrons to higher energy states that can then transfer to the Eu³⁺ ions. This type of charge transfer excitation does not require full bandgap energy and can occur with lower-energy photons.[175] In addition, the 394 nm light can directly excite the Eu³⁺ ions themselves. Eu³⁺ ions have multiple energy levels, and the 394 nm wavelength corresponds to the transition from the ground state to an excited state within the Eu³⁺ ion (specifically the ⁷F₀ → ⁵L₆ transition).[147] This direct excitation of Eu³⁺ does not depend on the bandgap of TiO₂. After initial excitation, non-radiative processes can transfer energy from TiO₂ to Eu³⁺ ions. Even if the 394 nm light initially excites electrons to sub-bandgap states, these electrons can further relax and transfer energy to the Eu³⁺ ions. The ⁵D₀ population is populated through multiphonon relaxation from ⁵L₆, a non-radiative energy transfer process involving exchange and multipolar interactions.[147] The energy is finally transferred from ⁵D₀ to the ⁷F_{*i*} (*i* = 0, 1, 2, 3, 4) levels of the Eu³⁺ ions through radiative transitions, and the

dominant emission wavelength is 613 nm. Alternatively, the excitation wavelength of 394 nm (corresponding to an energy of approximately 3.15 eV) used to excite the ETO thin films (scenario 1), is lower in energy than the 3.2 eV direct bandgap of anatase TiO₂. However, PL excitation is still possible due to several mechanisms associated with defects and impurity states within TiO₂. The incorporation of Eu³⁺ will introduce defect states or energy levels within the bandgap of TiO₂. These defects consist of oxygen vacancies which introduce indirect bandgap states.[176–178] Anatase TiO₂ features an indirect bandgap that is narrower than its direct bandgap, decreasing from 3.2 eV to 3.15 eV (scenario 2).[179] These states effectively reduce the energy required for electronic transitions, allowing sub-bandgap excitation at 394 nm to promote electrons from these defect states into the conduction band or from the valence band to these intermediate states. This mechanism may also facilitate energy transfer to Eu³⁺ ions resulting in PL due to sub-bandgap excitation. In anatase TiO₂, oxygen vacancies lead to the localisation of one or two electrons within the vacancy state, driven by the Madelung potential of the ionic crystal structure. These vacancies introduce energy levels 0.75–1.18 eV below the conduction band, creating localised trap states that affect the material's electrical and optical properties by modifying the bandgap (scenario 3).[177] Rutile TiO₂ has a bandgap of 3.0 eV and effectively absorbs photons at 394 nm, resulting in more efficient energy transfer without sub-bandgap transitions, leading to greater increases in emission intensity (scenario 4).[155] XRD analysis indicates that the thin film containing 7.2 at% Eu exhibits both anatase and rutile phases of TiO₂, promoting efficient absorption of low-energy photons. This absorption is followed by energy transfer to Eu³⁺ ions, leading to strong PL intensity, consistent with scenarios 1, 2, 3, and 4. Conversely, the films with 29.2 at% and 75.5 at% Eu lack crystalline phases, resulting in reduced photon absorption and diminished PL intensity, aligning with scenarios 1, 2 and 3. For the 100 at% Eu film, a monoclinic Eu₂O₃ lattice forms, where photon absorption is limited to Eu³⁺ ions, causing very weak emission, matching scenario 1.

Chen et al. compared the influence of PL intensity of ETO with different annealing temperature, the emission intensity progressively increased until reaching a peak at 700°C, after which it gradually decreased.[110] Both excitation and emission spectra of the 7.2 at% Eu/(Eu+Ti) thin film sample have the same transitions and peaks, when the sample is as-deposited, after annealing at 450°C and 600°C. Only the intensity of

excitation and emission are significantly affected by the annealing temperature. At a temperature below 300°C, the samples exhibit a low degree of crystallinity and a slightly yellowish tint, attributed to the residual presence of organic materials. These factors contribute to a reduction in the emission intensity of Eu^{3+} . However, at significantly higher annealing temperatures, there is a likelihood of segregation of Eu^{3+} ions within the phosphors and the formation of impurity phases such as rutile TiO_2 and $\text{Eu}_2\text{Ti}_2\text{O}_7$, resulting in a decline in Eu^{3+} emission.[110]

The optical bandgap of anatase TiO_2 is typically around 3.2 eV, while the bandgap of pure Eu_2O_3 has been reported to be approximately 4.3 eV. The variation in bandgap values between TiO_2 and the ETO can be attributed to the introduction of europium as a mixture. As the Eu concentration increases, the bandgap values of the ETO films gradually increase, falling between the bandgap values of pure TiO_2 and Eu_2O_3 . Specifically, the bandgap expands from 3.2 eV to 4.3 eV as the Eu concentration increases from 0 at% to 100 at% $\text{Eu}/(\text{Eu}+\text{Ti})$, demonstrating that a higher Eu content results in a larger bandgap value.

ETO luminescence thin films with lower europium ratios (less than 50% $\text{Eu}/(\text{Eu}+\text{Ti})$) will generate higher fluorescence intensity. The bandgap energy variation of the samples may be attributed to the europium ratios, and the bandgap energy change will affect the photon absorption. When considering PCE, transmittance, and bandgap results collectively, it is observed that samples with lower europium ratio yield lower bandgap and higher absorption.

5.4 Conclusion

The optical characteristics of the ETO thin films are assessed by UV-Vis, fluorescence spectroscopy and solar simulator before and after annealing. The range of europium ratio (at% $\text{Eu}/(\text{Eu}+\text{Ti})$) is from 0 at% to 100 at%, and the annealing temperatures are 450 °C and 600 °C, which are able to influence the structural properties and optical properties of the thin films. Transmittance and bandgap of the thin films are affected by the annealing temperature and the bandgap energy variation of the samples may be attributed to the europium ratios, which will influence the photon absorption and the luminescence properties of the films. Photoluminescence properties of the thin films are investigated by fluorescence spectroscopy. ${}^7F_0 \rightarrow {}^5L_6$ (394 nm) and ${}^7F_0 \rightarrow {}^5D_2$ (464 nm) are the most intense excitation peaks for films to absorb the photons. The

strongest emission intensity peak is at ${}^5D_0 \rightarrow {}^7F_2$ (613 nm), which has a higher branching ratio in fluorescence spectra. The peak maximum emission intensity of the sample is shown when the film is 9.1 at% Eu/(Eu+Ti) sample after annealing at 600°C, which is approximately 4 times higher than the sample as-deposited and annealing at 450°C. The samples with lower bandgap have lower power conversion efficiency, because more photons have been absorbed and scattered, and they escape from the edge of the substrate.

6 Degradation of ETO luminescence thin films

6.1 Introduction

PL materials are renowned for their fluorescence properties and have been the subject of extensive research across diverse applications over an extended duration. Additionally, Eu-doped NPs exhibit notably prolonged luminescence lifetimes, further enhancing their appeal for various technological and scientific endeavours.[180,181] Titania holds a distinguished reputation as an outstanding optoelectronic material, especially in the realm of photocatalysis.[182,183] Particularly, titania emits red luminescence with Eu dopant, a characteristic that renders it indispensable for augmenting PCE in solar cell applications.[184,185]

Lanthanides and semiconductor QDs are explored as promising materials for synthesising PL thin films, particularly for their potential in wavelength-shifting applications. Among these, tris(dibenzoylmethane) europium(III) ($\text{Eu}(\text{dbm})_3$) stands out with its remarkable attributes similar with Eu-doped NPs.[186,187] Notably, $\text{CuInS}_2/\text{ZnS}$ QDs exhibit Stokes shifts exceeding 150 nm, longer PL lifetimes, and broader full width at half maximum (FWHM) of approximately 125 nm compared to other QD types such as cadmium-based or indium phosphide (Cd-based or InP) QDs.[188]

Given the critical role of the position of triplet states (T) of ligands in the intramolecular energy transfer process of RE^{3+} -complexes, the DBM ligand serves as an effective "antenna" for Eu^{3+} ions, notably due to its lowest excited triplet state occurring at approximately $21,600 \text{ cm}^{-1}$. [189,190] The fluorescence spectra of the PMMA-complex doping exhibit a significant enhancement in the fluorescence intensity of Eu^{3+} attributed to the presence of Phen.[191] The encapsulation structure, comprising a PVA layer at the bottom doped with $\text{Eu}(\text{dbm})_3$ phen, demonstrated an augmentation in the overall delivered power compared to the scenario involving undoped PVA-coated cells.[192] Colloidal QDs encapsulation can passivate surface trap states and mitigate the degradation of optical properties involving capping the QDs or embedding them into polymers or oxides, such as PMMA and PVA[193]

The lifetime of PL thin films serves as a crucial gauge for their practical application. Some studies have documented the photobleaching phenomenon in Eu^{3+} luminescent

samples, characterised by a reduction in fluorescence intensity upon exposure to UV or visible light irradiation.[181,194–196] Lanthanide-doped inorganic nanoparticles exhibit remarkable physicochemical properties, including prolonged luminescence, high resilience to photobleaching, and minimal toxicity.[197] TiO_2 , renowned for its prowess in photocatalysis, demonstrates exceptional efficiency, albeit susceptible to photobleaching under UV irradiation.[198] Oxygen serves a pivotal function in optically induced PL decay, as evidenced by a diminished photobleaching effect observed under vacuum conditions.[199]

This research endeavours to investigate the photobleaching phenomenon in ETO thin films, $\text{CuInS}_2/\text{ZnS}$ and $\text{Eu}(\text{dbm})_3$ when embedded in PVA and PMMA thin films following degradation testing. Utilising combinatorial sputtering, ETO thin film samples with varying europium ratios are synthesised and subsequently annealed at 600 °C. The polymer thin films are synthesised using the drop-casting method. The chapter aims to discern the factors influencing the lifetime of these thin films, with degradation testing serving to swiftly explore their longevity under specific conditions of temperature, humidity, and UV irradiation intensity. Moreover, the research delves into the luminescence properties, transmittance, and bandgap of the thin films both before and after degradation testing, offering comprehensive insights into their behaviour under controlled environmental stresses.

6.2 Results

6.2.1 Visual inspection

The ETO thin films with various compositions exhibited PL properties after annealing at 600°C. In addition, $\text{CuInS}_2/\text{ZnS}$ and $\text{Eu}(\text{dbm})_3$ embedded with PVA and PMMA films illustrated red-colour fluorescence under the UV light. The thicknesses of ETO thin films after annealing at 600°C are roughly 3.48 μm , 3.01 μm , 3.12 μm and 3.95 μm relative to 7.2 at%, 29.2 at%, 75.5 at%, and 98.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ respectively. Otherwise, the thicknesses of $\text{CuInS}_2/\text{ZnS}$ and $\text{Eu}(\text{dbm})_3$ embedded with PVA are about 1 mm in the centre, and the thicknesses of $\text{CuInS}_2/\text{ZnS}$ and $\text{Eu}(\text{dbm})_3$ embedded with PMMA are about 100 μm when the films are fabricated.

Degradation testing was performed on all ETO luminescent thin films, as well as on $\text{CuInS}_2/\text{ZnS}$ and $\text{Eu}(\text{dbm})_3$ embedded with PVA and PMMA luminescent thin films,

within a controlled humidity chamber. The time-dependent behaviour observed in these materials was then compared with that of more commonly used fluorescent materials. Throughout the degradation testing, the maximum emission intensity demonstrates a decrease corresponding to the duration of UV exposure, as depicted in Figure 6-1 and Figure 6-2. In Figure 6-1, the x-axis denotes the Europium ratio of the samples, while the y-axis represents the duration of UV exposure in hours. Notably, at 0 hours, indicating samples after 600°C annealing and prior to UV exposure, the samples emitted a bright red colour. Among these, the region with approximately 9.1 at% Eu/(Eu+Ti) exhibited the highest brightness. Conversely, samples with approximately 88.4 at% Eu/(Eu+Ti) experienced delamination post-600 °C annealing, leading to the absence of fluorescence. In Figure 6-2, the x-axis denotes various samples, namely Eu(dbm)₃ with PMMA, Eu(dbm)₃ with PVA, CuInS₂/ZnS with PMMA, and CuInS₂/ZnS with PVA, respectively, while the y-axis represents the duration of UV exposure in hours. At 0 hours, corresponding to the point after curing and before UV exposure, the samples exhibit the highest brightness levels.

During the 40-hour degradation testing period with a 7500Wh/m² UV LED, conducted at a controlled temperature of 25°C and humidity of 45%, which closely simulates average real-world application conditions, the visual inspection of samples fluorescence under UV light, depicted in Figure 6-1 and Figure 6-2, elucidated the degradation process. In Figure 6-1 Samples with a europium ratio ranging between 4.7 and 9.1 at% Eu/(Eu+Ti) exhibit slow bleaching, retaining strong fluorescence even after 40 hours of UV exposure. Conversely, samples with a europium ratio between 19.0 and 44.4 at% Eu/(Eu+Ti) experience accelerated bleaching, nearing complete bleaching following the same duration of UV exposure. Interestingly, samples with a europium ratio spanning from 65.4 to 88.4 at% Eu/(Eu+Ti) initially display slow bleaching within the first 20 hours, followed by rapid bleaching in the subsequent 20 hours. Samples with a europium ratio between 96.3 and 99 at% Eu/(Eu+Ti) exhibit weak fluorescence intensity initially, with no discernible change observed after 40 hours of UV exposure.

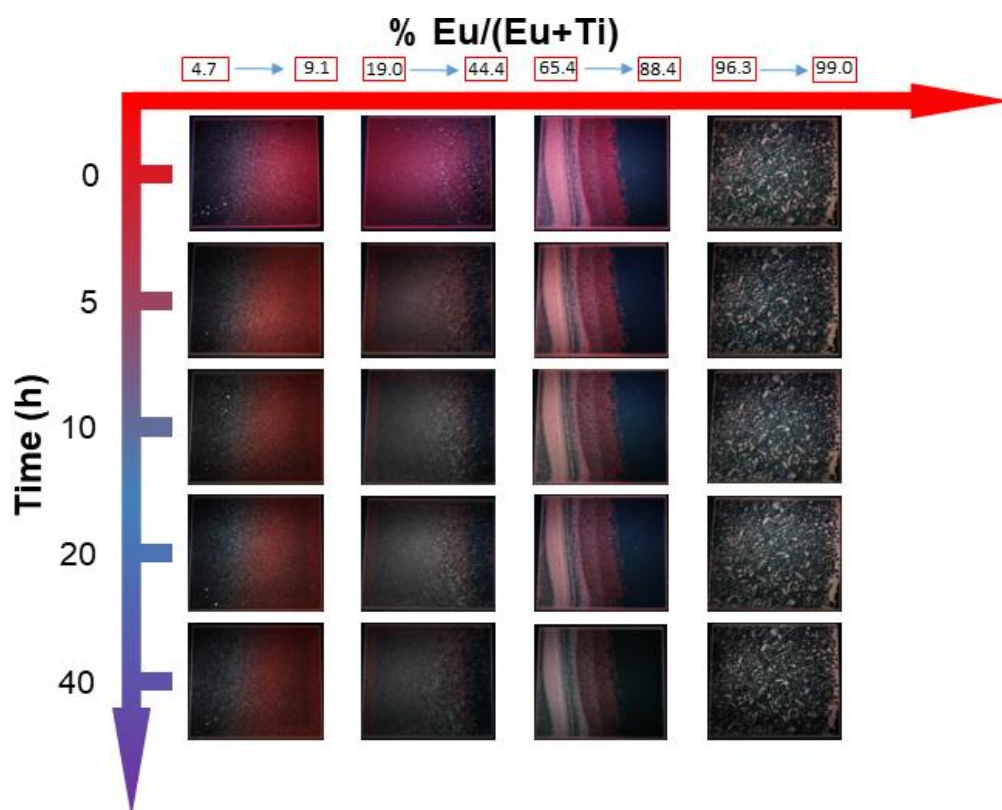


Figure 6-1 Visual inspection of luminescence thin films on quartz annealing at 600 °C for the degradation testing from 0 to 40 hours.

In Figure 6-2, During the 20 hours of UV exposure period, both $\text{CuInS}_2/\text{ZnS}$ with PVA and $\text{CuInS}_2/\text{ZnS}$ with PMMA exhibit gradual bleaching, demonstrating they retain fluorescence after degradation testing. Notably, $\text{Eu}(\text{dbm})_3$ with PVA before degradation testing displays the highest emission brightness, maintaining stable and strong emission intensity during the initial 5 hours of UV exposure. However, a significant decline in emission intensity is observed after 5 hours, with the sample nearly fully bleached by the end of the 10 hours of degradation testing. In contrast, the $\text{Eu}(\text{dbm})_3$ with PMMA sample exhibits an accelerated bleaching process within a short duration. Experiencing rapid bleaching within the first hour, this sample continues to undergo swift bleaching, nearing complete bleaching after 5 hours of degradation testing.

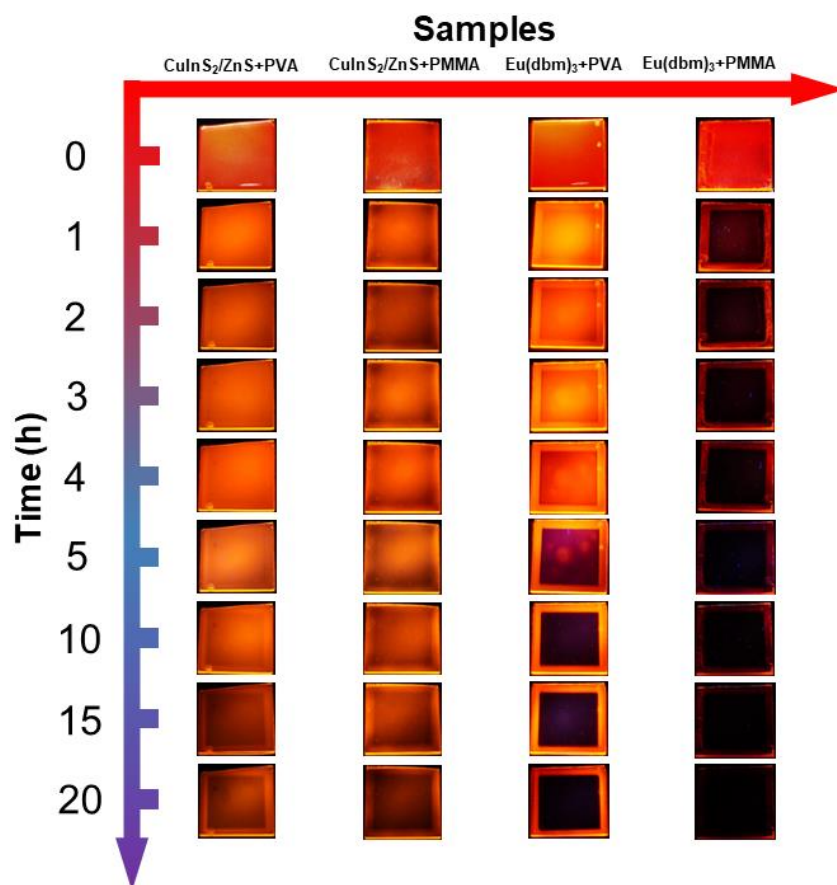


Figure 6-2 Visual inspection of $\text{Eu}(\text{dbm})_3$ with PMMA, $\text{Eu}(\text{dbm})_3$ with PVA, $\text{CuInS}_2/\text{ZnS}$ with PMMA, and $\text{CuInS}_2/\text{ZnS}$ with PVA luminescence thin films on glass after curing for the degradation testing from 0 to 20 hours.

6.2.2 Fluorescence properties during degradation testing

Following each degradation testing cycle, the fluorescence properties of the samples are evaluated using photoluminescence spectroscopy, focusing on specific areas of ETO thin films representing europium ratios of 7.2 at%, 29.2 at%, 75.5 at%, and 98.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ within the middle of the samples. The fluorescence properties of the $\text{Eu}(\text{dbm})_3$ with PMMA, $\text{Eu}(\text{dbm})_3$ with PVA, $\text{CuInS}_2/\text{ZnS}$ with PMMA, and $\text{CuInS}_2/\text{ZnS}$ with PVA samples are measured and compared with ETO thin films.

The normalised PL intensities of samples at 613nm emission wavelength, corresponding to different europium ratios, are recorded and depicted in Figure 6-3, employing an excitation wavelength of 393nm. This analysis facilitates a comprehensive examination and comparison of fluorescence variation among the samples. Notably, Figure 6-3 highlights the considerable influence of the europium ratio on fluorescence intensity. Particularly obvious is the observed increase in

fluorescence intensity in the majority of samples with lower europium ratios, especially those below 50 at% Eu/(Eu+Ti). The maximum PL intensity of ETO thin films at 0 hours was normalised to 1. However, following UV exposure, some of the normalised PL intensities exceeded 1, possibly indicating that the thin films were cured by UV light.

The sample with a europium ratio of 7.2 at% Eu/(Eu+Ti) exhibits the highest fluorescence intensity among all samples prior to UV exposure. It maintains remarkable stability throughout the 40-hour degradation testing, experiencing only a modest 10% reduction in emission intensity by the end of the testing period. Conversely, the sample with a europium ratio of 29.2 at% Eu/(Eu+Ti) demonstrates initially high emission intensity, but it rapidly bleaches within the first 5 hours, resulting in a nearly 50% decrease in emission intensity. Subsequently, the decrease in emission intensity of 29.2 at% Eu/(Eu+Ti) thin film stabilises and keeps at a lower level, for the remainder of the degradation testing. In contrast, both the 75.5 at% and 98.2 at% Eu/(Eu+Ti) samples display low and consistent emission intensity both before and after UV exposure. Notably, the emission intensities of the 7.2 at%, 29.2 at% and 75.5 at% Eu/(Eu+Ti) thin film is about twelve, eight and three times higher than that of the 98.2% Eu/(Eu+Ti) thin film before degradation testing respectively. However, the 75.5 at% Eu/(Eu+Ti) thin film has approximately a 50% reduction in emission intensity after 40 hours of UV exposure.

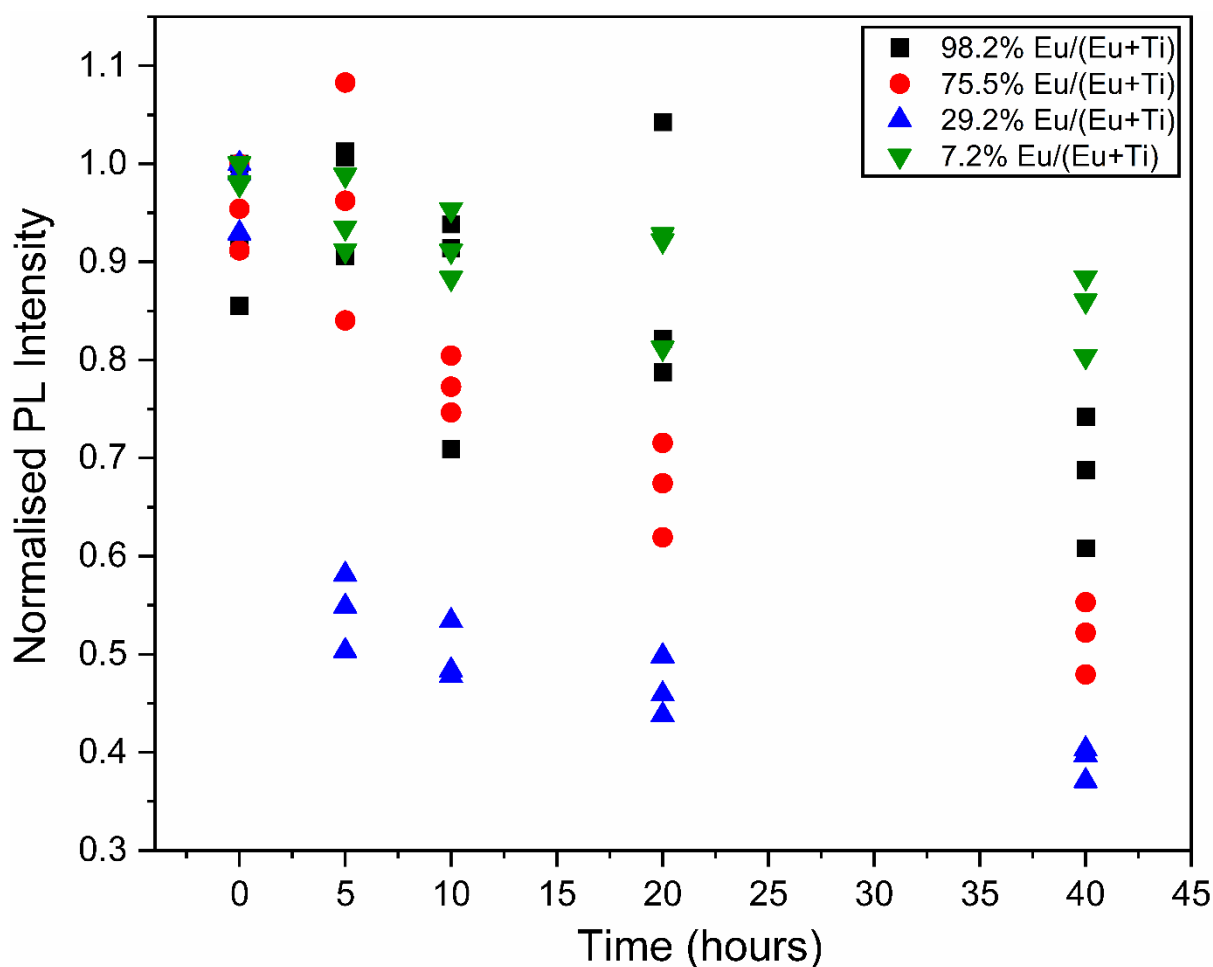


Figure 6-3 Normalised PL intensity of luminescence thin films with different at% Eu/(Eu+Ti) at 394nm excitation wavelength for 0 to 40 hours degradation testing.

