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# Influence of ferroelectricity of the photoelectric effect of $LiNbO_3$

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Abstract

A comparison between the influence of domain dependent photochemical and photoelectric cation reduction on the surface of $LiNbO_3$ is presented. The reduction of the photoelectric threshold for $LiNbO_3$ due to the polar nature of the crystal allows high energy UV irradiation to produce free electrons that can participate in photochemical reduction of silver nitrate on the surface. This is in addition to the previously understood phenomenon of domain directed photophysics, where influences on space charge layer due to the internal dipole of a ferroelectric determine the carrier at the surface. We show that the interaction of photoelectric and domain dependent influences can be observed in $LiNbO_3$ due to the low electron affinity (ca 2eV) and large band bending (0.8eV).

Body

There has been growing interest in the study of the photophysics and photochemical interactions of ferroelectric materials since the late 1990's. At this time some of the early confusion regarding the nature of the interaction between the semiconducting and ferroelectric properties of the materials where being resolved. Furthermore interesting work from Gioncondi and Rohrer[1] demonstrated that it was possible to spatially separate the reduction and oxidation processes on the surface of a ferroelectric. This was resolved by examining the influence of the internal dipole of a

poled ferroelectric on the space charge layer and has led to a number of publications highlighting the influence of semiconductor physics on the surface photochemistry of ferroelectric systems[2,3].

In the case of a $c^+$ domain then there is downward band bending and so $e^-$ are driven to the surface, while in a $c^-$ domain there is upward band bending and $h^+$ are driven to the surface. Where we have $e^-$ we have a surface that acts to reduce species in contact with the surface and a surface with $h^+$ is oxidative. The exact degree of reductive or oxidative power of this mobile carrier is determined by the relative position of the conduction and valence bands. It is now commonly accepted that the value of the NHE in electrochemical terms lies 4.5V (or 4.5eV) from vacuum[4]. It is, therefore, possible to map an electrochemical potential against the band structure of a semiconductor and determine whether there will be reduction or oxidation of solvated species on the semiconductor.

The degree of band bending that is influence by the dipole of the ferroelectric is determined by a number of factors which include the defect density and magnitude of remnant polarisation[5]. It must also be considered that a ferroelectric material can screen the internal polarisation by external screening which increasingly happens as the defect density reduces or remnant polarisation increases. Examples of opposite effects are lead zirconate titanate (PZT) where a high number of defects allow almost complete internal screening and $LiNbO_3$ where there is a significant degree of external screening due to low defect numbers. Interestingly there is also an influence on the photoelectric effect seen on poled semiconductor systems as was demonstrated by in 2004 by Yang *et al*[6].

The interesting questions that arise from the studies on $LiNbO_3$ that have been undertaken so far relate to the subtle differences seen in the work undertaken. Two different broad observations have been published – one shows photo assisted deposition on domian boundaries[7] and the other deposition across the bulk of a poled domain[8]. The differences in the results presented in these reports are in the wavelength of irradiation and power of the source used. In cases where a high power and therefore higher flux of photons is generated then complete domain decoration

according to domain dependent coverage is observed, when a lower power output is used then only domain boundaries are sites of nucleation[2].

In this work, we have used single crystal $LiNbO_3$ that has been poled to present either $c^+$ or $c^-$ faces. $LiNbO_3$ (z-cut from MTI Corporation) is known to exhibit an hexagonal structure below the Curie temperature of 1210ºC with polarization along the c-axis. Experiments were conducted using a high energy (400W) UV bulb produced by Honle that gives irradiation from 200nm to the band gap energy of the $LiNbO_3$ at *ca* 320nm[5]. Each sample was $0.5mm^2$ and adhered to a glass slide substrate using silver loaded epoxy. Irradiation was performed under 0.01M silver nitrate solution (Aldrich 99.99%) that was freshly prepared for each sample. A Veeco Dimension 3000 scanning probe microscope was used to investigate the coverage of the $LiNbO_3$ after irradiation with the UV and prior to deposition.

Fig 1 (a) shows the coverage of silver nanoparticles as deposited on the $c^+$ domain of the $LiNbO_3$. This image is consistent with previous work published in the field where the band bending of the semiconductor produces an interface to which either $e^-$ or $h^+$ are preferentially driven. The pattern of silver deposition in discrete particles is due to the localisation of free electrons at surface defects or subsurface defects. This is demonstrated in Fig 1 (b) where a localised nanowire has formed. The surface of the crystal was epi polished and prior to deposition no topographical features could be seen. It is likely that the feature of the nanowire has formed due to a sub-surface defect during polishing[9]. This subsurface feature acts to disturb the local crystal lattice and so interferes with the space charge layer. This interference can allow for a build up of free carriers in the vicinity.

The same experiment was performed on the $c^-$ face of the $LiNbO_3$ crystal, the results of which are shown in Fig 2. Fig 2 shows that although the space charge layer of the sample would inhibit $e^-$ reaching the surface there has still been reduction in silver cations to silver metal clusters. The size and distribution of the clusters is identical to the initial stages of metal cluster deposition where photogenerated carriers are responsible. We have already demonstrated[5] that it is possible to alter the space charge layer of a semiconductor by using high energy superband gap irradiation.

However, in the case of $LiNbO_3$ this would not be expected as the high $P_r$ and low defect density in $LiNbO_3$ generate a large space charge region.