The fluorescence exhibited by these films is primarily attributed to the presence of ETO, with variations in fluorescence spectra stemming from the diverse europium ratios within the films, as illustrated in Figure 6-4.

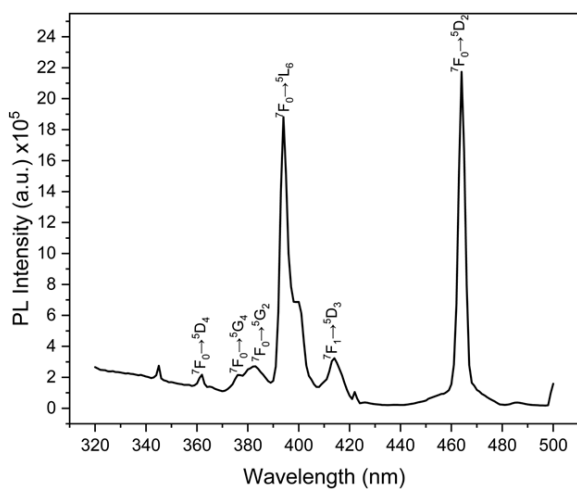
Excitation and emission spectra for analysing the photoluminescence properties of Eu^{3+} films, where the various europium ratios exert notable influence on the resulting PL spectra. Photoluminescence spectroscopy is employed to measure the fluorescence spectra of the samples, with particular attention directed towards specific areas corresponding to europium ratios of 7.2 at% (Figure 6-4 (a) &(b)), 29.2 at% (Figure 6-4 (c) &(d)), 75.5 at% (Figure 6-4 (e) &(f)), and 98.2 at% (Figure 6-4 (g) &(h)) Eu/(Eu+Ti) within the middle of the samples. In the excitation spectra (Figure 6-4 (a) (c) (e) (g)), a fixed typical emission wavelength of 613 nm is maintained, while the emission spectra (Figure 6-4 (b) (d) (f) (h)) are recorded with a fixed typical excitation wavelength of 394 nm. Leveraging the electronic structure and ensuing luminescent

characteristics of Eu^{3+} ions in evaluating luminescence spectra and discerning the local site symmetry of Eu^{3+} ions within the host matrix.[200] Notably, the ground state $^7F_0$ and the primary emitting level $^5D_0$ are non-degenerate, providing crucial insights into the photoluminescent behaviour of ETO luminescent thin films. These excitation wavelengths and transitions are observed across the excitation spectra of samples with varying europium ratios. Notably, the transitions $^7F_0 \rightarrow ^5L_6$ (394 nm) and $^7F_0 \rightarrow ^5D_2$ (464 nm) consistently exhibit strong intensities in the spectra. In particular, the $^7F_0 \rightarrow ^5L_6$ (394 nm) transition, consistently displays one of the highest intensities and is consequently selected as the fixed typical excitation wavelength for recording emission spectra. When excited under the 394 nm wavelength, Eu^{3+} ions transition to the $^5L_6$ level, while the emission spectra display transitions originating from the $^5D_0$ level. The fluorescence intensity increases as the at% $\text{Eu}/(\text{Eu}+\text{Ti})$ decreases, reaching its peak at a specific at% $\text{Eu}/(\text{Eu}+\text{Ti})$ value before declining. Furthermore, all the ETO samples exhibited identical emission wavelengths, with only the fluorescence intensity varying.

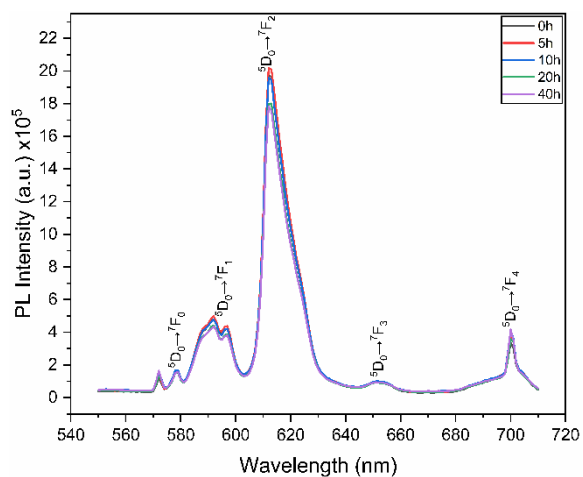
Figure 6-4 (b), (d), (f), and (h) present the emission spectra of samples featuring various europium ratios of 7.2 at%, 29.2 at%, 75.5 at%, and 98.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ respectively, measured at the centre of the samples. The emission spectra cover a wavelength range from 550 to 710 nm. For the investigation of emission spectra, the typical excitation wavelength corresponding to the $^7F_0 \rightarrow ^5L_6$ transition at 394 nm is employed. The emission spectra (550—710 nm) reveal several specific emission peaks located at 579, 592, 613, 652, and 700 nm, attributed to distinct $4f$ level transitions of Eu^{3+} ions, namely $^5D_0 \rightarrow ^7F_0$ (579 nm), $^5D_0 \rightarrow ^7F_1$ (592 nm), $^5D_0 \rightarrow ^7F_2$ (613 nm), $^5D_0 \rightarrow ^7F_3$ (652 nm), and $^5D_0 \rightarrow ^7F_4$ (700 nm). Upon comparing all transitions in the emission spectra, it is evident that the most intense and well-defined red emission peak at 613 nm corresponds to the electric-dipole (ED) allowed transition $^5D_0 \rightarrow ^7F_2$ (613 nm), commonly known as the "hypersensitive" transition.[201] This peak is chosen as the fixed typical emission wavelength for recording excitation spectra due to its high responsiveness to the local environment of Eu^{3+} . Conversely, the intensity of the peak at 592 nm, associated with the magnetic-dipole (MD) allowed $^5D_0 \rightarrow ^7F_1$ (592 nm) transition, demonstrates minimal variation relative to the crystal field strength surrounding Eu^{3+} ions. Before degradation testing, both excitation and emission spectra exhibit similar intensities. However, as the duration of the degradation testing

increases, the emission intensities of the samples decrease, indicating a degradation in their luminescent properties over time. After 5 hours of UV exposure, some samples exhibit an increase in maximum emission intensities, suggesting crystallisation or defect removal in the thin films, it needs more evidence. The figures provide more precise insights into the changes observed across the emission spectra, even as the intensity diminishes. Notably, the sample featuring a europium ratio of 7.2 at% Eu/(Eu+Ti) demonstrates the highest fluorescence intensity among all samples before and after UV exposure, only comparing 7.2 at%, 29.2 at%, 75.5 at% and 98.2 at% Eu/(Eu+Ti). Conversely, the thin film with a 29.2 at% Eu/(Eu+Ti) experiences rapid bleaching within the first 5 hours of exposure. In contrast, samples with ratios of 75.5 at% and 98.2 at% Eu/(Eu+Ti) exhibit a gradual decrease in fluorescence intensity throughout the degradation testing period, because those samples have weaker absorption.

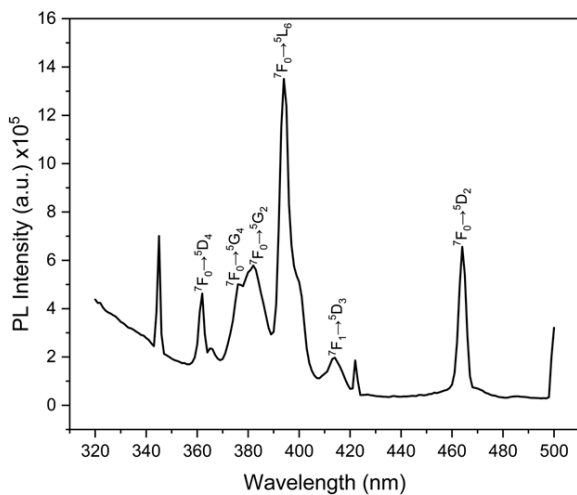
(a)



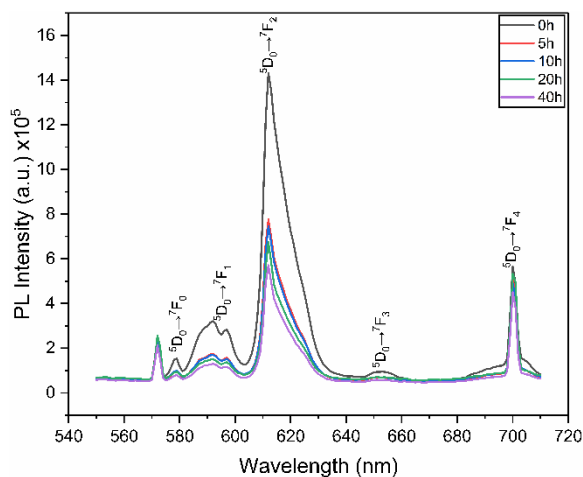
(b)



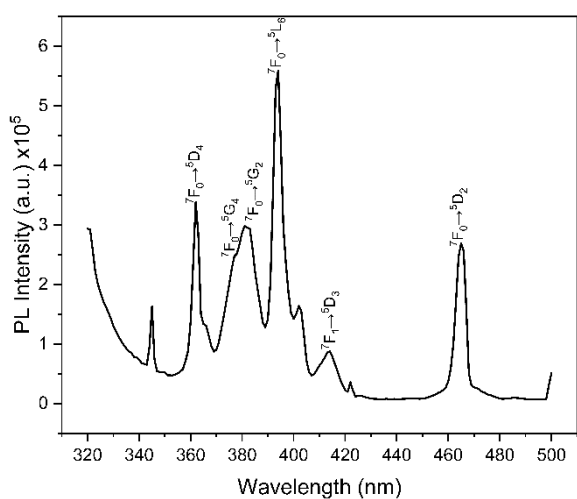
(c)



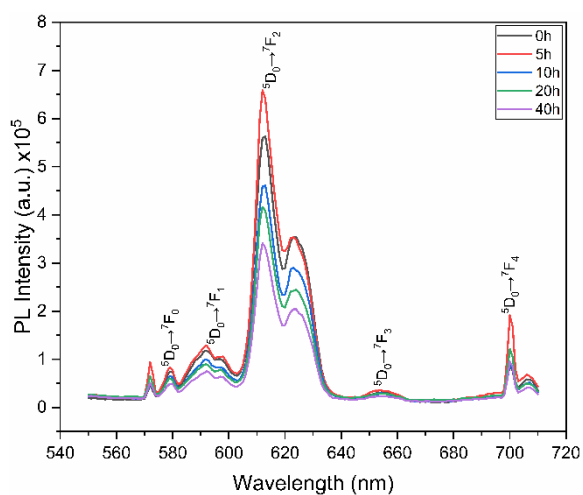
(d)



(e)



(f)



(g)

(h)

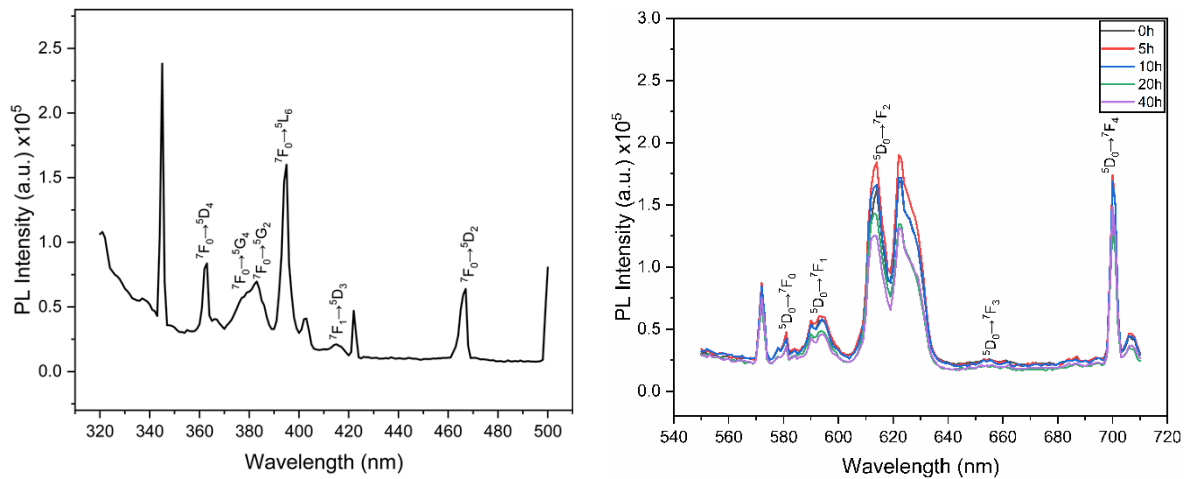


Figure 6-4 The excitation spectra of samples (a) 7.2 at%, (c) 29.2 at%, (e) 75.5 at%, and (g) 98.2 at% Eu/(Eu+Ti) after annealing at 600°C before degradation testing. The emission spectra of samples (b) 7.2 at%, (d) 29.2 at%, (f) 75.5 at%, and (h) 98.2 at% Eu/(Eu+Ti) before degradation testing (0 hour) and during degradation testing at 5, 10, 20 and 40 hours.

6.2.2.1 Fluorescence properties of polymer samples during degradation testing.

The normalised PL intensities corresponding to the $\text{Eu}(\text{dbm})_3$ with PMMA, $\text{Eu}(\text{dbm})_3$ with PVA, $\text{CuInS}_2/\text{ZnS}$ with PMMA, and $\text{CuInS}_2/\text{ZnS}$ with PVA luminescence thin film samples are meticulously recorded and illustrated in Figure 6-5, utilising distinct excitation wavelengths. The maximum PL intensities of the films at 0 hours were normalised to 1. This comprehensive analysis facilitates an in-depth examination and comparison of fluorescence variation across the samples. Notably, Figure 6-5 underscores the significant influence of the materials on fluorescence intensity and lifetime, with discernible higher values observed in fluorescence intensity within the samples containing $\text{Eu}(\text{dbm})_3$ without UV exposure. However, the samples with $\text{CuInS}_2/\text{ZnS}$ are observed with lower values in fluorescence intensity before degradation testing. Furthermore, the trendlines and device equations are included in Figure 6-5 for the comparison of the degradation of the films.

Before the degradation testing, the samples containing $\text{Eu}(\text{dbm})_3$ demonstrates notably stronger fluorescence intensity, with $\text{Eu}(\text{dbm})_3$ with PVA exhibiting the highest intensity among the samples. The luminescence materials are embedded with PVA and PMMA will exhibit diverse PL intensity.[202] This particular sample maintained stable and high emission intensity during the initial 5 hours of UV exposure. However, a

substantial decline in emission intensity occurred thereafter, reaching very low levels, with the sample exhibiting weak fluorescence. Similarly, $\text{Eu}(\text{dbm})_3$ with PMMA also displayed strong emission intensity at the onset of testing, similar to that of $\text{Eu}(\text{dbm})_3$ with PVA. However, the emission intensity of $\text{Eu}(\text{dbm})_3$ with PMMA exhibited rapid bleaching within a short timeframe, with swift bleaching observed within the first hour and nearing complete bleaching after 5 hours of degradation testing. Therefore, the trendline of $\text{Eu}(\text{dbm})_3$ with PMMA only describes the degradation process after the first hour. Conversely, both $\text{CuInS}_2/\text{ZnS}$ with PVA and $\text{CuInS}_2/\text{ZnS}$ with PMMA samples exhibited low and consistent emission intensity both before and after UV exposure, with these samples displaying similar and steady declines in emission intensity. Notably, $\text{Eu}(\text{dbm})_3$ and $\text{CuInS}_2/\text{ZnS}$ with PMMA samples experienced a drastic reduction in emission intensity within the first hour, followed by a consistent decline thereafter.

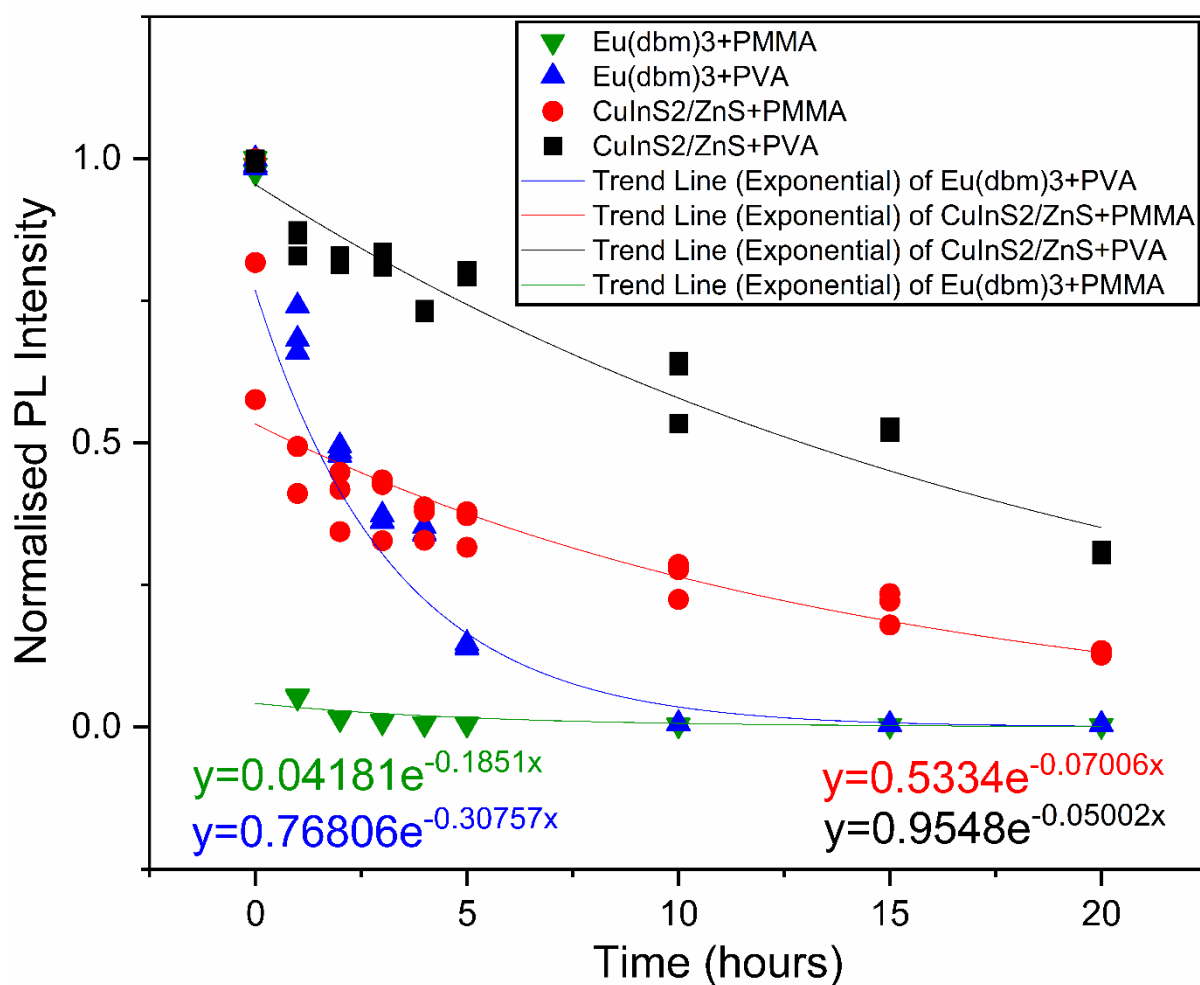


Figure 6-5 Normalised PL intensity of $\text{Eu}(\text{dbm})_3$ with PMMA, $\text{Eu}(\text{dbm})_3$ with PVA, $\text{CuInS}_2/\text{ZnS}$ with PMMA, and $\text{CuInS}_2/\text{ZnS}$ with PVA luminescence thin films with a fixed

typical excitation wavelength after 0 to 20 hours degradation testing. The trendlines and device equations for the degradation of the films.

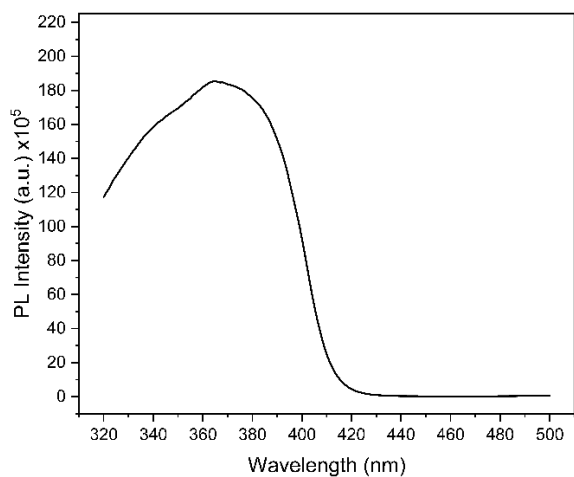
The synthesis process involving drop-casting and curing of these luminescence thin films results in distinct fluorescence characteristics. Figure 6-6 presents a comprehensive overview of the fluorescence spectra exhibited by thin films incorporating various materials, including $\text{Eu}(\text{dbm})_3$ with PMMA, $\text{Eu}(\text{dbm})_3$ with PVA, $\text{CuInS}_2/\text{ZnS}$ with PMMA, and $\text{CuInS}_2/\text{ZnS}$ with PVA. Notably, thin films incorporating $\text{Eu}(\text{dbm})_3$ and $\text{CuInS}_2/\text{ZnS}$ luminescent materials manifest diverse fluorescence properties. $\text{CuInS}_2/\text{ZnS}$ QDs have advantageous characteristics, including the use of non-toxic elements, cost-effective synthesis, and adjustable bandgap. In addition $\text{CuInS}_2/\text{ZnS}$ QDs and $\text{Eu}(\text{dbm})_3$ has similar maximum excitation and emission wavelengths. Specifically, $\text{Eu}(\text{dbm})_3$ -based thin films exhibit a wide range of excitation wavelengths and feature several narrow emission peaks, while $\text{CuInS}_2/\text{ZnS}$ -based thin films demonstrate broad excitation and emission wavelength ranges. The excitation processes involving Eu^{3+} ions are intricately linked to electronic transitions from the ground state $^7\text{F}_0$ to energy levels surpassing $^5\text{D}_0$. Energy originating from states higher than $^5\text{D}_0$ undergoes non-radiative transitions, ultimately relaxing to the $^5\text{D}_0$ state. The visible emissions of Eu^{3+} ions arise from radiative transitions from the lowest $^5\text{D}_0$ excited states to $^7\text{F}_J$ ($J = 0-4$) states, underscoring the complex luminescence mechanisms in these thin film materials.

Excitation and emission spectra of four distinct compositions— $\text{Eu}(\text{dbm})_3$ with PMMA (Figure 6-6 (a) &(b)), $\text{Eu}(\text{dbm})_3$ with PVA (Figure 6-6 (c) &(d)), $\text{CuInS}_2/\text{ZnS}$ with PMMA (Figure 6-6 (e) &(f)), and $\text{CuInS}_2/\text{ZnS}$ with PVA (Figure 6-6 (g) &(h))—are meticulously measured within the central regions of the samples. In the excitation spectra (Figure 6-6 (a) (c) (e) (g)), the fixed typical emission wavelengths of 612 nm for $\text{Eu}(\text{dbm})_3$ samples and 618 nm for $\text{CuInS}_2/\text{ZnS}$ samples are maintained. Conversely, the emission spectra (Figure 6-6 (b) (d) (f) (h)) are recorded with a fixed typical excitation wavelength of 363 nm for $\text{Eu}(\text{dbm})_3$ samples and 360 nm for $\text{CuInS}_2/\text{ZnS}$ samples. This systematic approach enables a comprehensive investigation and comparison of the fluorescence properties among the different luminescent thin film compositions.

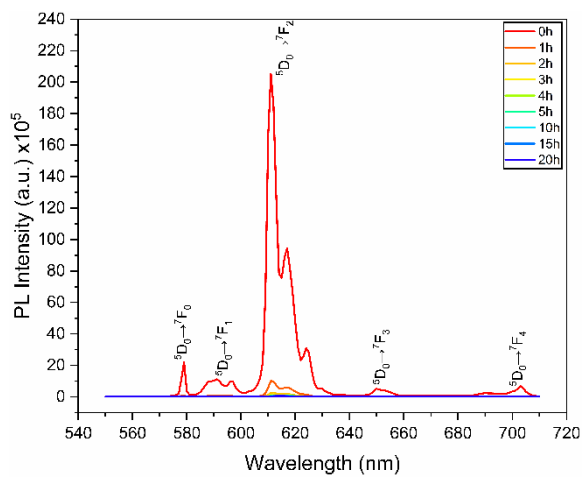
The excitation spectra (Figure 6-6 (a) (c) (e) (g)) span the range from 320 nm to 500 nm, revealing broad excitation spectra across all samples. Meanwhile, Figure 6-6 (b)

(d) (f) (h) depicts the emission spectra of samples ranging from 550 nm to 710 nm. While CuInS₂/ZnS samples exhibit wide emission spectra, Eu(dbm)₃ samples showcase several narrow emission peaks. To investigate the emission spectra of Eu(dbm)₃ samples, a typical excitation wavelength corresponding to 363 nm is utilised. The emission spectra (550—710 nm) unveil specific emission peaks at 579, 592, 612, 652, and 700 nm, attributed to distinct 4*f* level transitions of Eu³⁺ ions—namely $^5D_0 \rightarrow ^7F_0$ (579 nm), $^5D_0 \rightarrow ^7F_1$ (592 nm), $^5D_0 \rightarrow ^7F_2$ (613 nm), $^5D_0 \rightarrow ^7F_3$ (652 nm), and $^5D_0 \rightarrow ^7F_4$ (700 nm). Among these transitions, the most intense and well-defined red emission peak at 612 nm corresponds to the electric-dipole (ED) allowed transition $^5D_0 \rightarrow ^7F_2$ (612 nm), often referred to as the "hypersensitive" transition.[109]

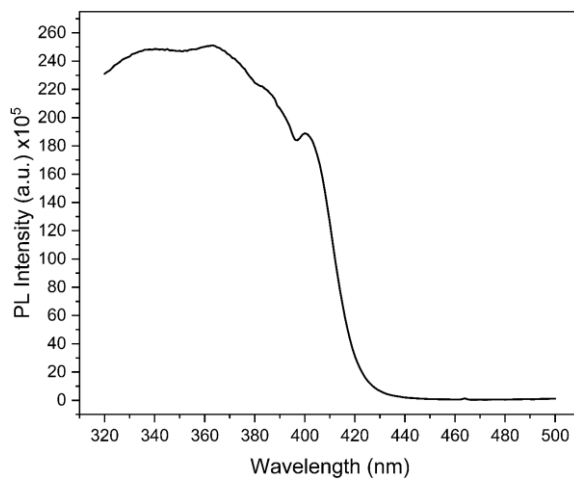
(a)



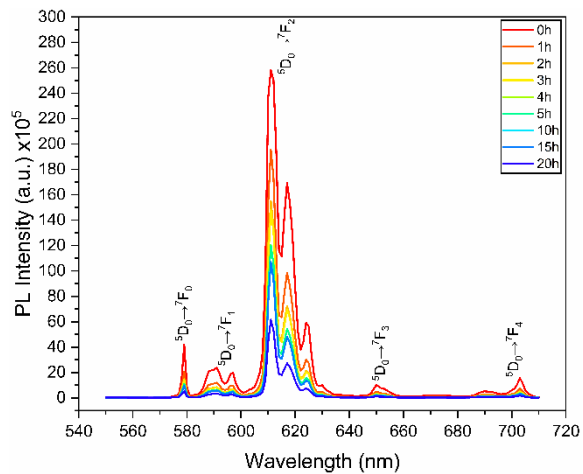
(b)



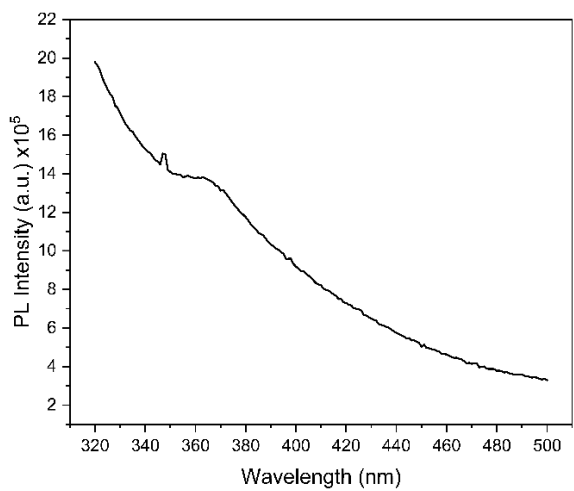
(c)



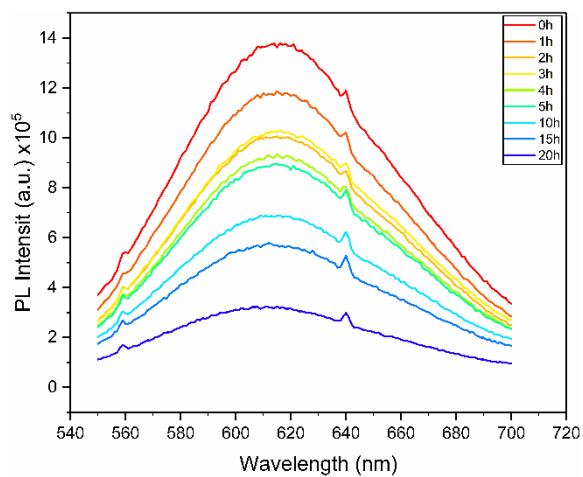
(d)



(e)



(f)



(g)

(h)

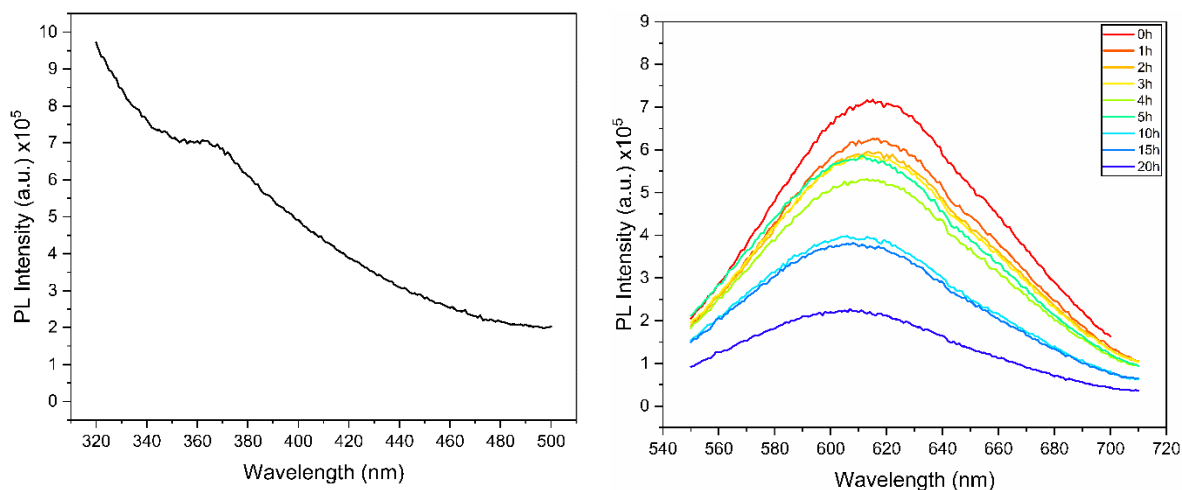
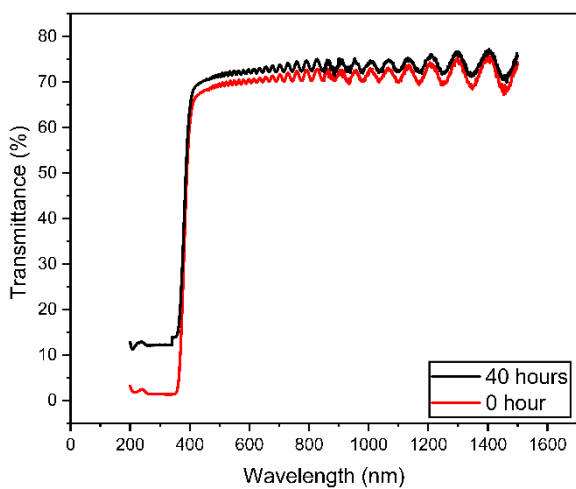


Figure 6-6 The excitation spectra of samples (a) $\text{Eu}(\text{dbm})_3$ with PMMA, (c) $\text{Eu}(\text{dbm})_3$ with PVA, (e) $\text{CuInS}_2/\text{ZnS}$ with PMMA, and (g) $\text{CuInS}_2/\text{ZnS}$ with PVA. The emission spectra of samples (b) $\text{Eu}(\text{dbm})_3$ with PMMA, (d) $\text{Eu}(\text{dbm})_3$ with PVA, (f) $\text{CuInS}_2/\text{ZnS}$ with PMMA, and (h) $\text{CuInS}_2/\text{ZnS}$ with PVA.

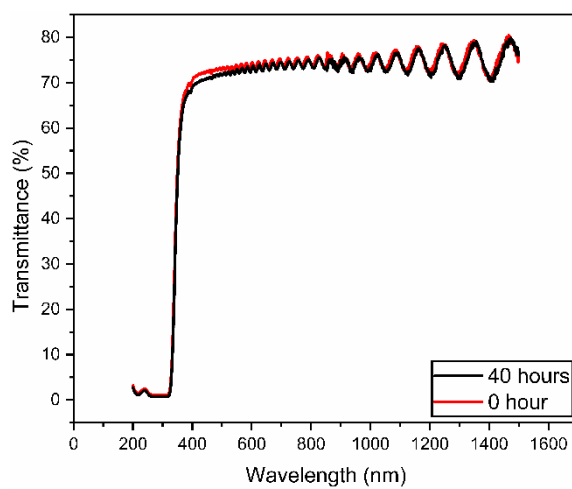
6.2.3 Transmittance and Bandgap of samples

The Tauc plot will be drawn by (5-1). Representative samples featuring different europium ratios (7.2 at%, 29.2 at%, 75.5 at%, and 98.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$) underwent UV-Vis testing for comparison purposes. Transmittance spectra and Tauc plots of the samples, both before and after degradation testing, are presented in Figure 6-7. Notably, samples with higher europium ratios exhibit higher transmittance (T%) values from 450 to 1500 nm, with percentages ranging from approximately 75T%, 78 T%, 82 T% and 90 T% for 7.2 at%, 29.2 at%, 75.5 at% and 98.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ samples respectively. Furthermore, all samples exhibit sharp absorption edges from 300 to 400 nm, enabling effective photon absorption in the UV region. Concurrently, the bandgap of each sample increases with the europium ratio, with values of 3.46, 3.72, 3.93, and 3.53 eV for 7.2 at%, 29.2 at%, 75.5 at%, and 98.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ samples respectively. Remarkably, transmittance spectra and bandgap measurements remain consistent before and after degradation testing, indicating minimal influence of UV exposure on the optical properties of ETO luminescence thin films.

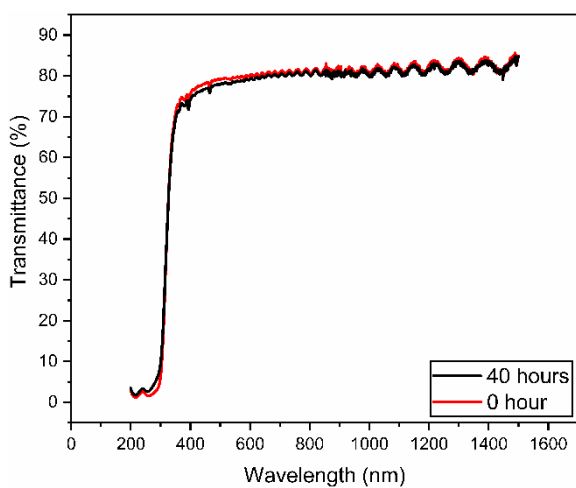
(a)



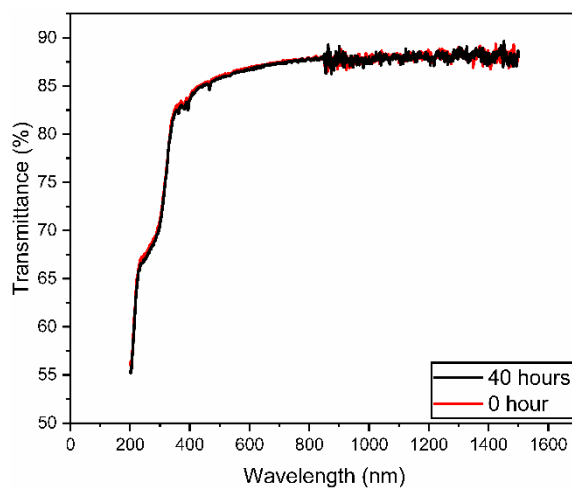
(b)



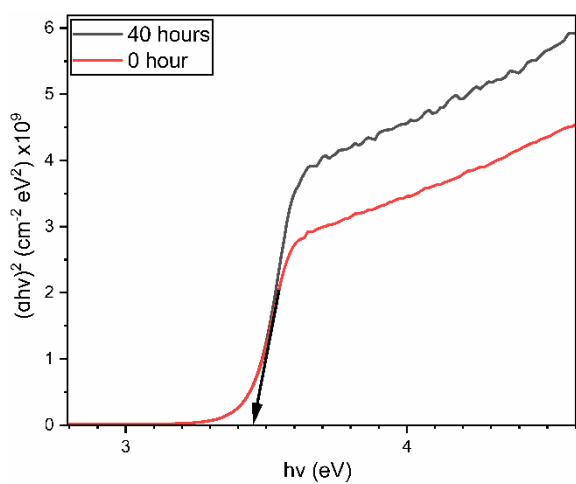
(c)



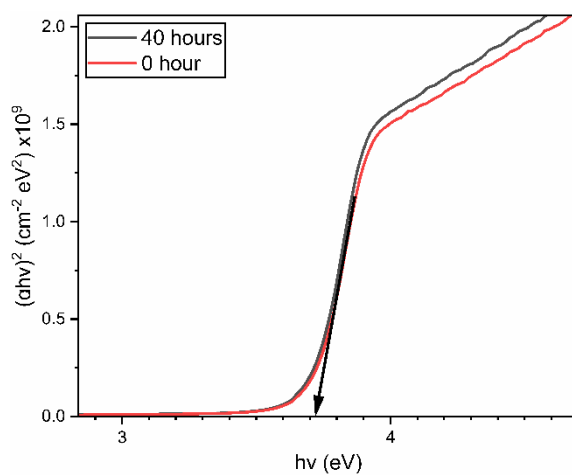
(d)



(e)



(f)



(g)

(h)

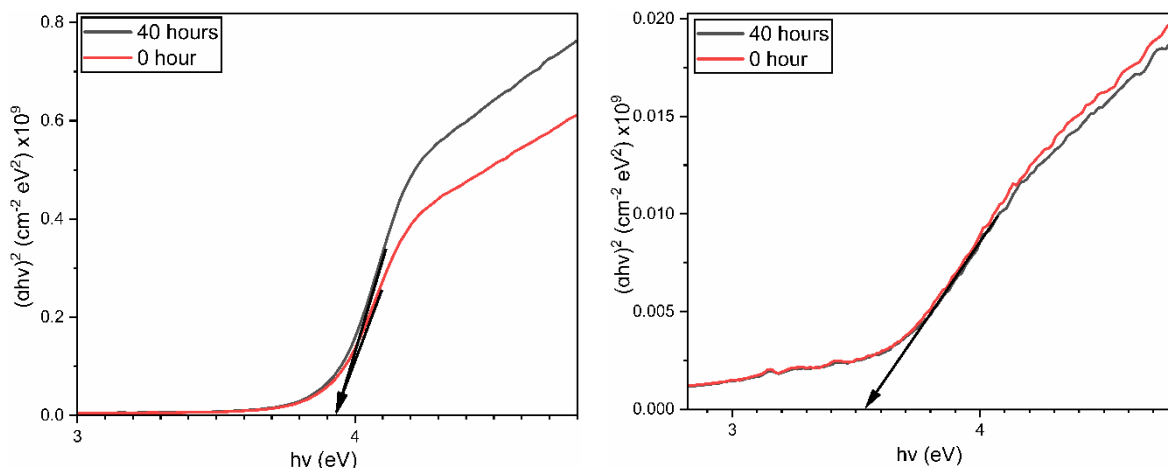


Figure 6-7 Transmittances of (a) 7.2 at%, (b) 29.2 at%, (c) 75.5 at%, and (d)98.2 at% Eu/(Eu+Ti) samples before and after 40 hours degradation testing. Tauc plots of (e)7.2 at%, (f) 29.2 at%, (g) 75.5 at%, and (h)98.2 at% Eu/(Eu+Ti) samples before and after 40 hours of degradation testing.

Upon exposure to UV radiation, significant alterations in transmittance and bandgap characteristics are observed in samples containing $\text{Eu}(\text{dbm})_3$, whereas samples with $\text{CuInS}_2/\text{ZnS}$ show minimal changes in these properties.[23,203,204] The bandgaps of the samples are determined using Tauc plots calculated from the transmittance spectra.

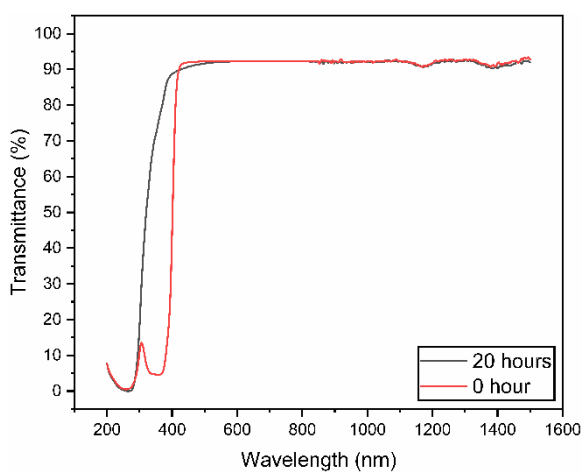
The Tauc plot will be drawn by (5-1), and the transmittance spectra are recorded before and after degradation testing to enable comparison. Figure 6-8 present transmittance spectra and Tauc plots of the samples, both before and after degradation testing. Notably, all samples— $\text{Eu}(\text{dbm})_3$ with PVA, $\text{Eu}(\text{dbm})_3$ with PMMA, $\text{CuInS}_2/\text{ZnS}$ with PVA, and $\text{CuInS}_2/\text{ZnS}$ with PMMA—exhibit higher transmittance (T%) values from 450 to 1500 nm both before and after degradation testing, with transmittance values averaging approximately 92 T%.

Two dramatic changes are evident in the transmittance spectra of $\text{Eu}(\text{dbm})_3$ with PVA and $\text{Eu}(\text{dbm})_3$ with PMMA thin films within the wavelength range of 200 to 450 nm before degradation testing. The $\text{Eu}(\text{dbm})_3$ with PVA sample demonstrates a rapid decrease in transmittance between 420 and 320 nm, with the transmittance plummeting from 92 T% to 5 T%, indicating strong absorption in this region. Conversely, a sharp decline occurs in the transmittance spectra of the $\text{Eu}(\text{dbm})_3$ with PMMA sample between 420 and 360 nm, where transmittance decreases from 92 T%

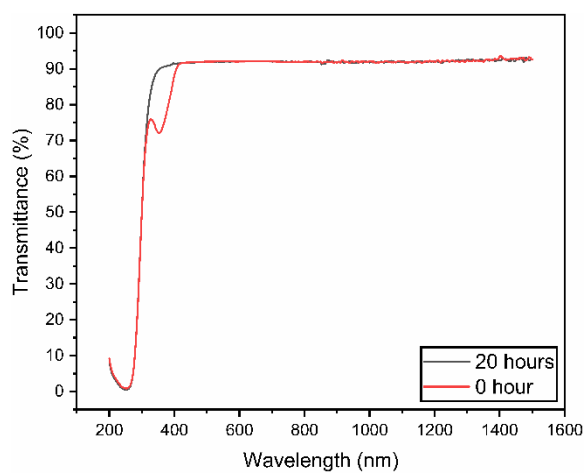
to 72 T%, indicative of photon absorption within this range. However, these discernible changes vanish after 20 hours of degradation testing due to photobleaching phenomena observed in these samples, resulting in the loss of photon absorption in this region. In contrast, CuInS₂/ZnS with PVA and CuInS₂/ZnS with PMMA exhibit higher transmittance (T%) values before and after degradation testing. However, the transmittance spectra of these samples resemble that of the substrate, suggesting that these two samples lack significant absorption capability.

Simultaneously, the bandgap values of these samples are determined through calculation. Before the degradation testing, all samples—Eu(dbm)₃ with PVA, Eu(dbm)₃ with PMMA, CuInS₂/ZnS with PVA, and CuInS₂/ZnS with PMMA—exhibit similar main bandgap values of 4.16, 4.40, 4.38, and 4.41 eV, respectively, but Eu(dbm)₃ with PVA illustrated the second bandgap at 3.14 eV. The bandgap values have slight changed observed after UV exposure for all samples. Following degradation testing, the bandgap values for Eu(dbm)₃ with PMMA, Eu(dbm)₃ with PVA, CuInS₂/ZnS with PMMA, and CuInS₂/ZnS with PVA samples are 4.46, 4.48, 4.38, and 4.46 eV, respectively. Notably, the Eu(dbm)₃ with PVA sample presents two bandgap values: one at 4.16 eV and the other at 3.14 eV. The bandgap value of 3.14 eV corresponds to strong absorption observed in the Eu(dbm)₃ with PVA sample between 420 and 320 nm, but this bandgap is missed after degradation testing.