In the case of PZT we found that only certain irradiation spectrums produced the anomalous deposition on the $c^-$ domain. In the case of $LiNbO_3$ both the low intensity and high intensity at high energy bulbs produced silver decoration, see reference 5 for a full spectrum. We believe that the silver being deposited on the $c^-$ domains of $LiNbO_3$ is being produced as a result of the photoelectric effect. If we accept that the electron affinity is between 1.1 and 1.5eV and the band gap ($E_g$) is 3.9eV[6] we find that photoelectrically generated photons will be able to interact with the $Ag^+$ that are bound to the $c^-$ surface when photons above *ca* 4.6eV are incident on the surface. It is known that photons of this wavelength are capable of penetrating the silver nitrate[2] solution. In Fig 3 we show the proposed mechanism for deposition of silver nanoparticles through reduction of silver cations on the surface of a $c^+$ and $c^-$ $LiNbO_3$ domain.

Using the arguments presented above it should be possible to see evidence of the photoelectric effect producing metal nanoparticles on other ferroelectric systems. A body of work has been published on perovskite systems such as $BaTiO_3$ and $PbZr_{(x)}Ti_{(1-x)}O_3$ and so some comparisons can be drawn. Taking PZT as a comparative system a number of electron affinities and band diagrams have been presented in the literature[10]. Additionally the system has been reasonably well studied using photochemical techniques. It has been shown that energy ranging from 3.8 to 4.5eV is required to deposited silver nanoparticles on the $c^+$ domains and that only under exceptional circumstance can silver reduction occur on the $c^-$ domain[3,5]. Similar results have also been obtained for $BaTiO_3$[11].

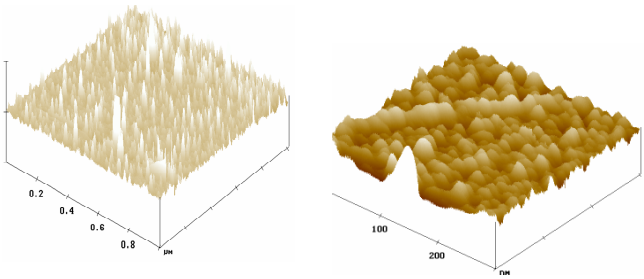
In the case of PZT there has been further experimental work, using photochemical analysis using salts of various reduction potentials[12], that has shown the conduction band ($E_c$) for PZT lies around 3.5eV from the vacuum and that the band bending associated with polarisation is in the order of 0.5eV. The value of band bending due to polarisation is fixed at less than 0.8eV as this the location of the acceptor level generated by oxygen defects; a value of bending greater then 0.8eV would produce a degenerate semiconductor. We are at present unable to explain some of the PEEM

results produced for PZT as PEEM and surface photochemical studies are consistent for $LiNbO_3$. However, it would seem likely that the differences in the band structure and mechanisms of polarisation screening are responsible for the observed differences.

We have demonstrated that it is possible to use the photoelectric effect to reduce metal cations on the surface of $LiNbO_3$ $c^-$ domains. The effect is shown to be dependent on the location of valence band with respect to the vacuum and degree of band bending caused by the internal dipole and mechanism of screening polarisation charge.

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Figures




(a) (b)

FIG. 1. (a) SPM image of silver nanoparticle growth on the $c^+$ domain of $LiNbO_3$, (b) localised nanowire formation due to subsurface defects.

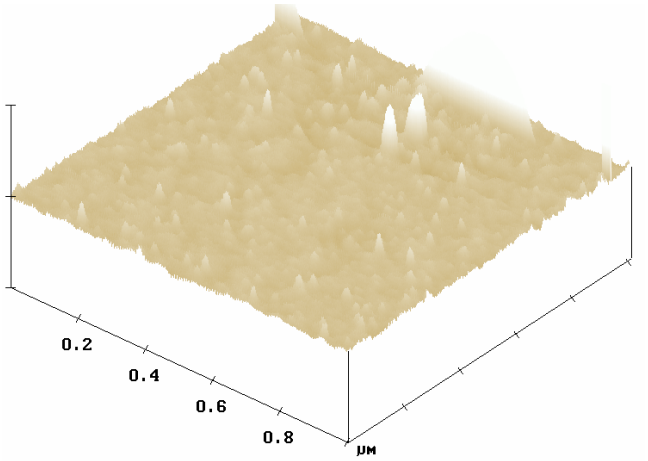



FIG. 2. Surface of $c^-$ $LiNbO_3$ showing evidence of production of silver nanoparticles.

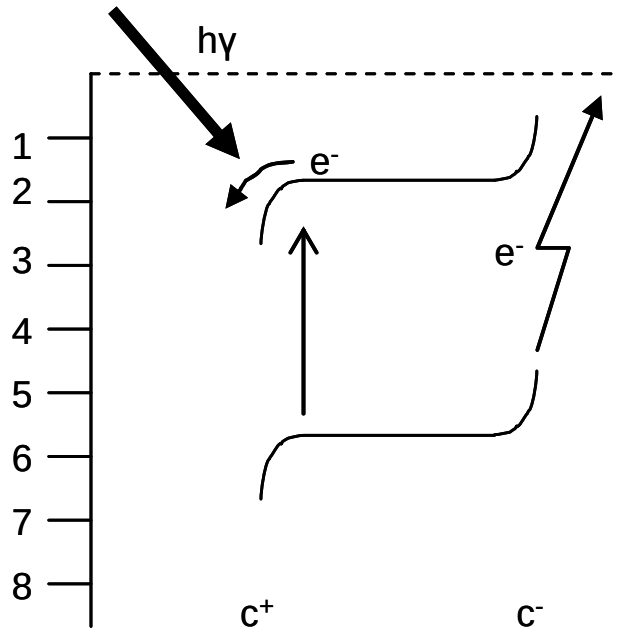



FIG.3 Proposed schematic for photoreduction of silver cations over $c^+$ domain and photoelectric reduction of silver cations over $c^-$ domain. Here we have used $E_g$ as 3.9eV and $X_s$ as 1.5eV.

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