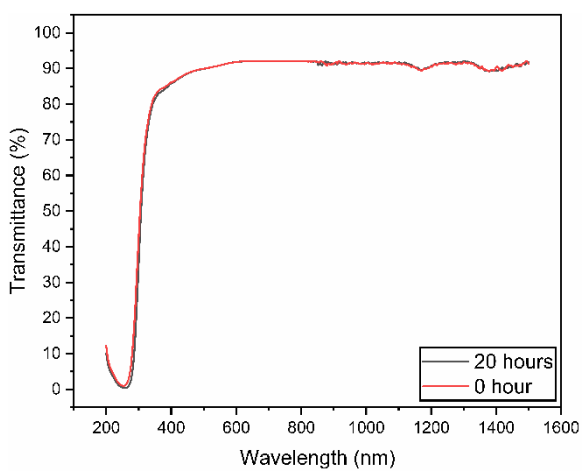
(a)



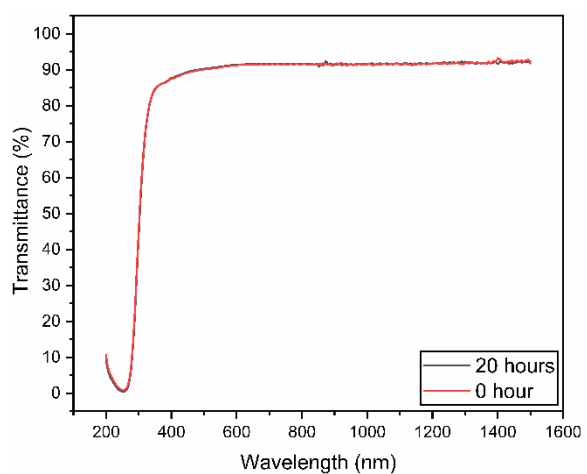
(b)



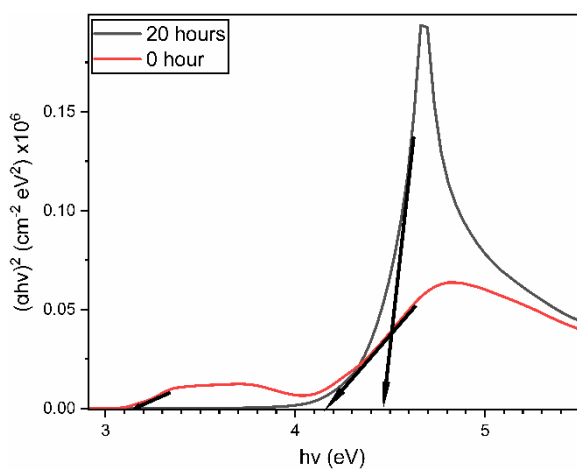
(c)



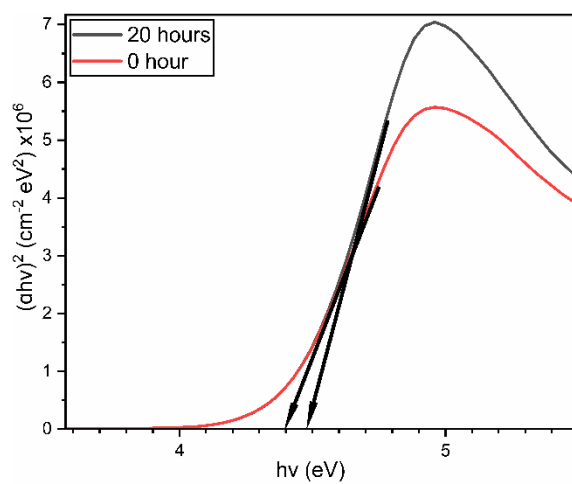
(d)



(e)



(f)



(g)

(h)

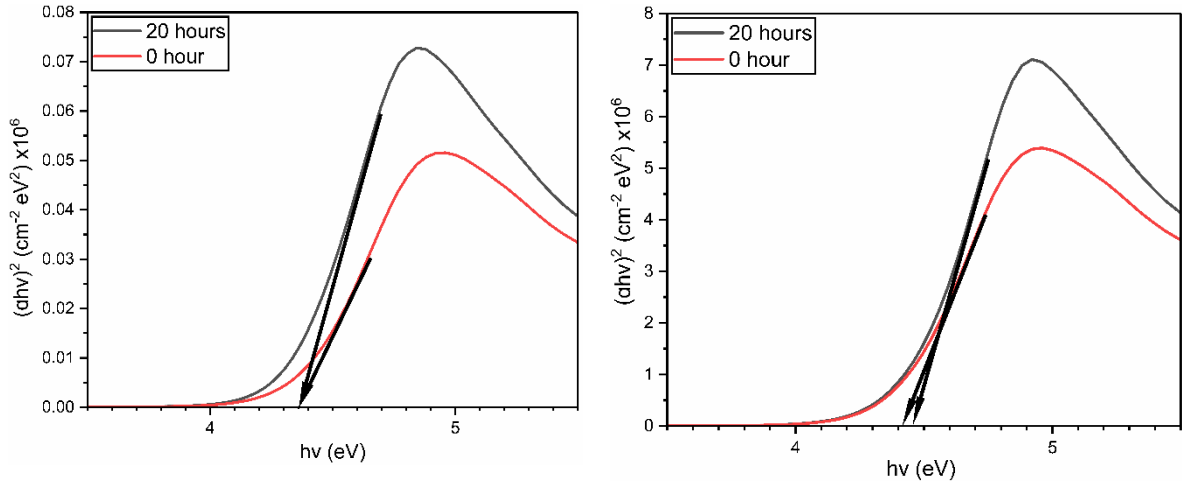


Figure 6-8 Transmittances of (a) $\text{Eu}(\text{dbm})_3$ with PVA, (b) $\text{Eu}(\text{dbm})_3$ with PMMA, (c) $\text{CuInS}_2/\text{ZnS}$ with PVA, and (d) $\text{CuInS}_2/\text{ZnS}$ with PMMA samples before and after 20 hours degradation testing. Tauc plots of (e) $\text{Eu}(\text{dbm})_3$ with PVA, (f) $\text{Eu}(\text{dbm})_3$ with PMMA, (g) $\text{CuInS}_2/\text{ZnS}$ with PVA, and (h) $\text{CuInS}_2/\text{ZnS}$ with PMMA samples before and after 20 hours degradation testing.

6.2.4 Power conversion efficiency of solar cells with luminescence thin films

The utilisation of luminescence thin films atop solar cells aims to enhance the PCE, making the evaluation of their lifetime through degradation testing crucial.[205] To assess the PCE performance, the Oriel LCS-100 solar simulator will be employed. Representative samples featuring various europium ratios (7.2 at%, 29.2 at%, 75.5 at%, and 98.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$) (Figure 6-9) and polymer samples ($\text{Eu}(\text{dbm})_3$ with PMMA, $\text{Eu}(\text{dbm})_3$ with PVA, $\text{CuInS}_2/\text{ZnS}$ with PMMA, and $\text{CuInS}_2/\text{ZnS}$ with PVA) (Figure 6-10) have been selected for PCE testing to facilitate comparison. This investigation into PCE aims to gauge the effectiveness of these luminescent thin films in enhancing solar cell performance, thereby contributing to advancements in photovoltaic technology.

During the operational process of the solar cell, power, current, and voltage are generated. The formula for calculating the output power (P_{out}) involves multiplying the current (I) by the voltage (V), as demonstrated in the following equation (3-1).

The characterisation of solar cells relies on fundamental parameters such as Short Circuit Current (I_{sc}), Open Circuit Voltage (V_{oc}), Maximum Current (I_{max}), Maximum Voltage (V_{max}), and Maximum Power (P_{max}). The determination of the Maximum Power

is conventionally achieved by measuring both the Maximum Current and Maximum Voltage, as outlined in the following equation (3-2):

Upon calculation using the equation (3-2), distinct maximum output powers are observed for all samples, as depicted in the I-V plot. Specifically, the maximum output powers before degradation testing are recorded as 43.08, 46.02, 50.07, and 55.39 mW for ETO samples with 7.2 at%, 29.2 at%, 75.5 at%, and 98.2 at% Eu/(Eu+Ti) respectively. Furthermore, following degradation testing, the maximum output powers are measured as 43.22, 45.19, 50.97, and 55.05 mW for the corresponding samples. The maximum output powers before degradation testing are recorded as 56.34, 55.52, 54.52, and 55.95 mW, and after degradation testing are recorded as 56.99, 57.10, 57.15, and 57.55 mW for samples Eu(dbm)₃ with PMMA, Eu(dbm)₃ with PVA, CuInS₂/ZnS with PMMA, and CuInS₂/ZnS with PVA respectively.

The PCE is a critical parameter that signifies the ratio of Maximum Output Power ($P_{\max}$) to Sunlight Power Intensity (P_{Sunlight}). This pivotal relationship can be mathematically expressed as follows (3-3):

The PCE values for ETO samples with europium ratios of 7.2 at%, 29.2 at%, 75.5 at%, and 98.2 at% Eu/(Eu+Ti) before degradation testing are recorded as 10.77%, 11.50%, 12.52%, and 13.85% respectively. Post-degradation testing, the PCE values for these samples are measured as 10.81%, 11.30%, 12.74%, and 13.76% respectively. These results underscore the inverse relationship between the europium ratio and PCE in ETO samples, wherein lower ratios correlate with diminished PCE values. Furthermore, when considering PCE alongside transmittance and bandgap outcomes, it becomes apparent that samples featuring lower europium ratios exhibit reduced bandgaps and increased absorption. This phenomenon suggests increased photon absorption and scattering, leading to more photons escaping from the substrate's edge. The PCE values for the samples exhibit similar values both before and after degradation testing, suggesting that these thin films possess consistent optical properties. Furthermore, the similarity in PCE values implies weaker emission intensity, leading to lower scattering effects of the thin films.

PCE values for samples Eu(dbm)₃ with PMMA, Eu(dbm)₃ with PVA, CuInS₂/ZnS with PMMA, and CuInS₂/ZnS with PVA before degradation testing are recorded as 14.09%, 13.88%, 13.63% and 13.99% respectively. Moreover, the PCE after degradation

testing are recorded as 14.25%, 14.28%, 14.29% and 14.39% respectively. The PCE values for the samples exhibit similar values, which means these films do not affect the PCE significantly.

The Fill Factor (FF) within a solar cell is a crucial metric defined as the ratio of Maximum Output Power ($P_{\max}$) to the product of Short Circuit Current (I_{sc}) and Open Circuit Voltage (V_{oc}). It serves as a vital representation of the actual characteristics depicted by the I-V curve and provides insights into the quality of the solar cell. The Fill Factor formula is expressed as follows (3-4):

Following calculation, the Fill Factor (FF) results for the 7.2 at%, 29.2 at%, 75.5 at%, and 98.2 at% Eu/(Eu+Ti) samples are determined to be 72.42%, 72.93%, 73.06%, and 73.37% respectively. Additionally, the FF values for these samples after degradation testing are measured as 72.05%, 72.43%, 72.66%, and 73.13%. The Fill Factor (FF) results for the samples Eu(dbm)₃ with PMMA, Eu(dbm)₃ with PVA, CuInS₂/ZnS with PMMA, and CuInS₂/ZnS with PVA before degradation testing are determined to be 73.33%, 73.28%, 73.15% and 73.34% respectively. In addition, The Fill Factor (FF) results for the samples Eu(dbm)₃ with PMMA, Eu(dbm)₃ with PVA, CuInS₂/ZnS with PMMA, and CuInS₂/ZnS with PVA after degradation testing are determined to be 72.86%, 73.53%, 73.04% and 73.41% respectively.

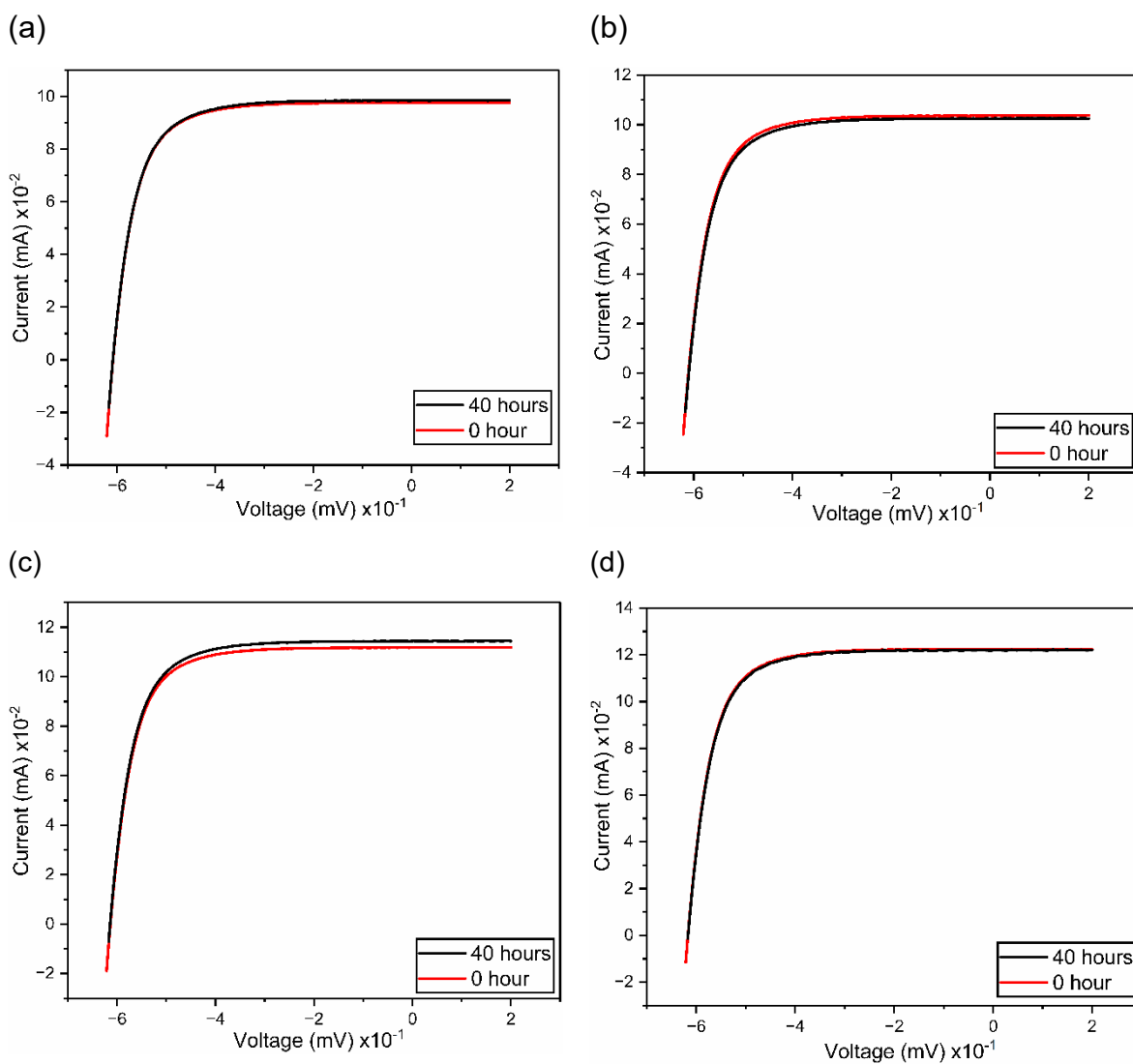


Figure 6-9 Power conversion efficiency of (a) 7.2 at%, (b) 29.2 at%, (c) 75.5 at% and (d) 98.2 at% Eu/(Eu+Ti) samples before and after 40 hours degradation testing.

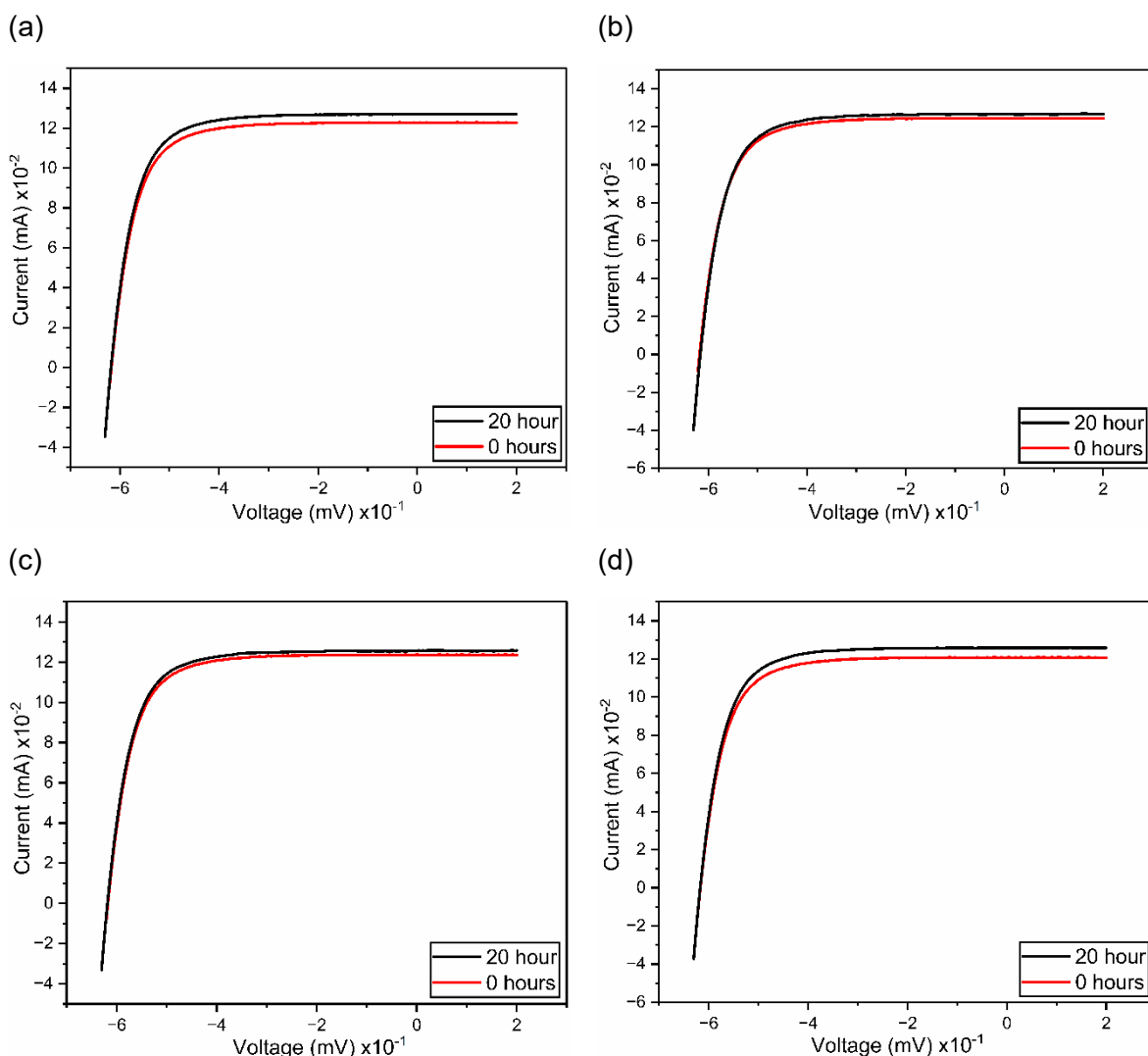


Figure 6-10 Power conversion efficiency of (a) $\text{Eu}(\text{dbm})_3$ with PVA, (b) $\text{Eu}(\text{dbm})_3$ with PMMA, (c) $\text{CuInS}_2/\text{ZnS}$ with PVA, and (d) $\text{CuInS}_2/\text{ZnS}$ with PMMA samples before and after 20 hours degradation testing.

6.3 Discussion

This study not only explores ETO but also compares it with $\text{Eu}(\text{dbm})_3$ with PVA, $\text{Eu}(\text{dbm})_3$ with PMMA, $\text{CuInS}_2/\text{ZnS}$ with PVA, and $\text{CuInS}_2/\text{ZnS}$ with PMMA as promising candidates for producing photoluminescent thin films, especially in the realm of wavelength-shifting applications. Eu-doped thin films exhibited luminescence properties are particularly noteworthy, characterised by narrow emission bands resulting from $f-f$ electron transitions.[186,187] $\text{CuInS}_2/\text{ZnS}$ QDs have garnered significant attention due to their environmentally friendly, cost-effective nature, along with their remarkable optical properties in the long-wavelength spectrum. The tunable emission wavelength of CuInS_2 QDs, achievable through size or composition

modulation, spans from the visible to the NIR region. Strategies such as the fabrication of CuInS₂ QDs with thicker shells, the selection of more durable surface ligands, and integration with advanced packaging technologies hold promise for enhancing their stability and longevity. Moreover, the high absorption coefficient of CuInS₂ QDs ($\sim 10^5 \text{ cm}^{-1}$) positions them as compelling candidates for applications in solar energy conversion.[22]

Visual inspection of the samples was conducted by capturing images with a camera under 365 nm UV excitation. For the ETO thin films only compared 7.2 at%, 29.2 at%, 75.5 at% and 98.2 at% Eu/(Eu+Ti). The fluorescence of the ETO samples appears in a dark red colour, while that of the Eu(dbm)₃ samples manifests in a bright red shade. This is attributed to PL intensity, the Eu(dbm)₃ samples have about 10 times higher PL intensity than ETO samples. These differences in colour can be attributed to the varying host materials utilised in each sample. Throughout the degradation testing process, a noticeable reduction in emission brightness intensity is observed, which correlates with the duration of UV exposure. Visual examination of the samples during the degradation testing reveals significant differences in the extent of bleaching among the various specimens. Specifically, Eu(dbm)₃ samples exhibit near-complete bleaching by the conclusion of the 10-hour degradation testing period, while CuInS₂/ZnS samples experience substantial bleaching after 20 hours of testing. In contrast, ETO samples maintain fluorescence even after 40 hours of degradation testing. Particularly noteworthy is the slow bleaching observed in samples containing 7.2 at% Eu/(Eu+Ti) (23 mm sputtering position), which exhibit strong fluorescence even after 40 hours of UV exposure.

The fluorescence intensities of all samples underwent noticeable changes following degradation testing. Particularly noteworthy is the ETO sample featuring a europium ratio of 7.2 at% Eu/(Eu+Ti), which demonstrated the highest fluorescence intensity both before and after 40-hour degradation testing. Conversely, the thin film with a 29.2 at% Eu/(Eu+Ti) experienced rapid bleaching within the initial 5 hours of exposure. In contrast, samples with ratios of 75.5 at% and 98.2 at% Eu/(Eu+Ti) exhibited a gradual decrease in fluorescence intensity throughout the degradation testing period. Of particular interest are the Eu(dbm)₃ samples, which displayed distinctive degradation rate. The Eu(dbm)₃ with PMMA sample exhibited a reduction of over 95% in emission intensity after just 1 hour of degradation testing. Similarly, the Eu(dbm)₃ with PVA

sample experienced a comparatively gradual decline during the degradation testing, yet still exhibited a reduction of over 75% after 20 hours of UV exposure. Furthermore, the reduction in fluorescence intensity observed in CuInS₂/ZnS samples, accompanied by a slight blue shift in the emission spectra, the blue shift in the maximum emission intensities of CuInS₂/ZnS thin films with PVA and PMMA during the degradation testing is illustrated in Figure Apx D - 1. This study underscores the stability of Eu:TiO₂ compared with Eu(dbm)₃ and CuInS₂ during degradation testing is illustrated and highlights the influence of fluorescence intensity by materials.

In the transmittance spectra and tauc plot suggest that ETO samples with lower europium ratios (less than 50 at% Eu/(Eu+Ti)) tend to exhibit superior absorption capabilities. Despite visual inspection of reduced fluorescence brightness following degradation testing, the bandgap values remain relatively stable before and after testing. This suggests that while the samples may experience diminished emission intensity, their fundamental optical properties, as represented by transmittance and bandgap, are largely unaffected by the degradation process. The bandgap of all samples before and after degradation testing are listed in Table 6-1 and Table 6-2. Thus, it can be inferred that the samples retain their ability to absorb photons while experiencing a loss in emission efficiency. For the Eu(dbm)₃ with PVA and Eu(dbm)₃ with PMMA samples, their absorption feature diminishes following degradation testing, indicating alterations in the bandgap characteristics of the sample. For Eu(dbm)₃, the DBM and Phen molecules are excited and transfer non-radiatively the energy to Eu³⁺. Changes in transmittance and bandgap suggest degradation of DBM and Phen molecules.[206] Additionally, the transmittance and bandgap characteristics of the Eu(dbm)₃ with PMMA and Eu(dbm)₃ with PVA thin films undergo noticeable changes post-degradation testing, attributed to observable alterations resulting from photobleaching phenomena. These changes ultimately contribute to the loss of photon absorption capability in the affected samples.

Table 6-1 Bandgap values of ETO thin films before and after degradation testing.

	7.2 at% Eu/(Eu+Ti)	29.2 at% Eu/(Eu+Ti)	75.5 at% Eu/(Eu+Ti)	98.2 at% Eu/(Eu+Ti)
Before degradation testing	3.46 eV	3.72 eV	3.93 eV	3.53 eV
After degradation testing	3.46 eV	3.72 eV	3.93 eV	3.53 eV

Table 6-2 Bandgap values of Eu(dbm)₃ with PVA, Eu(dbm)₃ with PMMA, CuInS₂/ZnS with PVA, and CuInS₂/ZnS with PMMA thin films before and after degradation testing.

	Eu(dbm) ₃ with PVA		Eu(dbm) ₃ with PMMA	CuInS ₂ /ZnS with PVA	CuInS ₂ /ZnS with PMMA
Before degradation testing	3.14 eV	4.16 eV	4.40 eV	4.38 eV	4.41 eV
After degradation testing	4.46 eV		4.48 eV	4.38 eV	4.46 eV

When comparing the characteristics of the ETO samples with those of Eu(dbm)₃ and CuInS₂/ZnS with polymer samples, notable differences emerge. Specifically, the polymer samples exhibit higher transmittance levels, averaging approximately 92 T%, across the visible and NIR regions. Conversely, these polymer-based samples demonstrate higher bandgap values compared to the ETO samples with lower europium ratios (less than 50 at% Eu/(Eu+Ti)). This discrepancy suggests that the polymer samples possess weaker absorption of UV light. Notably, all samples demonstrate consistently high FF results before and after degradation testing in the I-V curves from the solar simulator, with differences of within 2%.

The degradation mechanisms of these luminescent thin films are expected based on the analysis of characteristic results. It is understood that different materials used in the fabrication of luminescent thin films may lead to varied degradation mechanisms. Following annealing at 600°C, clusters of anatase and rutile phases form within the amorphous TiO₂ matrix and a portion of the Eu³⁺ ions diffuse into these clusters. This allows the thin films with 7.2 at% Eu/(Eu+Ti) to exhibit significantly higher excitation efficiency due to energy transfer from the crystalline TiO₂ to the Eu³⁺ ions. Note that anatase TiO₂ possesses a wider bandgap at ~3.2 eV compared to its rutile counterpart at ~3.0 eV.[165] The presence of rutile TiO₂ crystallites allows for the effective absorption of photons at 394 nm, as they are more likely to be excited than the anatase

crystallites. These absorptions are followed by energy transfer to Eu^{3+} ions, which then relax to the $^5D_0$ band edge through non-radiative cascading single/multi-phonon relaxation from $^5L_6$. [147] This is followed by radiative transitions from $^5D_0$ to ^7F_J ($J = 0, 1, 2, 3, 4$) with the transition of $^5D_0 \rightarrow ^7F_2$ at 613 nm to be the most intense and well-defined red emission observable in the visible spectral range. Annealing at 600°C results in the formation of anatase and rutile crystallites of TiO_2 at the thin films with 7.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$. Conversely, ETO films with 29.2 and 75.5 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ lack crystalline phases even after annealing. This results in reduced photon absorption and diminished PL intensity. For 100 at% (pure Eu_2O_3) film, the formation of monoclinic Eu_2O_3 crystallites with a bandgap of 4.3 eV limits the photon absorption to Eu^{3+} ions and causes very weak emission. [175]

Although less likely, the anatase phase of TiO_2 present in the ETO thin film with 7.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ may also be, in principle, excited by the 394 nm UV light. The incorporation of Eu_2O_3 in the TiO_2 forms oxygen vacancies, which for anatase TiO_2 leads to the localisation of one or two electrons within the vacancy state due to the Madelung potential of the ionic crystal structure. [176–178] These vacancies may introduce energy levels 0.75–1.18 eV below the conduction band and create localised trap states that affect the bandgap of the material. [177] These states effectively reduce the energy required for electronic transitions, allowing sub-bandgap excitation at 394 nm to promote electrons from these defect states into the conduction band or from the valence band to these intermediate states. [179] This mechanism may also facilitate energy transfer to Eu^{3+} ions resulting in PL even with sub-bandgap excitation. It is also possible that excitation at 394 nm induces a charge transfer process in the TiO_2 from the O 2p states to the Eu^{3+} 4f states. [175] As this process involves the absorption of photons by the O atoms and subsequent energy transfer to the Eu^{3+} ions, this form of charge transfer excitation can occur with lower-energy photons without sub-bandgap transitions and may potentially lead to a greater increase in emission intensity. [175] [155]

A portion of Eu^{3+} ions integrates into anatase and rutile phases crystalline clusters, enhancing the PL properties of the film. Specifically, ETO thin films with a composition of 7.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ exhibit significantly higher excitation efficiency due to efficient energy transfer from the crystalline TiO_2 matrix to the Eu^{3+} ions. This crystallisation process not only improves the UV absorption of the films but also contributes to

structural stability, reducing photobleaching effects. As a result, the 7.2 at% Eu/(Eu+Ti) film demonstrated the lowest degradation rate, retaining its photoluminescent properties after 40 hours of UV exposure, thus indicating its potential for prolonged application in UV-exposed environments.

[207]

In contrast, Eu(dbm)₃ and CuInS₂/ZnS have different degradation mechanisms during the UV exposure. In the transmittance spectra and Tauc plot (figure), CuInS₂/ZnS with polymer thin films exhibited the consistent values of transmittance, but the bandgap values have slightly changed. The reasons for that could be trap states changed, which includes size of particle change, dopant and purity variety of the quantum dots. In this case, the QDs may have the quantum confinement effect to influence the degradation mechanism.[208] During the degradation testing, the size of the QDs may be reduced to generate the blue shift in emission spectra.[203] Moreover, removal of Cu dopant and impurities of QDs, such as OH⁻ into the trap state from the moisture testing surrounding. In addition, the organic bond in the Eu(dbm)₃ Phen will be broken by UV exposure to modify the bandgap. For example, the Eu(dbm)₃ with PVA thin films loss the bandgap at 3.14 eV after degradation testing, means the absorbers DBM and/or Phen lost during the UV exposure.[203]

The defect states of Cu⁺ and Cu²⁺ can be modulated by adjusting the stoichiometry of QDs, with +1 representing stoichiometric QDs and +2 indicating Cu-deficient QDs. The emission mechanism of Cu¹⁺ is influenced by both hole and electron trapping, and stoichiometric QDs appear to favour the formation of Cu¹⁺ states, possibly in conjunction with charge-compensating In³⁺ defects in the form of anti-site defect pairs (CuIn–InCu). Oxidising a portion of the QDs leads to the deactivation of bright Cu⁺ centres, while the presence of Cu²⁺ cations result in PL quenching, attributed to efficient trap-assisted Auger recombination.[209]

6.3.1 Degradation behaviour of Eu(dbm)₃ and CuInS₂/ZnS

Photobleaching phenomena observed in this study are attributed to optically induced damage to the ligands,[79] which introduces defect states at the surface of CuInS₂/ZnS QDs, thus promoting nonradiative recombination channels. Additionally, the PL blue-shifts of CuInS₂/ZnS samples are explained by photooxidation

mechanisms.[210] Under illumination, the surface of CuInS₂/ZnS undergoes oxidation facilitated by oxygen diffusion through the passivating layer of ZnS, resulting in a reduction in average QD sizes and a broadening of the size distribution.[211] The decreased QD sizes induce a blue-shift owing to enhanced quantum confinement effects. Concurrently, the amplitude of the emission peak of the film exhibits a continuous decrease over the irradiation duration. Furthermore, irradiation of Eu(dbm)₃ with UV light leads to a reduction in the maximum luminescence intensity. The initial abrupt decline in maximum luminescence intensity is linked to photocatalytic oxidation processes occurring during exposure to ultraviolet light, which leads CuInS₂/ZnS and Eu(dbm)₃ particles to be oxidised.

The decline observed in the emission spectra can be attributed to a reduction in the population of photogenerated holes and electrons within the samples.[209] Exposure to UV light led to a decrease in the photoluminescence intensity across all exposed samples. This decline commenced with a relatively steep initial decrease, followed by a plateau in the case of polymers containing Eu³⁺ samples. Specifically, the Eu(dbm)₃ with PMMA sample exhibited a reduction of over 95% in emission intensity after just 1 hour of degradation testing, with the intensity continuing to decrease with prolonged UV exposure. Similarly, the Eu(dbm)₃ with PVA sample experienced a comparatively gradual decline during the degradation testing, yet still exhibited a reduction of over 75% after 20 hours of UV exposure. Furthermore, the reduction in fluorescence intensity observed in CuInS₂/ZnS samples, accompanied by a slight blue shift in the emission spectra, is linked to the diminished size of the quantum dots.[212] This study underscores the superior photostability of CuInS₂/ZnS samples compared to those containing Eu(dbm)₃.

Beyond core size, the shape of quantum dots absorption spectrum is largely influenced by structural characteristics of the QDs surface, particularly the type and integrity of the capping layer.[188] The importance of coating integrity has been underscored in elucidating the observed photoinduced reduction in the optical density of QDs, which is ascribed to the gradual diminishment of the stabilising effect of the ligands. The emergence of densely packed aggregates leads to a decline in PL intensity via a self-quenching mechanism, thereby diminishing the PL quantum yield in thin films containing higher concentrations of QDs. Luminescence quenching during

exposure has been associated with defect formation arising from ligand detachment and spontaneous aggregation.[213]

6.4 Conclusion

ETO luminescence thin films with various europium ratios are synthesised by combinatorial sputtering on Quartz substrates and annealed in air at 600°C after deposition. In addition, $\text{Eu}(\text{dbm})_3$ and $\text{CuInS}_2/\text{ZnS}$ are blended with PVA and PMMA by Liquid Chemical Drop-casting method. Subsequently, degradation testing will be performed on the lifetime of samples. Optical properties and application on solar cells for these thin films are tested and compared before and after degradation testing. ETO samples have different fluorescence intensity after annealing, and the emission intensity are influenced and reduced during the degradation testing as the time increases. And the strongest emission intensity peak is at $^5D_0 \rightarrow ^7F_2$ (613 nm) has higher branching ratio in fluorescence spectra. Moreover, $\text{Eu}(\text{dbm})_3$ samples have the same transitions at $^5D_0 \rightarrow ^7F_2$ (612 nm), but $\text{CuInS}_2/\text{ZnS}$ samples have broad emission spectra. Following degradation testing, the spectra of these thin films remain similar, with the only noticeable alteration being a change in photoluminescence intensity. Transmittance and bandgap of the ETO thin films do not have dramatically changed after degradation testing, that means the samples are able to absorb the photons but lose emission. The discernible changes in transmittance after degradation testing due to photobleaching phenomena observed in $\text{Eu}(\text{dbm})_3$ samples, resulting in the loss of photon absorption in this region. The ETO thin films with lower bandgap have lower power conversion efficiency, because more photons have been absorbed and scattered to escape from the edge of the substrate, it is keeping the same before and after degradation testing. Overall, ETO thin films with europium ratios 5—10 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ have longest lifetime, keep strong fluorescence intensity after 40 hours degradation testing, and $\text{Eu}(\text{dbm})_3$ with PMMA has the shortest lifetime, nearly fully photobleached after 10 hours degradation testing, during the degradation testing.

Combining the optical properties with the fluorescence data can provide insights into the degradation mechanism of ETO thin films. It is expected that an increased number of trap states of Eu^{3+} may have been generated, leading to lower emission intensity.[214] Furthermore, the occurrence of oxygen substoichiometric and oxygen

vacancy within the thin film may potentially impact the emission intensity, although additional evidence is required to prove this claim.

The efficient Auger recombination in $\text{CuInS}_2/\text{ZnS}$ involves the electron combining with the excess hole and the photogenerated hole in the valence band edge, leading to additional non-radiative recombination and subsequent PL quenching.[209] In the $\text{Eu}(\text{dbm})_3$ thin film, a strong interaction exists among Phen, DBM, and the Eu^{3+} ions, facilitating transitions from higher energy states of the Eu^{3+} ion. Energy transfer is from the singlet level of Phen to DBM, and subsequently from both the singlet and triplet levels of DBM to Eu^{3+} via short-range interactions.[215] $\text{Eu}(\text{dbm})_3$ thin film has oxidation phenomenon during degradation testing, due to both DBM and Phen are organic compounds which are easily oxidised by the UV light in air.[216,217]

7 Overall Conclusion and Future Work

7.1 Overall Conclusion and contribution to knowledge

The aim of this study is to Investigate the effect of Eu^{3+} doping concentration and annealing temperature on photoluminescent properties and degradation behaviour. The precise composition of thin films to achieve the desired photoluminescence properties is synthesised by combinatorial sputtering. In addition, to elucidate the effect of microstructure and cross-sectional morphology on photoluminescence and optical properties. Moreover, the degradation properties of these thin films synthesised by combinatorial sputtering with various concentrations will be measured and compared with the luminescence films from the chemical method. Through a comprehensive analysis, we have examined ETO thin films, synthesised using combinatorial sputtering (PVD).

There are five key findings.

1. Our finding shows that the combinatorial co-sputtering of TiO_2 and Eu_2O_3 produces a variation in the $\text{Eu}/(\text{Eu}+\text{Ti})$ ratio as a function of sample positioning. we employed combinatorial sputtering to fabricate ETO films with varying $\text{Eu}/(\text{Eu}+\text{Ti})$ compositions ranging from 0 at% to 100 at% in a single deposition process, investigating their effect on film crystallography and PL properties. The XRD pattern of as-deposited TiO_2 (0 at% $\text{Eu}/(\text{Eu}+\text{Ti})$) thin films, which exhibit the anatase phase of TiO_2 , the XRD patterns of as-deposited ETO thin films with $x>0$ exhibit broad peaks, which indicate that these films are dominated by amorphous matrix with anatase TiO_2 nanocrystallites are either absent or present in minimal amounts with diameters of <2 nm.[163] This strongly suggests that the incorporation of a small amount of Eu^{3+} is sufficient to suppress the formation of anatase TiO_2 crystallites. This contrasts with the previously reported studies that reported the formation of rutile TiO_2 by magnetron sputtering or the presence of cubic phases of Eu_2O_3 without annealing.[164] Our PL and XRD data indicate that the ETO films with 4.7 at%–44.4 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ are mildly luminescent despite being amorphous. At 7.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$, nearly all Eu^{3+} ions reside within the amorphous TiO_2 matrix. These Eu^{3+} ions can be directly excited through the charge transfer band (CTB) of $\text{O}_2 \rightarrow \text{Eu}^{3+}$ (280 nm) or the ${}^7F_0 \rightarrow {}^5L_6$ transition (394 nm) of Eu^{3+} itself, albeit

with very low excitation efficiency.[165]

2. In this study, we found that the excitation wavelength for ETO film is 394 nm, which corresponds to the excitation from the $^7F_0$ ground state to the $^5L_6$ excited state of the Eu^{3+} ion.[147] This direct excitation of Eu^{3+} does not require energy transfer from TiO_2 and, hence, is independent of the TiO_2 bandgap. After initial excitation, the electrons relax to the $^5D_0$ band edge through non-radiative cascading single/multi-phonon relaxation from $^5L_6$. [147] This is followed by the distinctive radiative transition in the visible spectral range from $^5D_0$ to ^7F_J , with $J = 0, 1, 2, 3$, and 4.[218] Note that the PL emission intensity from the $^5D_0 \rightarrow ^7F_2$ transition at 613 nm reaches a maximum at 9.1 at% $\text{Eu}/(\text{Eu}+\text{Ti})$, for both as-deposited and annealed films. This is similar to the previous study where 7--10 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ showed the optimum PL emission intensity, as it has the most available Eu^{3+} emitting centres in the amorphous TiO_2 matrix.[145,147] The emission intensity of the film with a 7.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ increases significantly by 5 times after annealing at 600°C. As discussed above, this enhancement is attributed to the formation of rutile TiO_2 that facilitates energy transfer to Eu^{3+} and ultimately leads to an increase in emission from the $^5D_0 \rightarrow ^7F_2$ transition. However, after annealing, the film with 7.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ forms clusters of anatase TiO_2 and nano-sized rutile TiO_2 crystallites in a 68:32 ratio.
3. While the findings presented herein are constrained to the demonstration of the effect of composition on PL properties and crystallography of ETO films, the combinatorial sputtering approach can be extrapolated to systematically investigate the correlation between film characteristics and properties of many other model systems. Nevertheless, this work provides a foundation for the rational development of luminescent thin films, essential for wide applications ranging from solar photovoltaics to electronic displays. The combinatorial sputtering approach employed here can be expanded to systematically explore other model systems that critically depend on the composition of the constituent elements.
4. Upon observing and comparing the microstructure and fluorescence characteristics of ETO thin films, notable differences have been discerned across various europium ratios. Specifically, thin film samples featuring lower europium ratios (<50 at% $\text{Eu}/(\text{Eu}+\text{Ti})$) exhibit a vertically oriented columnar

microstructure, which are matched with the zone 1 and 2 in the Thornton diagram (Figure 4-14), as evidenced by SEM analysis. Moreover, after annealing at 600°C, these samples display a narrower and sharper average columnar size, which are the zone 1 and 2 shown in the Thornton diagram (Figure 4-14). Furthermore, it is observed that thin films with columnar microstructures consistently exhibit fluorescence, spanning from as-deposited samples to those annealed at 600°C, even prior to annealing with intensity increases by annealing. These findings shed light on the relationship between microstructure and fluorescence properties in ETO thin films.

5. The comparative analysis of ETO thin films with varying Eu/(Eu+Ti) concentrations before and after degradation testing reveals significant differences in fluorescence intensity and stability. The sample with a 7.2 at% Eu/(Eu+Ti) ratio demonstrates superior fluorescence intensity prior to UV exposure and maintains remarkable stability, with only a modest 10% reduction in emission intensity after 40 hours of testing. Conversely, the sample with a 29.2 at% Eu/(Eu+Ti) ratio exhibits rapid bleaching within the first 5 hours, resulting in nearly a 50% decrease in emission intensity. Overall, samples with 4-10 at% Eu/(Eu+Ti) exhibited the most extended lifetime and consistently retained the highest fluorescence intensity throughout the degradation testing period. This observation is supported by both visual inspection and fluorescence spectra analysis. These findings elucidate the nuanced relationship between Eu-doping concentration and fluorescence stability. In contrast, Eu(dbm)₃ and CuInS₂/ZnS samples represent diverse degradation properties. Eu(dbm)₃ with PVA showcased the highest emission intensity among the polymer-based samples, maintaining stable and strong emission levels during the initial 5 hours of UV exposure. However, a notable decline thereafter led to a substantial reduction in fluorescence intensity, ultimately resulting in weak fluorescence. Similarly, Eu(dbm)₃ with PMMA initially exhibited strong emission intensity yet experienced rapid bleaching within the first hour of testing, progressing towards near-complete bleaching after 5 hours of degradation. In contrast, both CuInS₂/ZnS with PVA and CuInS₂/ZnS with PMMA samples displayed consistently low emission intensity levels both before and after degradation testing, indicating relatively stable fluorescence characteristics throughout the testing period.

6. Various degradation mechanisms are observed among ETO, $\text{Eu}(\text{dbm})_3$, and $\text{CuInS}_2/\text{ZnS}$ thin films. In ETO, the generation of trap states of Eu^{3+} may contribute to decreased emission intensity. Additionally, the presence of oxygen substoichiometry and oxygen vacancies within the film may further impact emission intensity.[214] Furthermore, $\text{CuInS}_2/\text{ZnS}$ experiences efficient Auger recombination, where excess holes and photogenerated holes in the valence band edge combine with electrons, leading to non-radiative recombination and subsequent photoluminescence quenching.[209] Meanwhile, in $\text{Eu}(\text{dbm})_3$, a significant interaction between Phen, DBM, and Eu^{3+} ions facilitates energy transfer from higher energy states of the Eu^{3+} ion. This process involves cascading energy transfer from Phen to DBM, followed by transfer from both singlet and triplet levels of DBM to Eu^{3+} via short-range interactions.[215]
7. The power conversion efficiency of the thin films is measured by solar simulator with c-Si solar cell, and the thin films are placed above the solar cell. The solar simulator measurements indicated that ETO samples with lower bandgaps demonstrate lower PCE. For instance, the thin film with a 7.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ ratio exhibited the lowest bandgap at 3.46 eV, resulting in the lowest PCE of 10.770%. Conversely, the thin film with a 98.2 at% $\text{Eu}/(\text{Eu}+\text{Ti})$ ratio displayed the highest bandgap at 5.29 eV, yielding the highest PCE of 13.848%. This phenomenon can be attributed to the increased absorption and scattering of photons, resulting in a higher likelihood of photons escaping from the substrate edge. Notably, this trend remained consistent both before and after degradation testing.

7.2 Future Work

In the ensuing phases of this research, considerable attention should be directed towards enhancing the efficiency of luminescence thin films while also exploring their practical deployment. Efforts may concentrate on several pivotal areas to bolster the performance of these films and facilitate their seamless integration into real-world applications.

1. The ETO thin films demonstrated commendable fluorescence characteristics when engineered to a thickness ranging between 3 and 4 μm . Further exploration with thicker films presents an opportunity to conduct comparative analyses against established luminescence thin films, potentially unveiling enhancements in both fluorescence and optical attributes.

2. Following the evaluation of fluorescence and degradation testing outcomes, it was observed that ETO thin films containing 7.2 at% to 9.1 at% Eu/(Eu+Ti) ratio showcased robust fluorescence intensity and prolonged lifetime. Nonetheless, the synthesis of these thin films via combinatorial sputtering methods presents a multifaceted and cost-intensive manufacturing approach. Streamlining the fabrication process to mitigate sputtering duration and expenses is imperative for large-scale production. Furthermore, precise control over thin film composition at elevated levels of accuracy is paramount to ensuring sustained high quality.
3. Trivalent lanthanide ions offer a rich energy-level configuration, rendering them exceptionally well-suited for spectral conversion applications. Encompassing a range from lanthanum (La) to lutetium (Lu), the lanthanide series encompasses 15 elements characterised by 4*f* orbitals. While this study primarily examines Europium ions (Eu³⁺), there exists a compelling need to explore the fluorescence and degradation properties of other lanthanide elements. Additionally, investigating thin films co-doped with two or more lanthanide elements presents an intriguing avenue for research inquiry.
4. Further evidence is needed to fully elucidate the degradation mechanism of internal luminescence thin films. This could involve investigating parameters such as trap states within the semiconductor materials, the particle size of QDs, and the oxidation process. These aspects may be explored through additional experiments utilising techniques such as transmission electron microscopy (TEM), XRD, and fluorescence spectroscopy to measure decay time.
5. ETO thin films manifest diminished power conversion efficiency when characterised by lower bandgaps. This observation is attributed to the phenomenon wherein photons are absorbed and diffused from the substrate edge. Subsequent investigations should prioritise strategies aimed at agglomerate photon propagation towards solar cells. Mitigating scattering losses necessitates the application of reflective tape along the substrate edge, alongside the incorporation of anti-reflective layers or hot mirrors to augment the influx of photons directed towards the solar cells. Hot mirrors, renowned for their heightened transmission within visible light wavelengths, present a particularly promising avenue in this regard.

Moreover, luminescence thin films possess versatile applications beyond the enhancement of solar cell power conversion efficiency, extending into diverse domains

such as agriculture. Certain plant species require protection from prolonged UV exposure while benefiting from exposure to red or NIR light for optimal growth conditions. Consequently, leveraging luminescence thin films offers a promising avenue to cater to such requirements, thereby facilitating advancements in agricultural practices.

8 Reference

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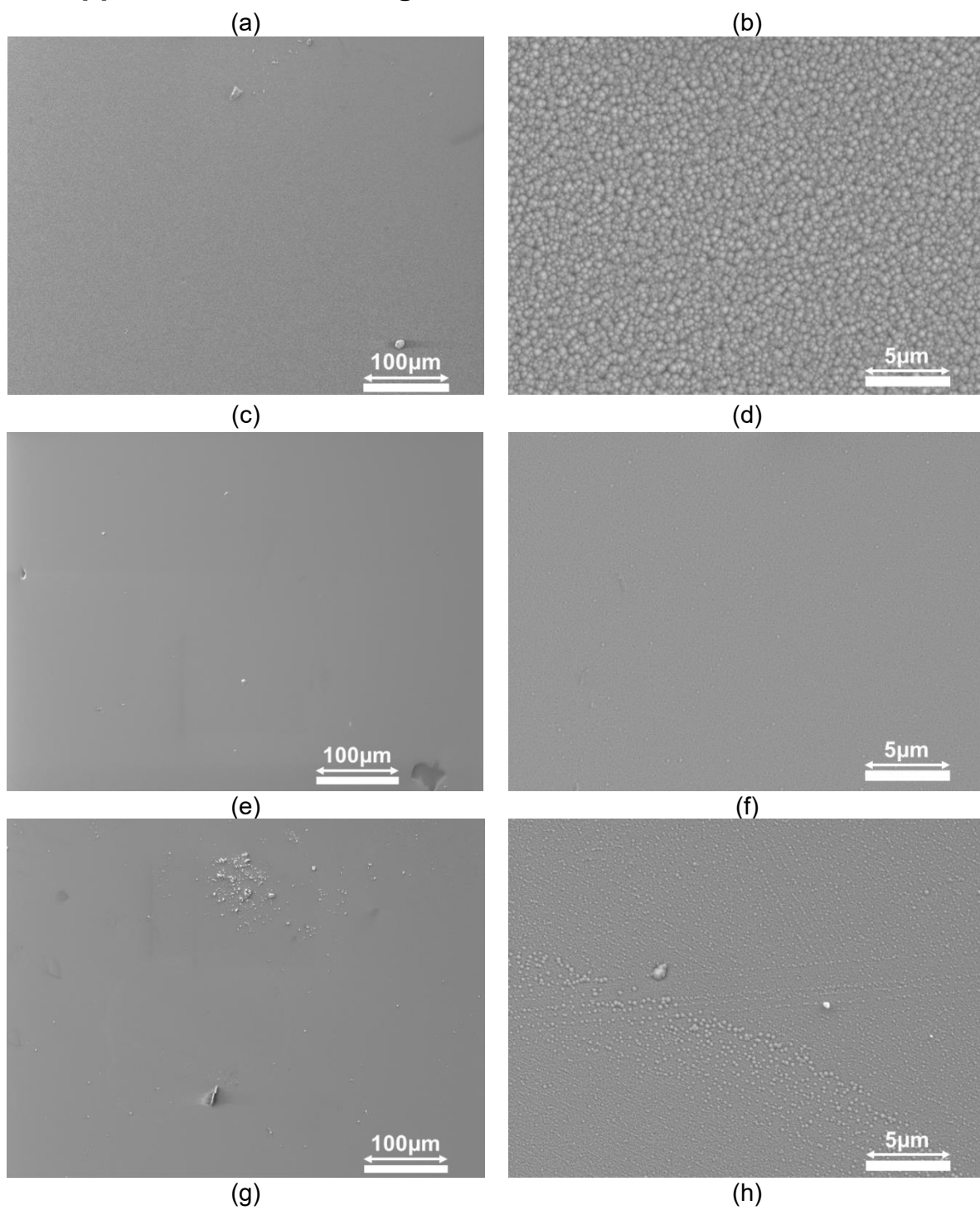
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9 APPENDICES

9.1 Appendix A -- SEM images for surface of ETO thin films



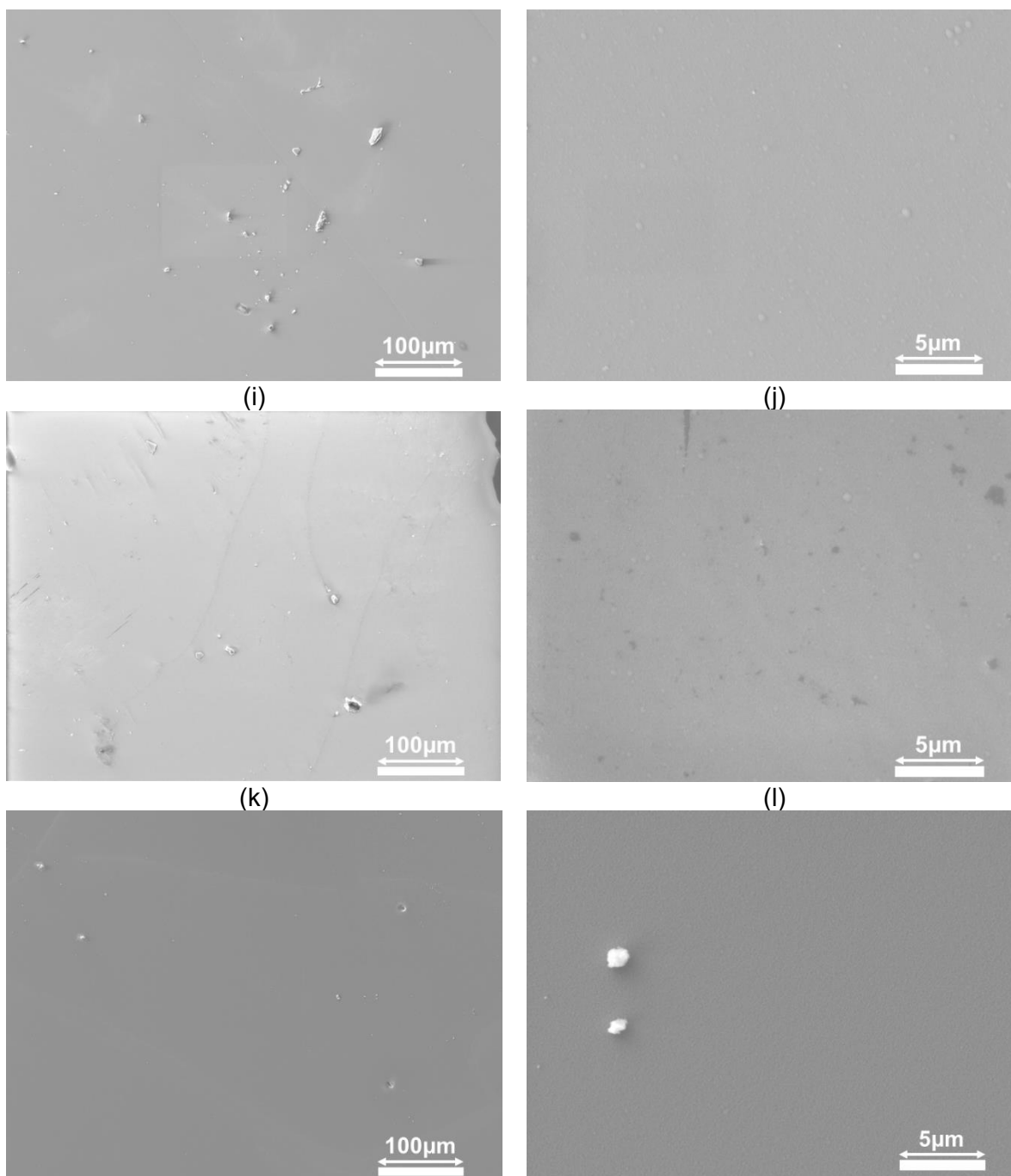
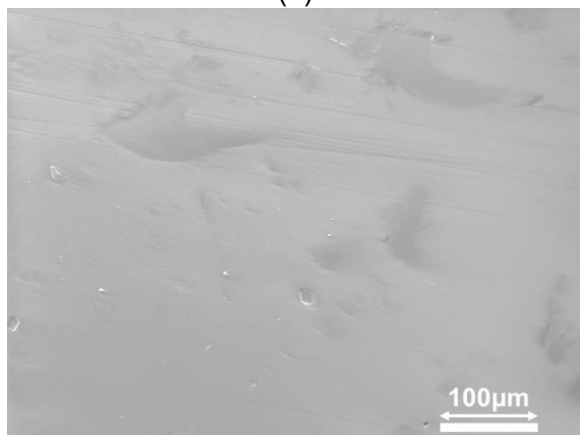
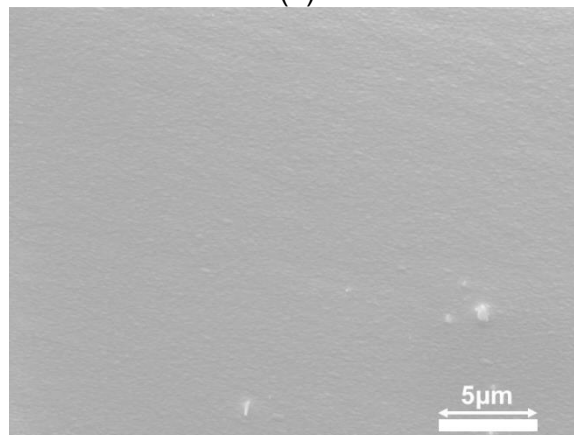


Figure Apx A - 1 SEM images for surface of the ETO as-deposited in different sputtering positions, (a) & (b) 10.5, (c) & (d) 23, (e) & (f) 35.5, (g) & (h) 54.5, (i) & (j) 67, (k) & (l) 79.5 mm

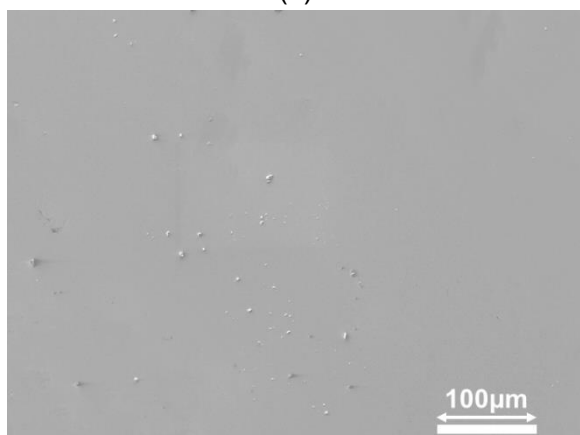
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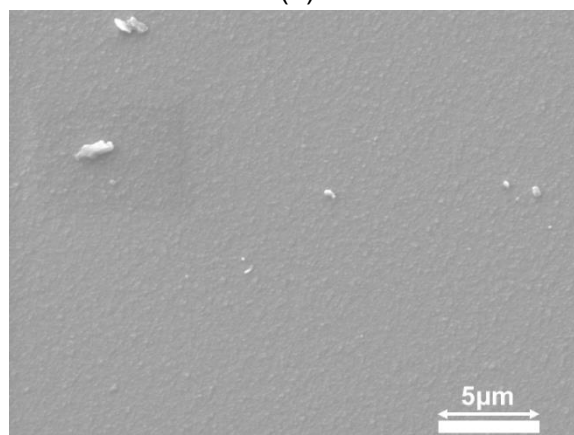
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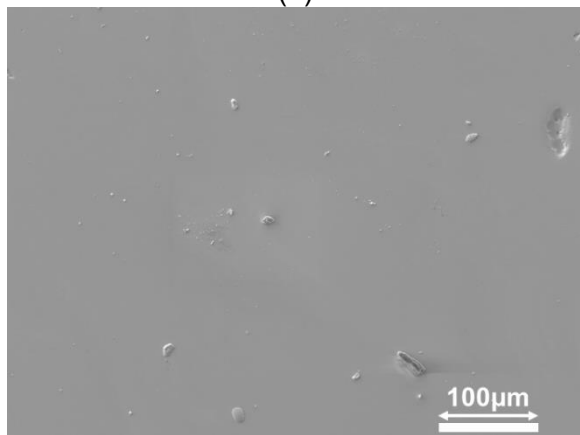
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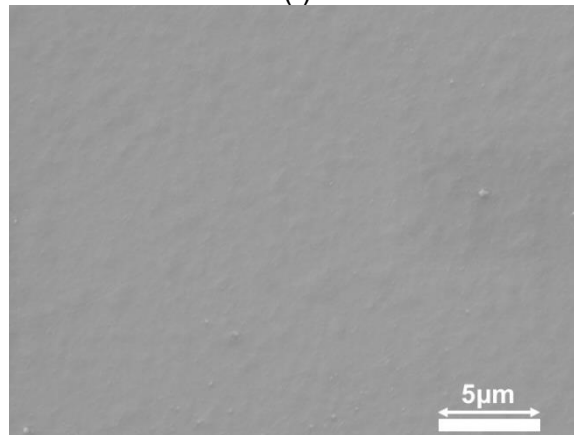
(d)



(e)



(f)



(g)

(h)

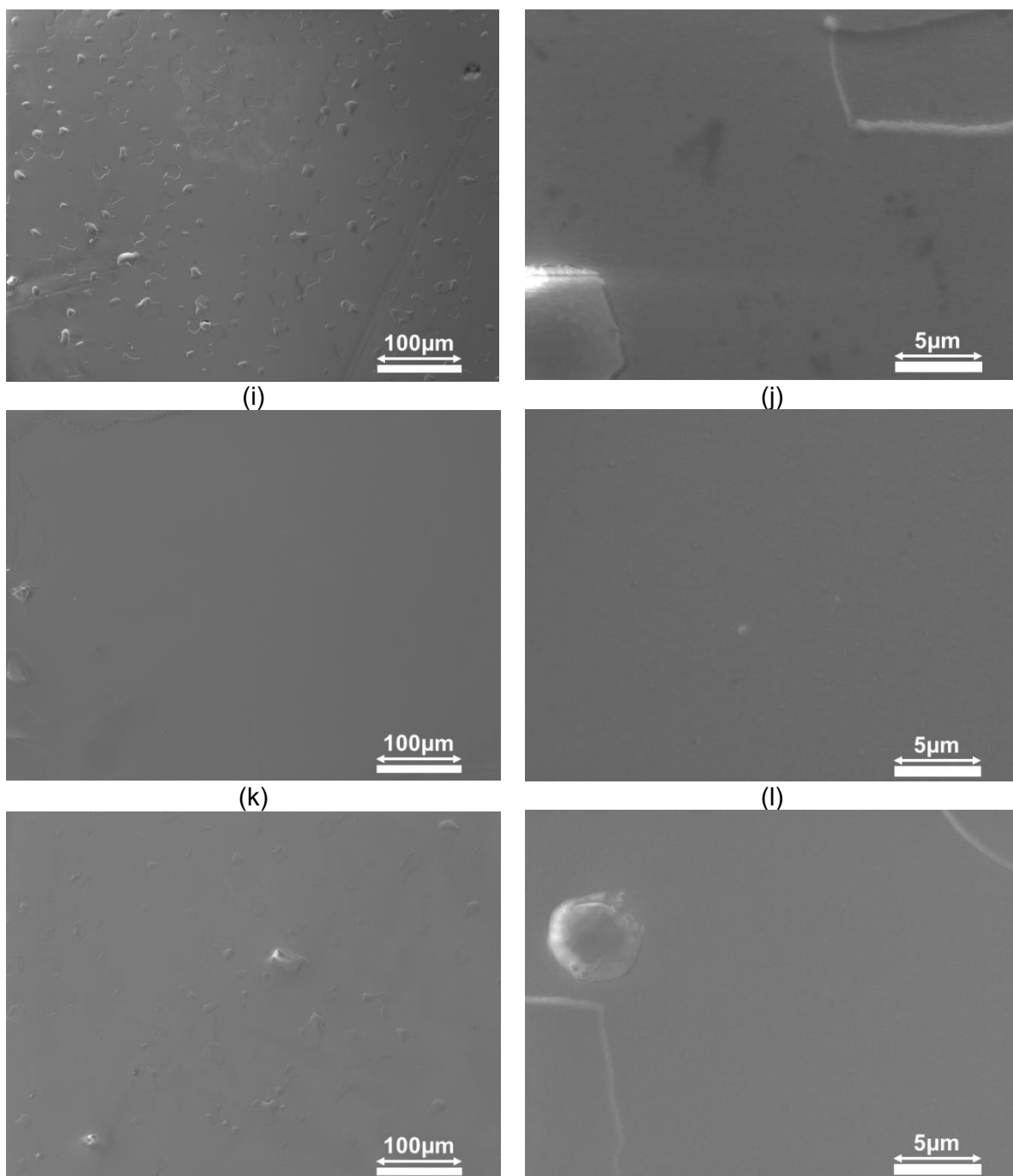
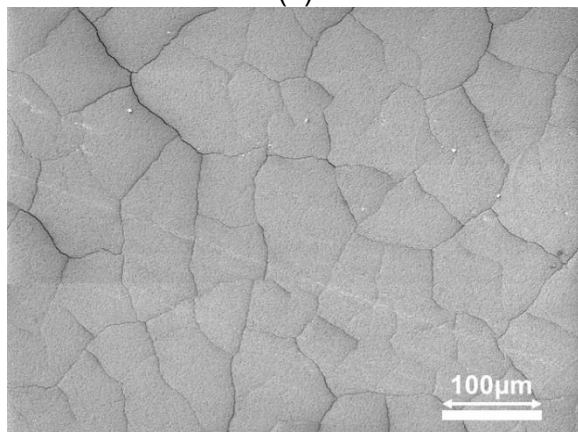
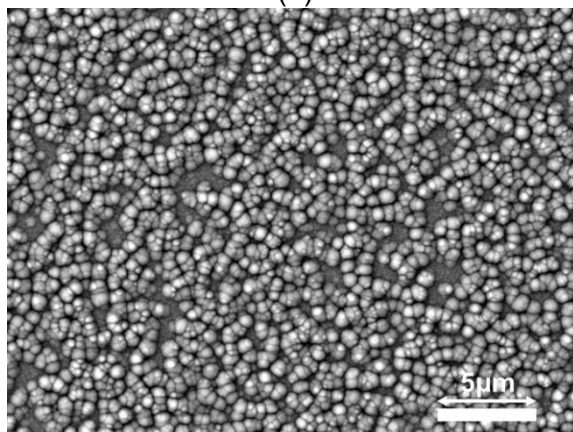


Figure Apx A - 2 SEM images for surface of the ETO as-deposited in different sputtering positions (a) & (b) 98.5, (c) & (d) 111, (e) & (f) 123.5, (g) & (h) 142.5, (i) & (j) 155, (k) & (l) 167.5 mm.

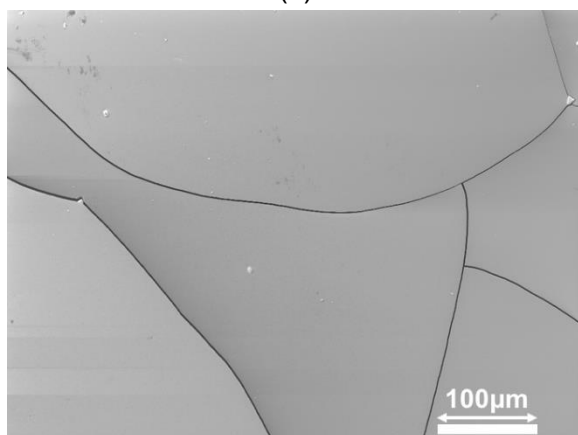
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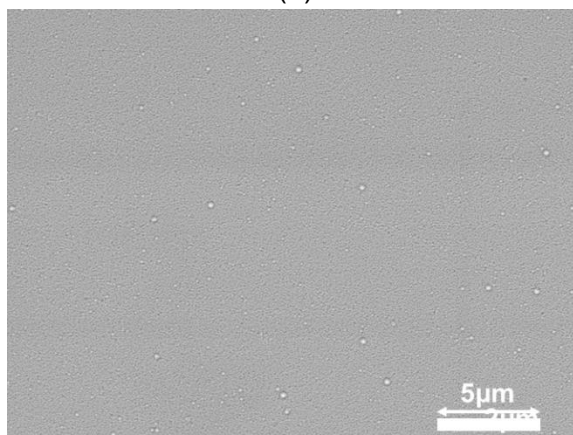
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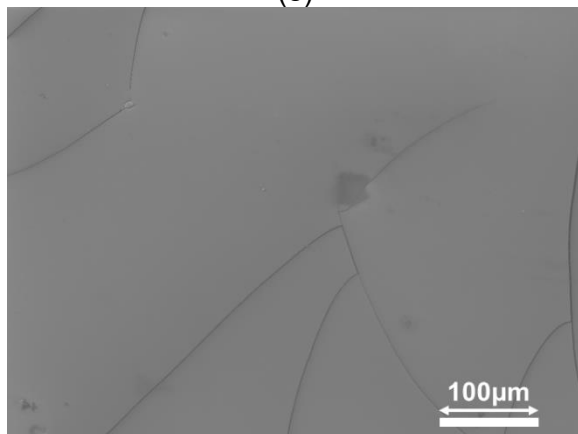
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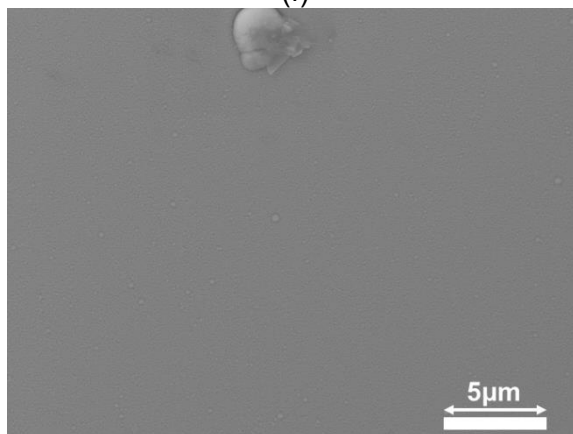
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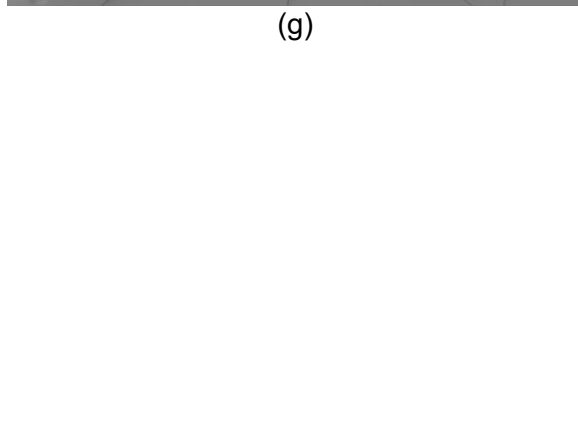
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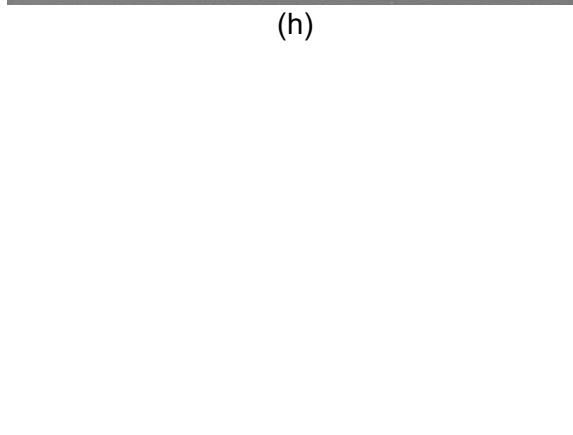
(f)

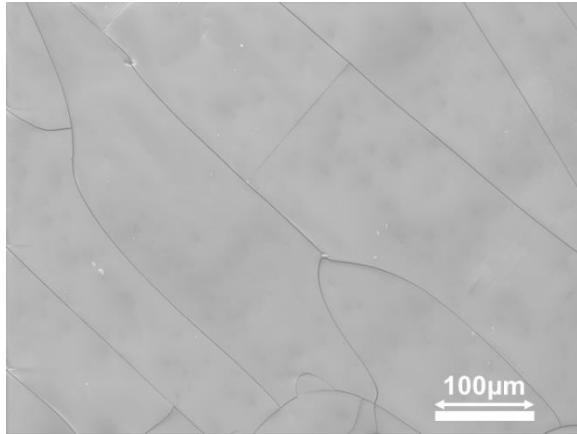


(g)

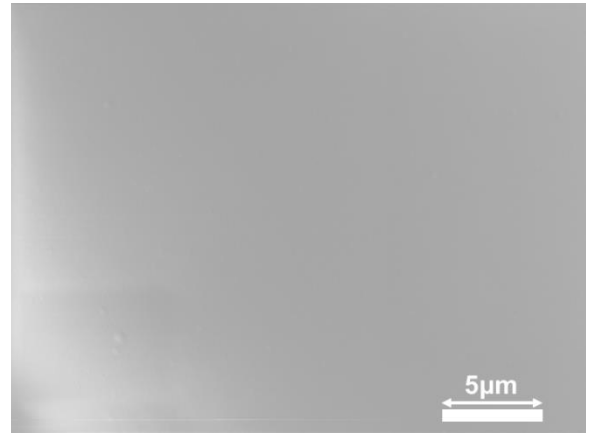


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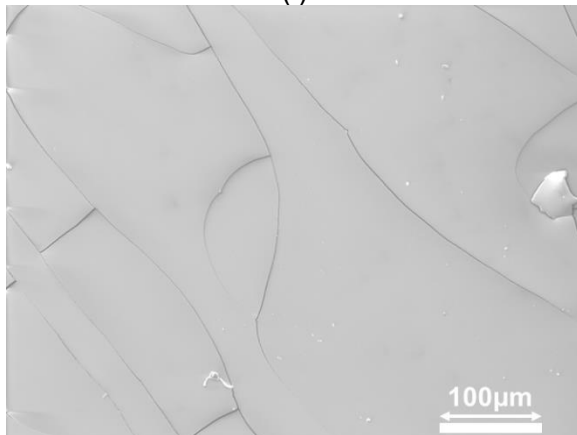




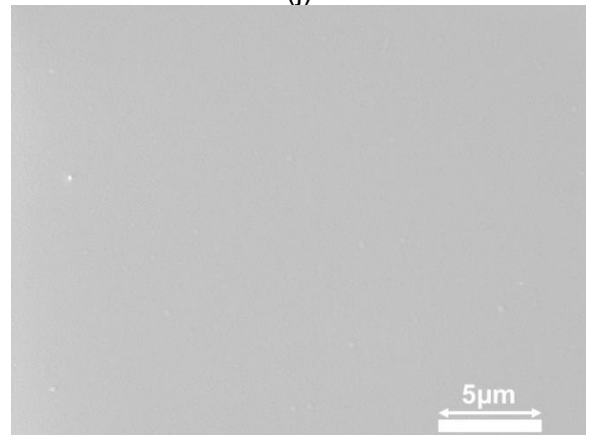
(i)



(j)



(k)



(l)

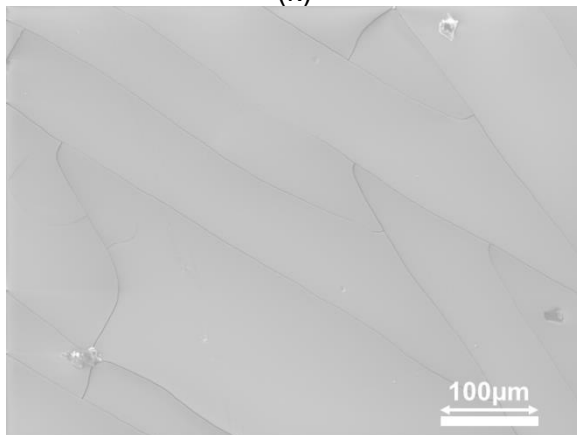
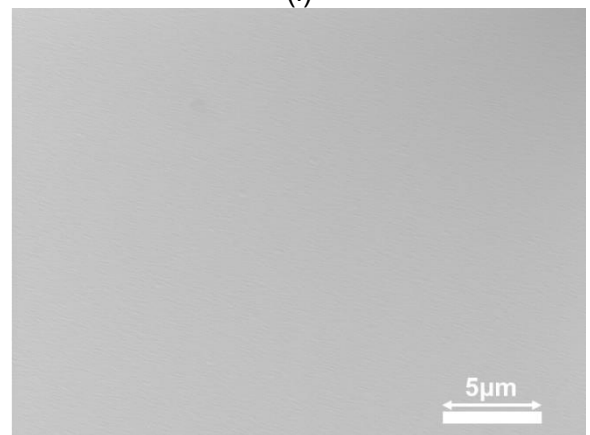
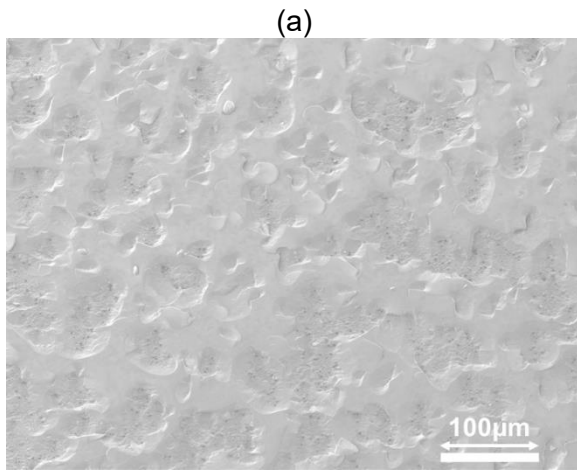
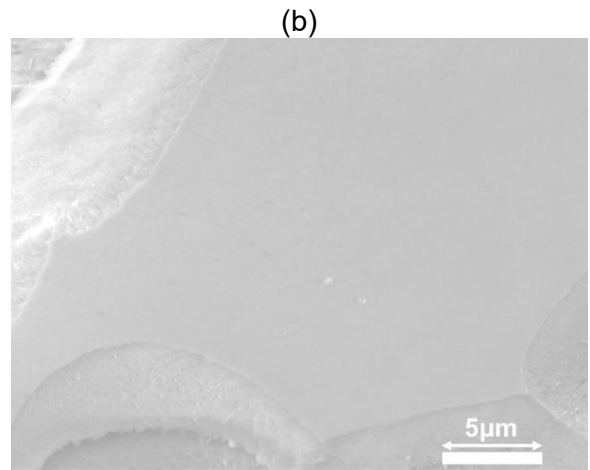
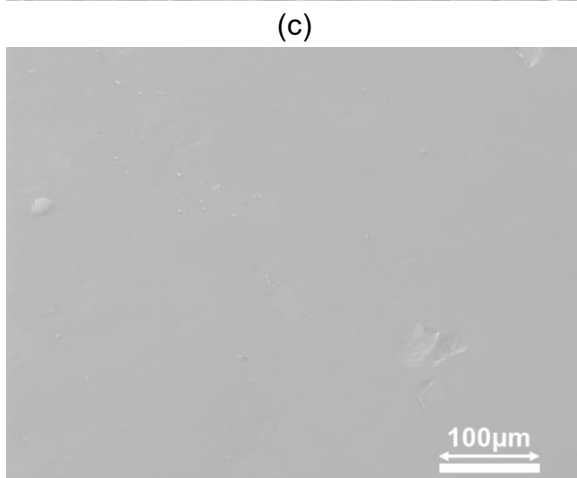
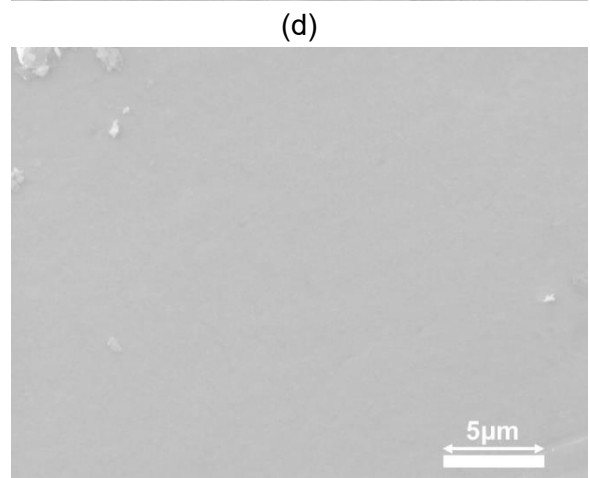
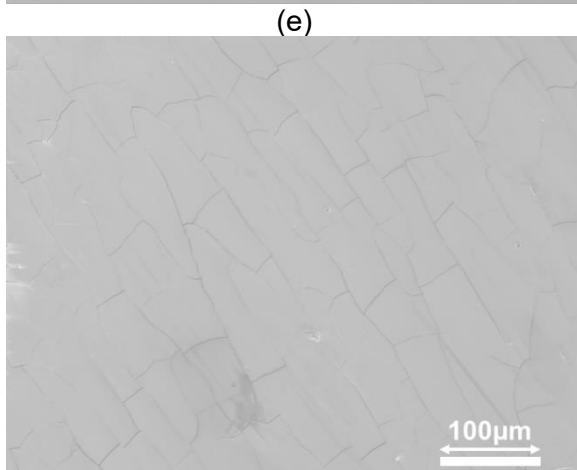
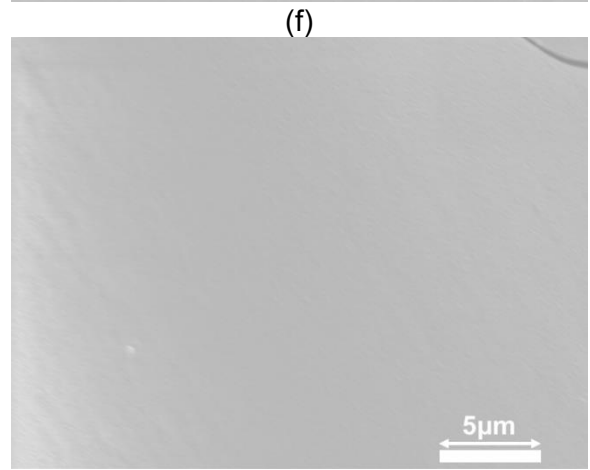
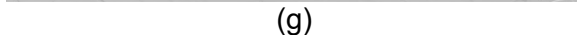
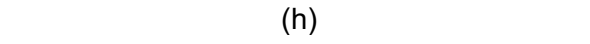


Figure Apx A - 3 SEM images with 500 and 10k magnification for surface of the ETO after annealing at 600°C in different sputtering positions, (a) & (b) 10.5, (c) & (d) 23, (e) & (f) 35.5, (g) & (h) 54.5, (i) & (j) 67, (k) & (l) 79.5 mm



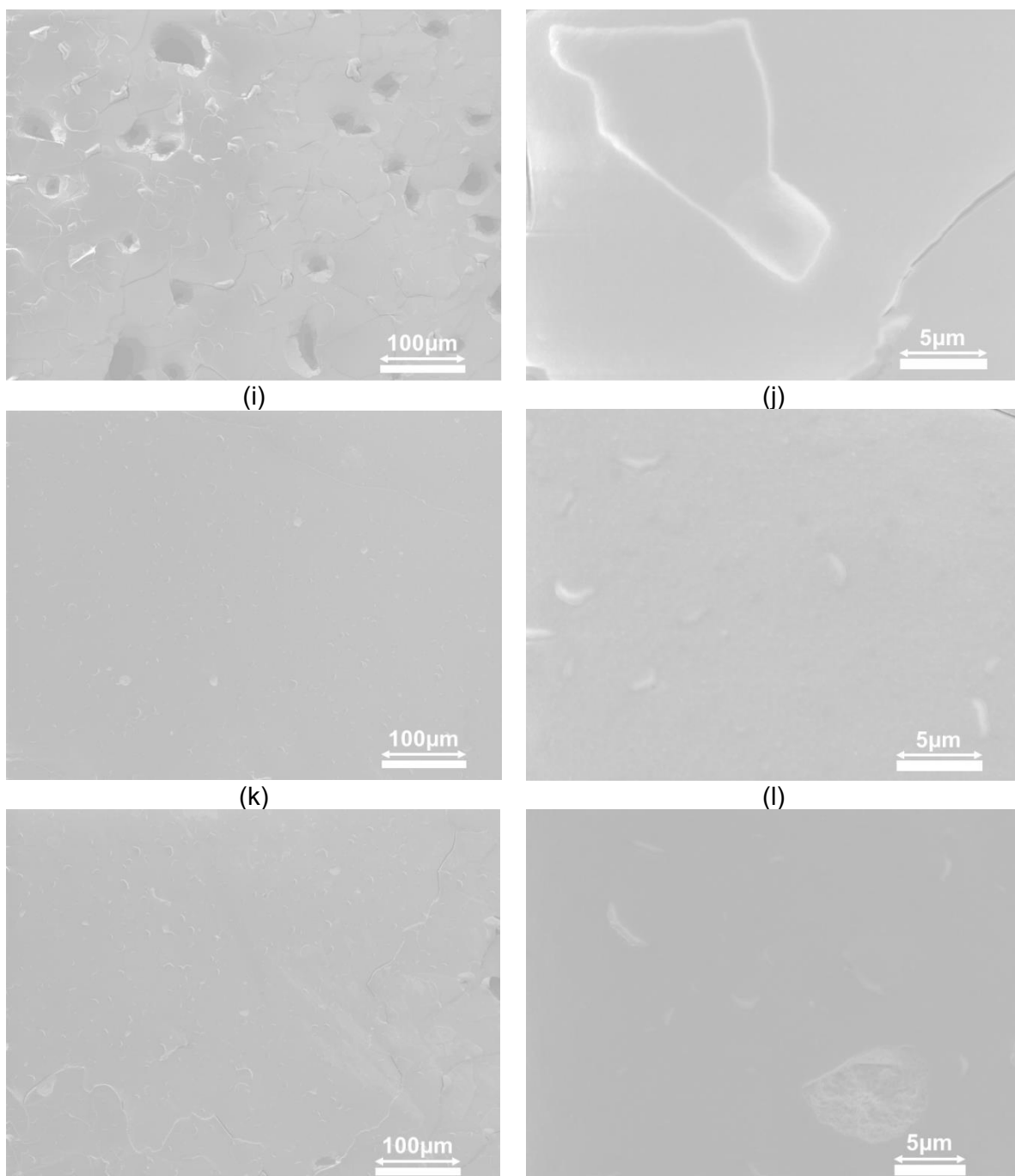
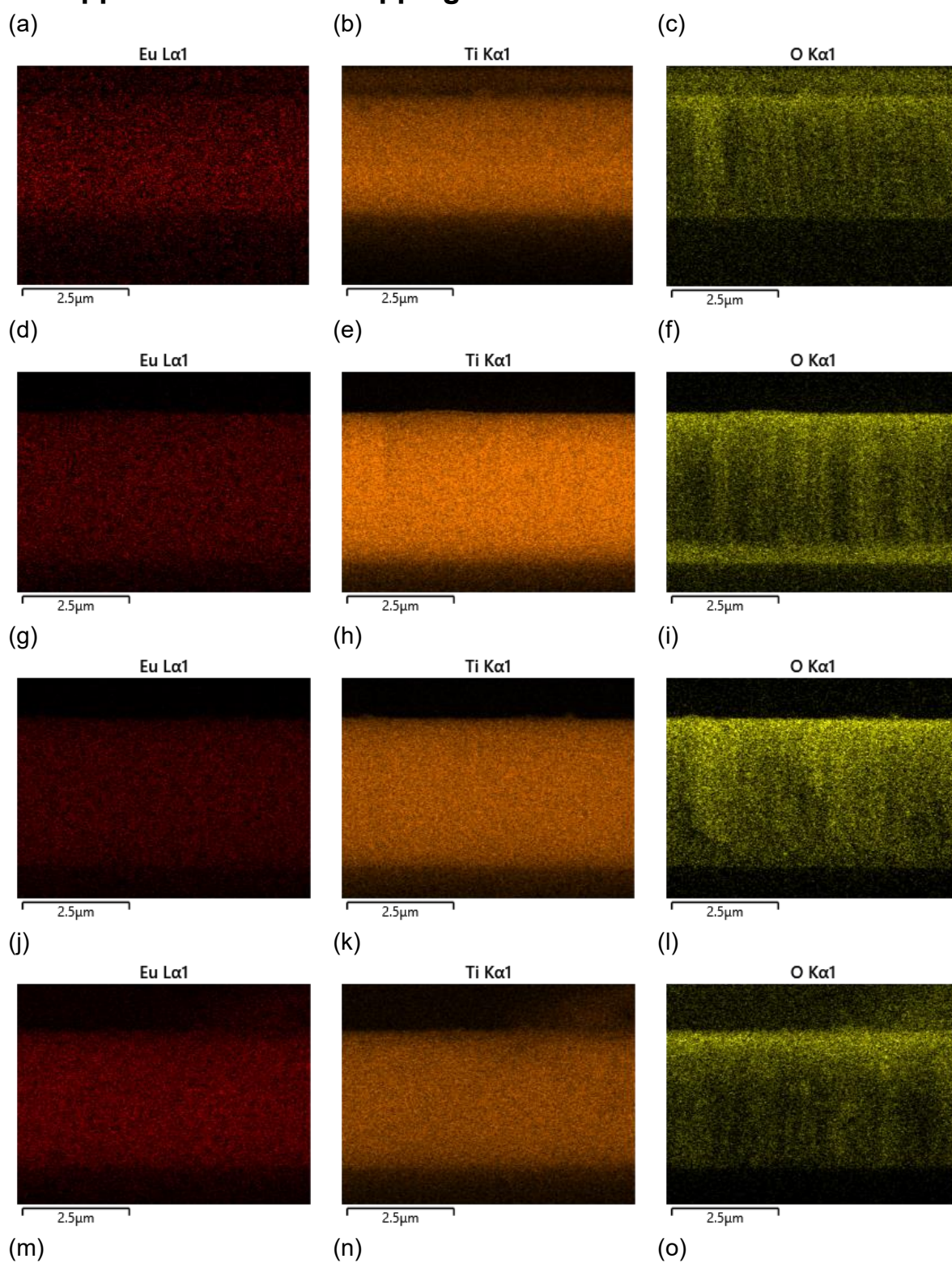


Figure Apx A - 4 SEM images with 500 and 10k magnification for surface of the ETO as-deposited in different sputtering positions (a) & (b) 98.5, (c) & (d) 111, (e) & (f) 123.5, (g) & (h) 142.5, (i) & (j) 155, (k) & (l) 167.5 mm.

9.2 Appendix B -- EDX mappings of ETO thin films



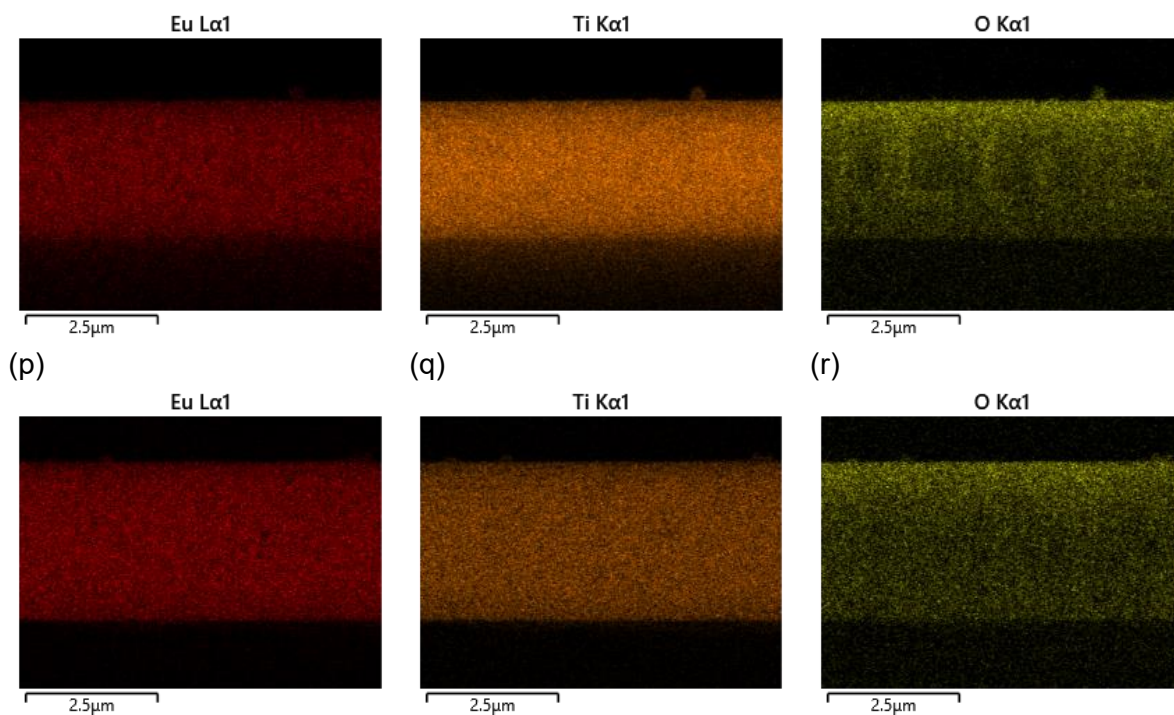
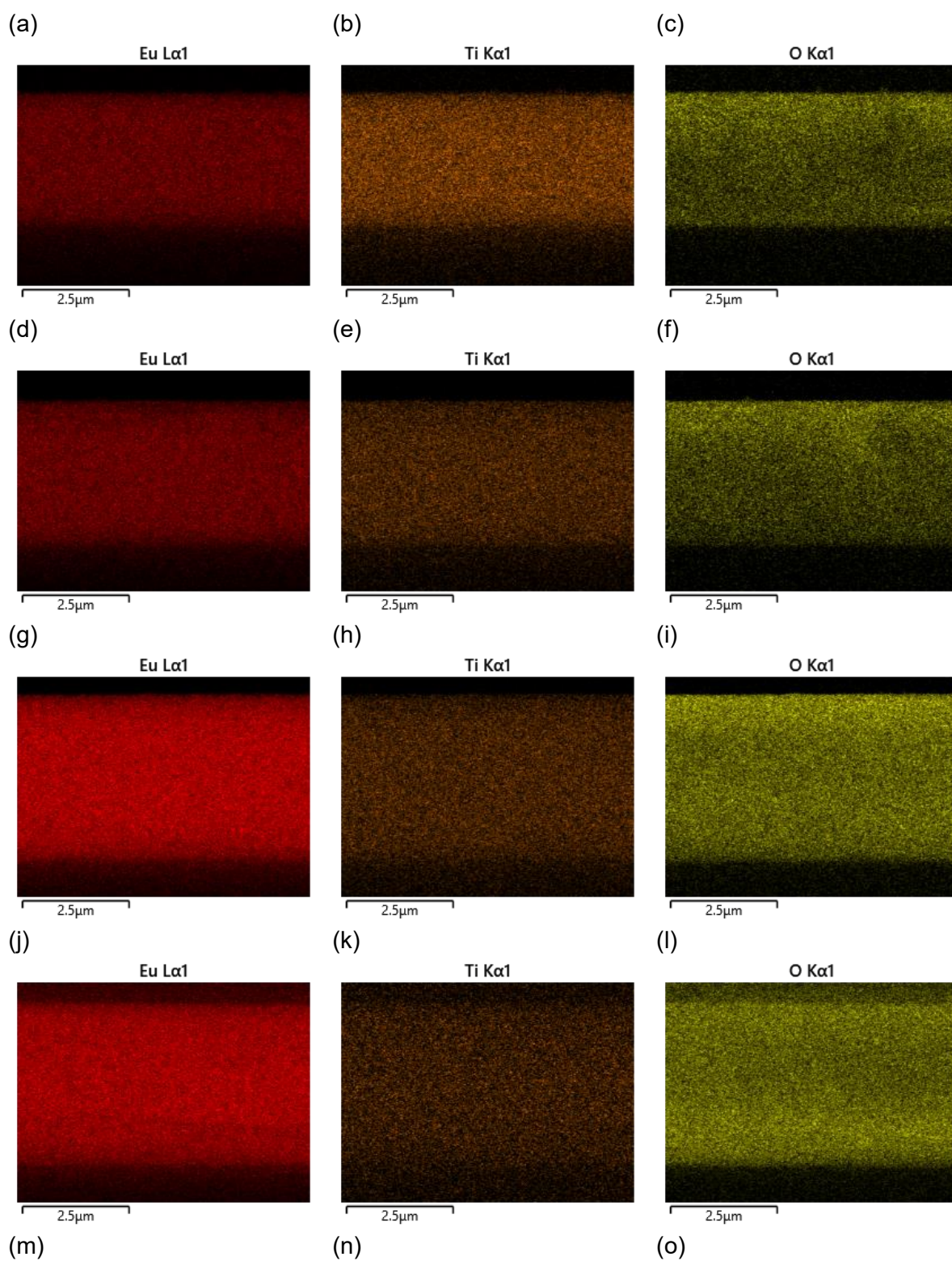


Figure Apx B - 1 EDX mapping for the samples As-deposited with Eu, Ti and O composition in thin films at different concentration, (a) (b) (c) 4.7 at% Eu/(Eu+Ti), (d) (e) (f) 7.2 at% Eu/(Eu+Ti), (g) (h) (i) 9.1 at% Eu/(Eu+Ti), (j) (k) (l) 19 at% Eu/(Eu+Ti), (m) (n) (o) 29.2 at% Eu/(Eu+Ti), (p) (q) (r) 44.4 at% Eu/(Eu+Ti).



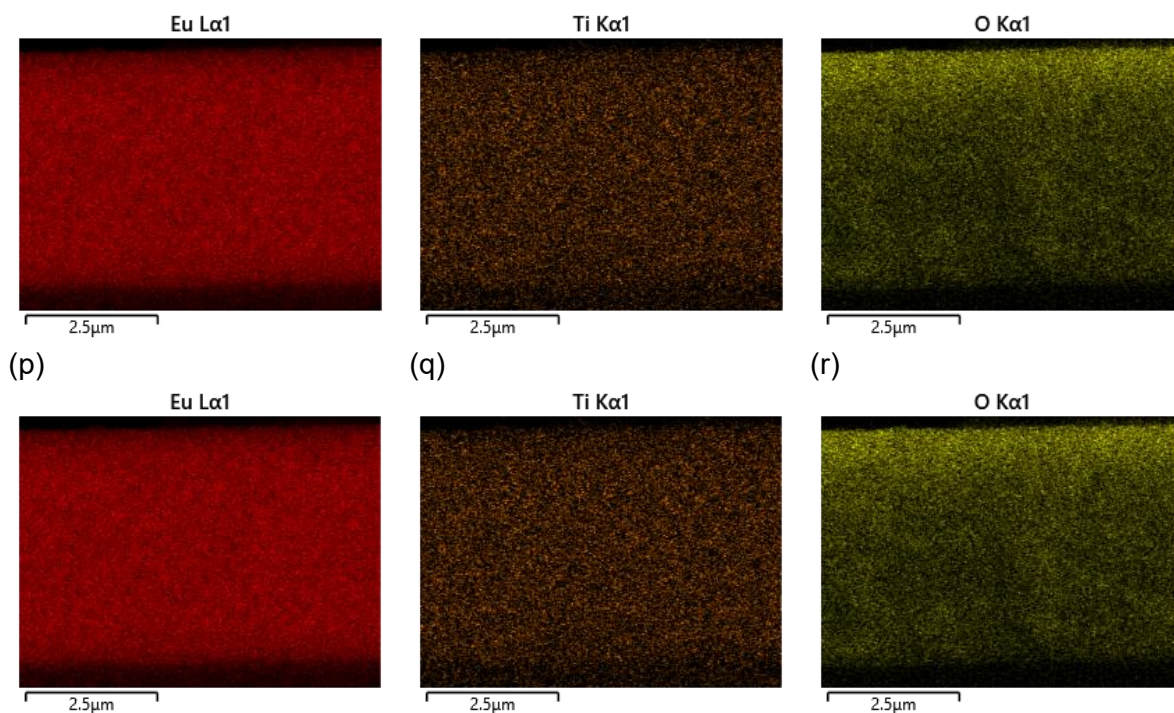
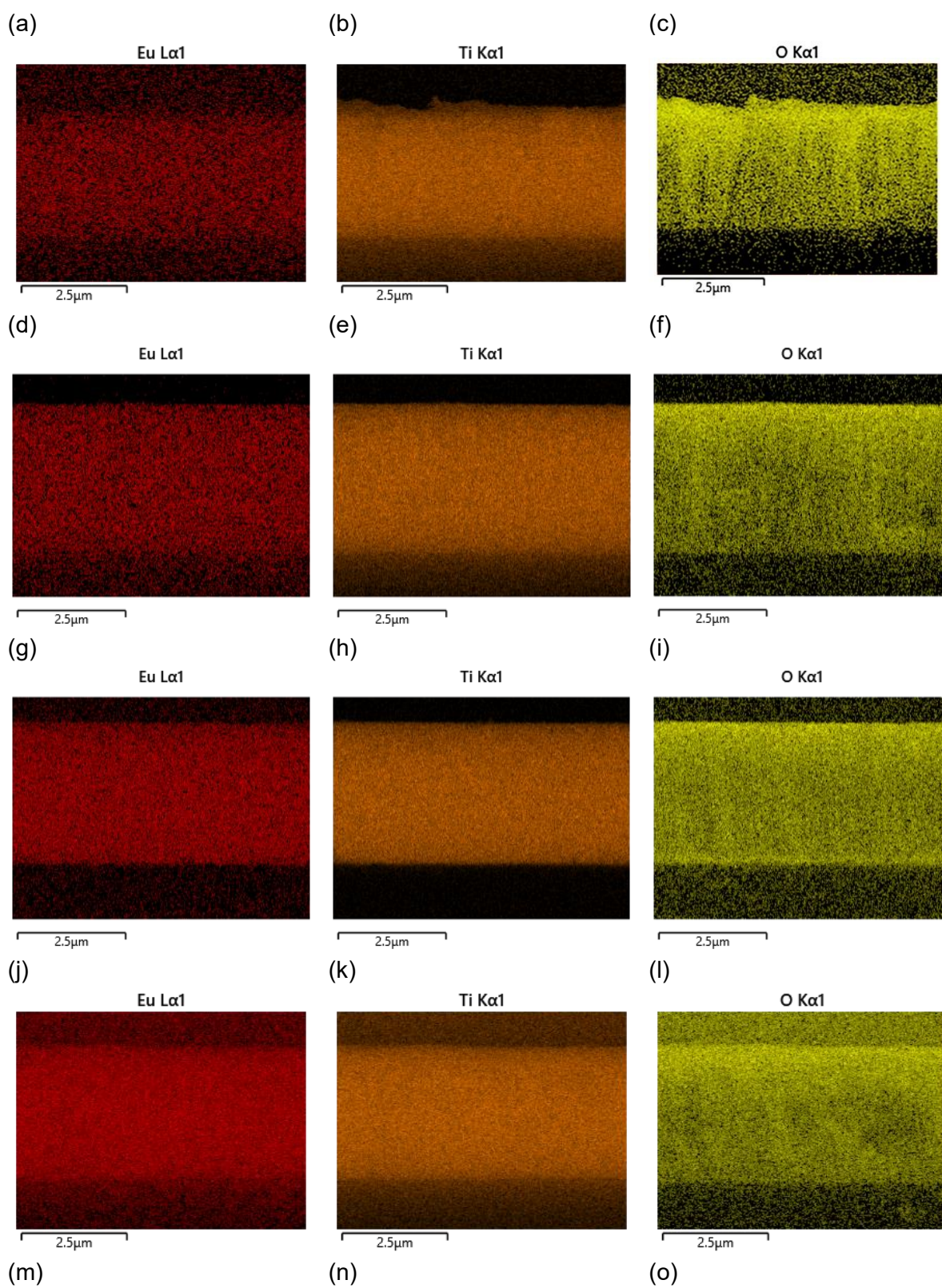


Figure Apx B - 2 EDX mapping for the samples as-deposited with Eu, Ti and O composition in thin films at different concentration, (a) (b) (c) 65.4 at% Eu/(Eu+Ti), (d) (e) (f) 75.5 at% Eu/(Eu+Ti), (g) (h) (i) 88.4 at% Eu/(Eu+Ti), (j) (k) (l) 96.3 at% Eu/(Eu+Ti), (m) (n) (o) 98.2 at% Eu/(Eu+Ti), (p) (q) (r) 99 at% Eu/(Eu+Ti).



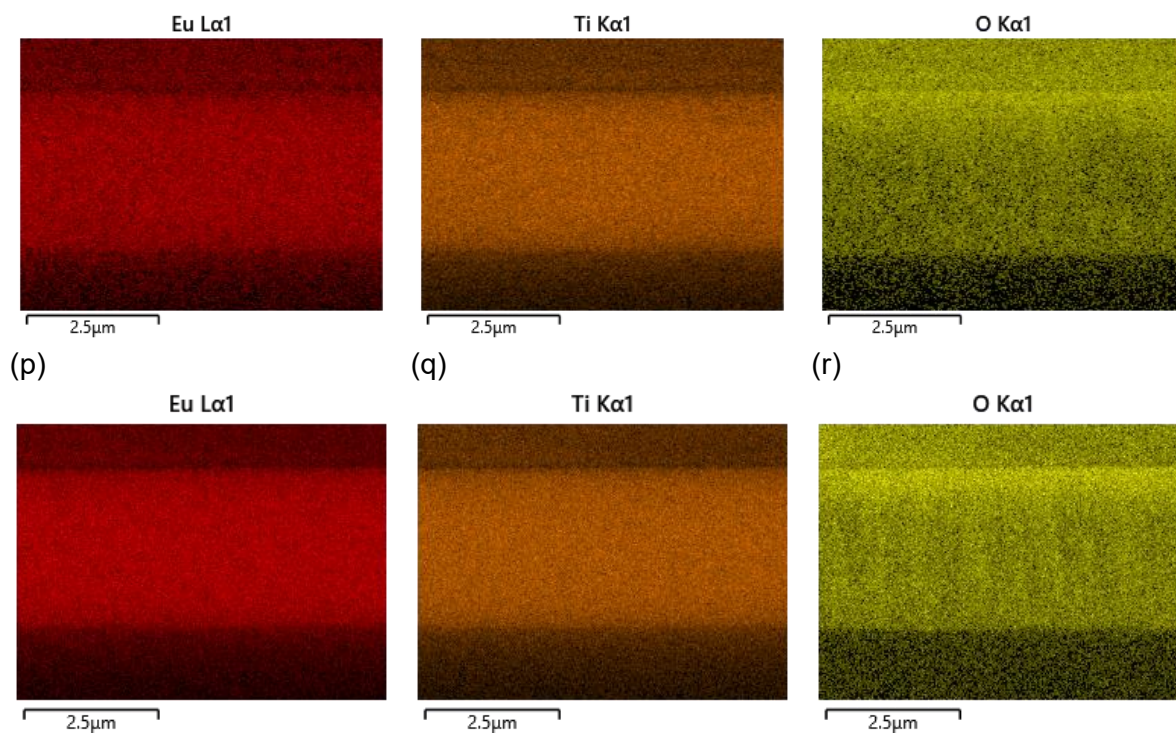
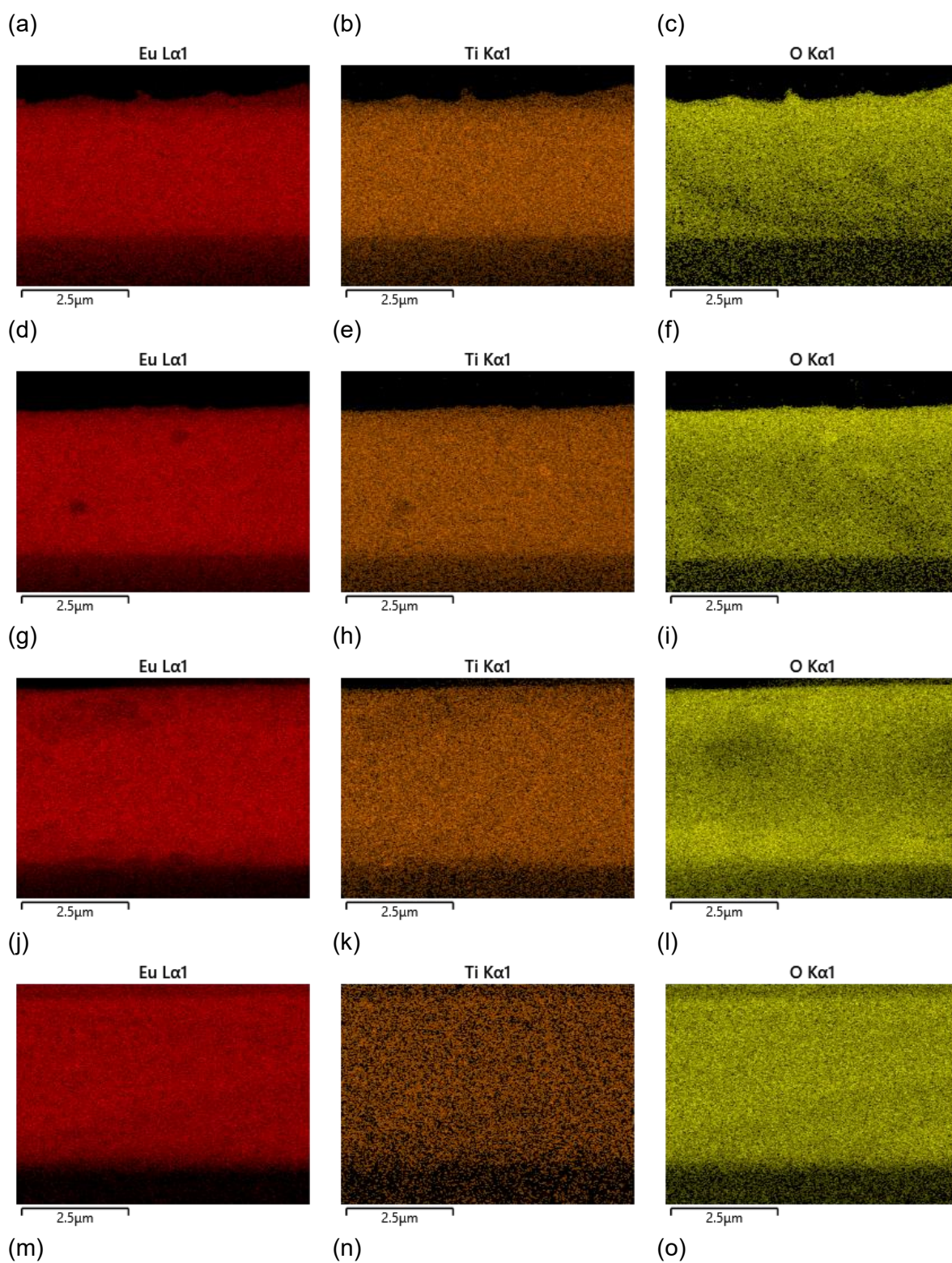


Figure Apx B - 3 EDX mapping for the samples after annealing at 600°C with Eu, Ti and O composition in thin films at different concentration, (a) (b) (c) 4.7 at% Eu/(Eu+Ti), (d) (e) (f) 7.2 at% Eu/(Eu+Ti), (g) (h) (i) 9.1 at% Eu/(Eu+Ti), (j) (k) (l) 19 at% Eu/(Eu+Ti), (m) (n) (o) 29.2 at% Eu/(Eu+Ti), (p) (q) (r) 44.4 at% Eu/(Eu+Ti).



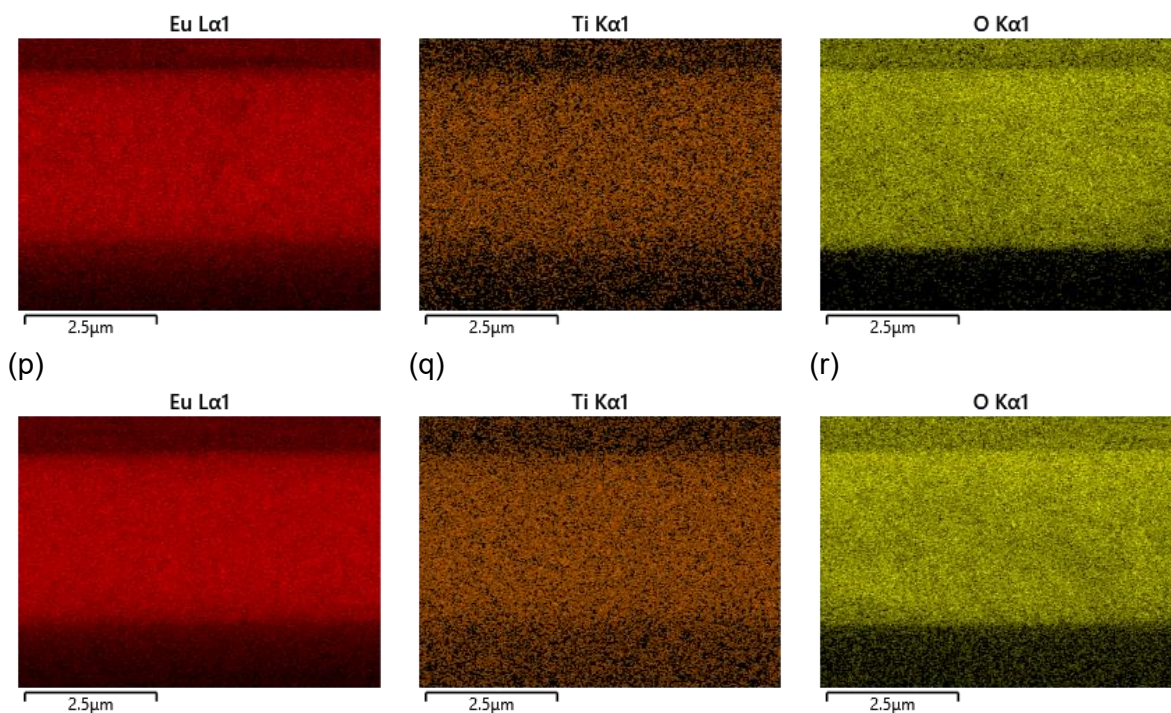


Figure Apx B - 4 EDX mapping for the samples after annealing at 600°C with Eu, Ti and O composition in thin films at different concentration, (a) (b) (c) 65.4 at% Eu/(Eu+Ti), (d) (e) (f) 75.5 at% Eu/(Eu+Ti), (g) (h) (i) 88.4 at% Eu/(Eu+Ti), (j) (k) (l) 96.3 at% Eu/(Eu+Ti), (m) (n) (o) 98.2 at% Eu/(Eu+Ti), (p) (q) (r) 99 at% Eu/(Eu+Ti).

9.3 Appendix C -- EDX Oxygen element Line scan for the cross-section of the ETO thin films

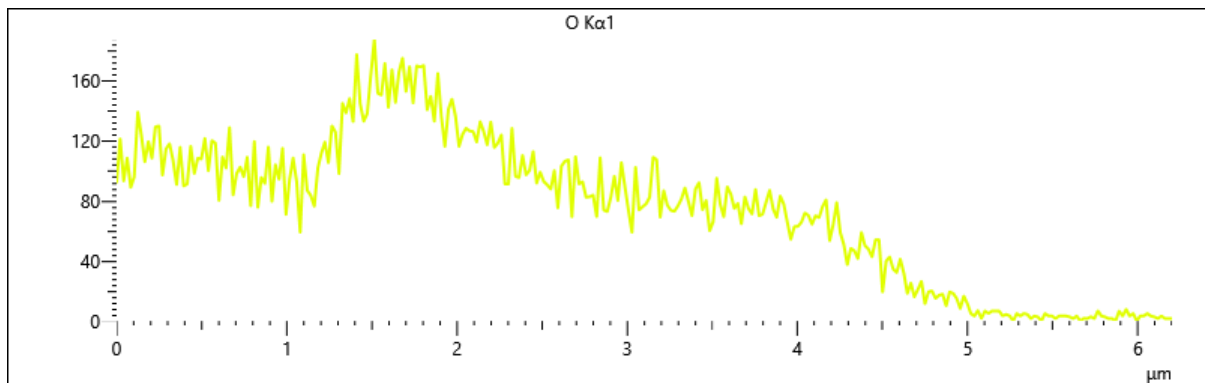


Figure Apx C - 1 EDX Oxygen element Line scan for the cross-section of the 7.2 at% Eu/(Eu+Ti) thin films

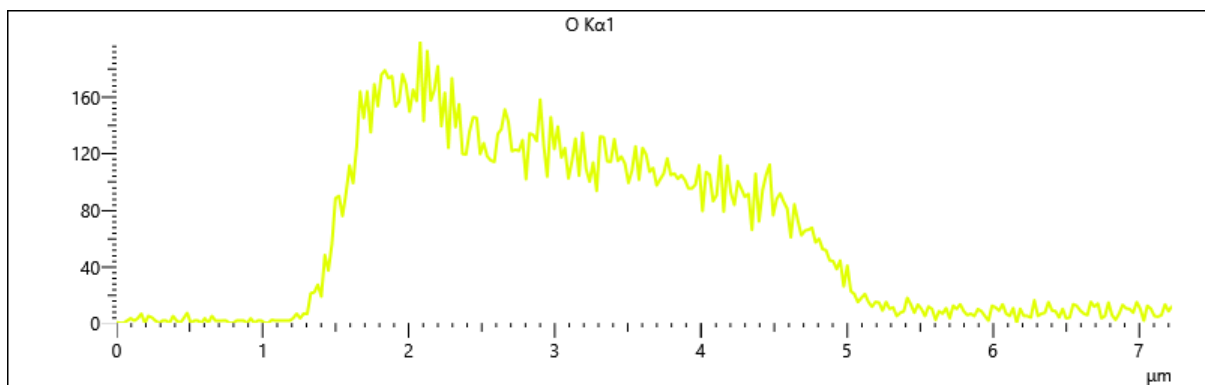


Figure Apx C - 2 EDX Oxygen element Line scan for the cross-section of the 29.2 at% Eu/(Eu+Ti) thin films

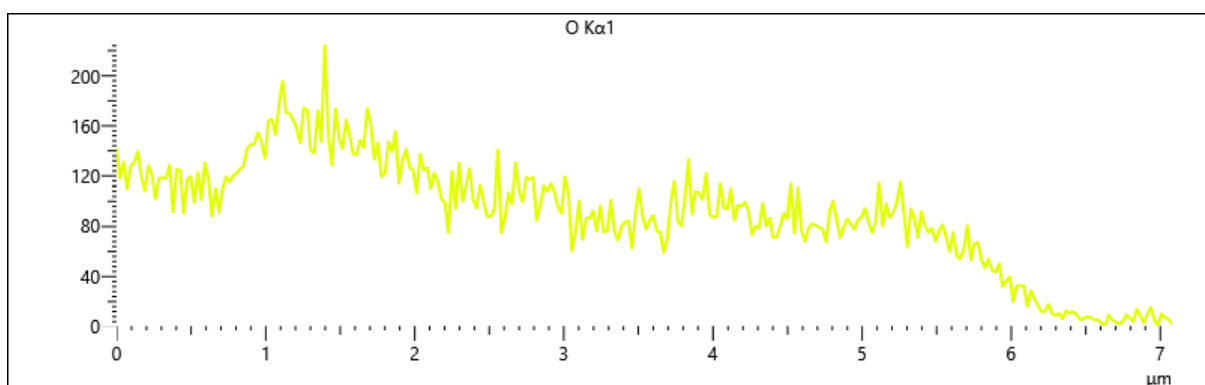


Figure Apx C - 3 EDX Oxygen element Line scan for the cross-section of the 75.5 at% Eu/(Eu+Ti) thin films

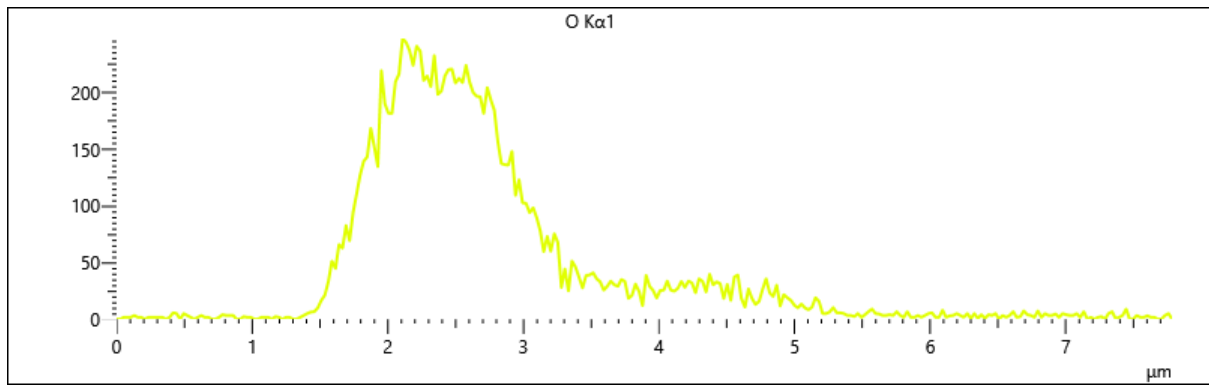


Figure Apx C - 4 EDX Oxygen element Line scan for the cross-section of the 98.2 at% Eu/(Eu+Ti) thin films

9.4 Appendix D -- Blue shift of $\text{CuInS}_2/\text{ZnS}$ with PVA and PMMA

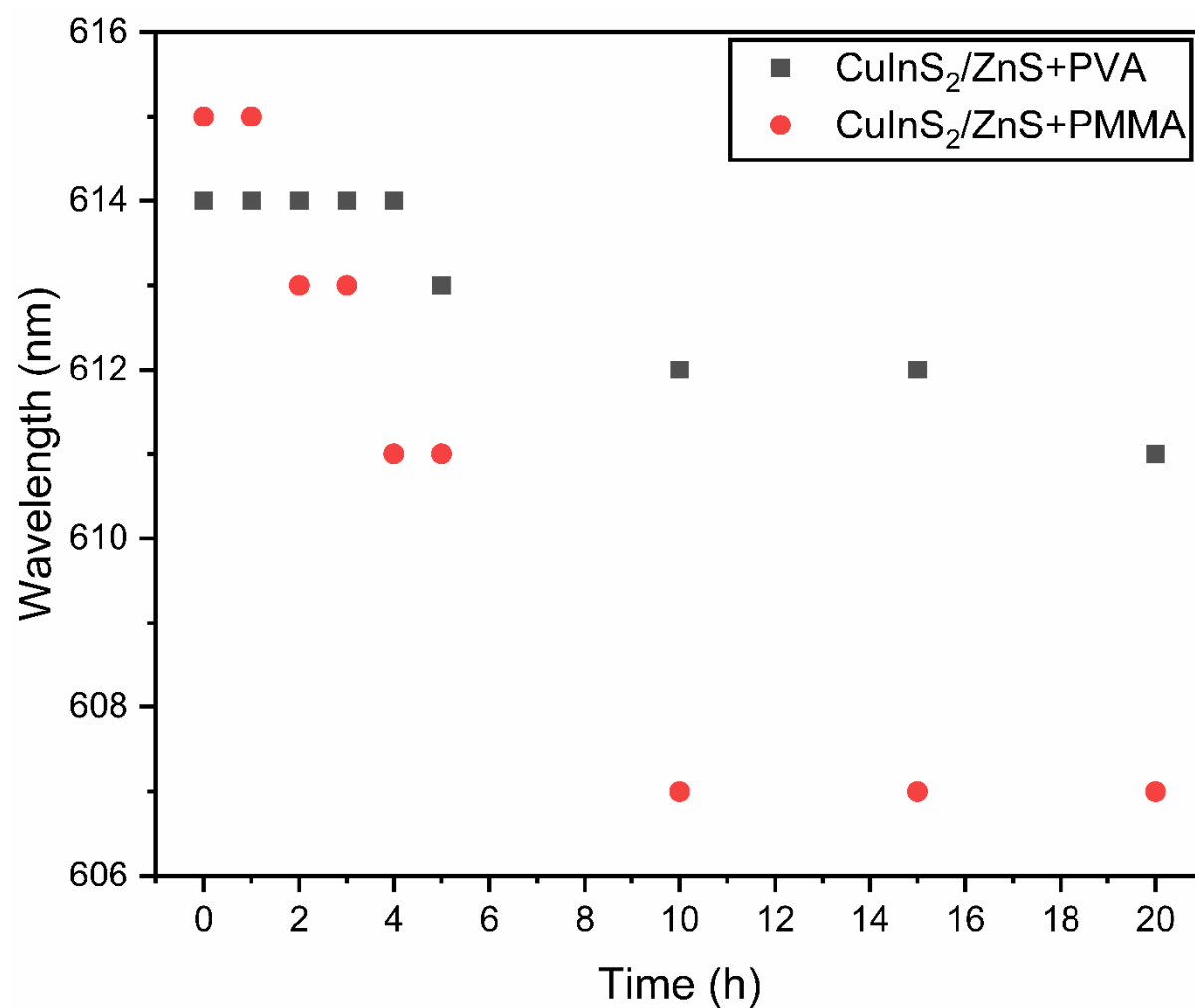


Figure Apx D - 1 The blue shift in maximum emission intensities of $\text{CuInS}_2/\text{ZnS}$ with PVA and PMMA thin films during the degradation testing.