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COMPARATIVE STUDIES OF PST THIN FILMS AS PREPARED BY SOL-GEL, LDCVD AND SPUTTERING TECHNIQUES

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Lead scandium tantalate (PST) thin films for pyroelectric applications have been deposited by using liquid delivery chemical vaporise deposition (LDCVD), sputtering and sol-gel techniques. These films were annealed by using rapid thermal annealing to improve their electrical properties. Their microstructures and electrical properties such as permittivity ε_r, dielectric loss $\tan\delta$, pyroelectric coefficient p, and thermal detection figure of merit F_d were studied. It is suggested to use a combination of methods to depositing films and then use rapid thermal annealing to produce high quality PST thin films.

Keywords: PST; thin films; sol-gel; sputtering; liquid delivery CVD.

1. **INTRODUCTION**

Lead scandium tantalate (PST) is a very promising candidate for the application of uncooled thermal imaging because of its high figure of merit for infrared detection [1]. Recent effort has been focused on the growth of PST as thin films directly onto silicon wafers in order to lower cost and improve device performance [2].

The magnetron sputtering technique has been widely employed for the deposition of ferroelectric thin films. It is a dry technique compatible with IC-technology but is capital intensive and the film composition is difficult to modify. The metal-organic liquid delivery chemical vapour

deposition (LDCVD) technique has a higher deposition rate and more flexible control of composition than the sputtering method. It also has very good step coverage and capable of coating onto large-area substrates. However, it is also capital intensive, and it is sometimes difficult to obtain appropriate precursors. On the other hand, sol-gel is relatively low cost to set up and simple to apply, confers easily control of composition, but being a wet chemical process with poor step-coverage properties is perhaps less acceptable in a semiconductor device processing context. In this communication we will report the deposition of PST films by using different techniques such as sputtering, LDCVD, and sol-gel. Their respective microstructures and electrical properties before and after the post-deposition anneal will be presented.

2. EXPERIMENTAL

LDCVD was carried out using $Pt/Ti/SiO_2/Si$ substrates. Heptane was used as the solvent and nitrogen as the carrier gas. The vaporiser and substrate temperatures were 200 °C and 600 °C respectively. In order to encourage nucleation of the perovskite phase, a thin seed layer of $PbTiO_3$ was initially deposited onto the Pt surface. For more details see reference [3].

Sputtering deposition was carried out in a custom sputtering system which uses dual RF magnetron sputtering targets in an argon/10% oxygen atmosphere. More details have been published elsewhere [4, 5]. Films were deposited at 300 °C

For sol-gel deposition, precursors were first prepared. $Pb(OAc)_2{\cdot}3H_2O$ was mixed with IPA with the ratio of $Pb(OAc)_2{\cdot}3H_2O$: IPA 1g:1ml. $Ta(OEt)_5$ and $Sc(OAc)_3$ was mixed in IPA with the ratio of $Ta(OEt)_5$: IPA 1g: 60ml. A lead zirconate titanate (PZT) layer was first coated on a $Pt/Ti/SiO_2/Si$ substrate as a seeding layer in an attempt to reduce PST crystallisation temperature. PST layers were spun onto the top of PZT. Each coating went through drying (200 °C, 30 s) and annealing (580 °C, 10 min.) procedures. 1% Mn was doped into both the PZT and PST layers to improve film electrical properties. For more details see reference [3].

Rapid thermal annealing (RTA) of the samples was carried out using an AG Associates Minipulse Rapid Thermal Processor system with a heating ramp rate of 50 °C/s and natural cooling.

Where possible electrical characterisation has been carried out on both as-deposited and annealed films. Top electrode of Au(100 nm)/Cr(10 nm) was deposited by thermal evaporation through a shadow mask. A Component Analyser was used to measure pyroelectric and dielectric properties (permittivity $\varepsilon_0\varepsilon_r$, dielectric loss tanδ) at 35 °C and 50 °C and in addition permittivity and dielectric loss were measured as functions of temperature – all in an inert atmosphere of 300 mbar N_2.

3. RESULTS AND DISCUSSION

Figure 1a shows the XRD patterns for the as-deposited sol-gel and LDCVD films. The intensity is in logarithm scale. The spectrum for the LDCVD film is moved up by one unit to improve visibility. Both films were mainly perovskite (Pe), with the sol-gel film mainly (222) oriented and the LDCVD film a mixed orientation. There is a recognizable peak of pyrochlore (Py) phase in the LDCVD film but hardly any in the sol-gel film. The as-deposited sputtering films were pyrochlore and amorphous.

It is a surprise to observe the B-site ordering Pe(111) peak at $2\theta < 20°$ for the as-deposited sol-gel film. It is generally believed that B-site ordering in PST starts at temperatures of 700 °C or higher.

The XRD patterns for the RTA treated films are shown in Figure 1b. Perovskite peaks grew stronger for all three films after RTA. For sol-gel film, the increase for normal perovskite peaks was moderate. However, the ordering peak Pe(111) was more than doubled, from 136 to 324. Extra peaks were observed for the LDCVD film after the RTA. These peaks could be indexed as $PbTiO_3$, and were labeled PT in figure 1b. This is not surprising since a seeding layer of $PbTiO_3$ was deposited prior to the deposition of the PST layer. No sign of ordering was observed even after RTA annealing at 850 °C for 120 s for the LDCVD films. The sputtered film after RTA treatment was strongly (222) oriented perovskite, with other orientations like (200) and (220) 100 times less in intensity. Ordering was also observed for this film.

The cross-section transmission electron microscope (TEM) images for the RTA annealed films are shown in figure 2 for (a) sol-gel; (b) LDCVD and (c) sputtered films respectively. The sol-gel prepared films had a very smooth surface. The PZT seeding layer was about 60 nm thick. Each layer of the following PST was about 41 nm thick. The PST

was well columnar structured. There were voids in the PST, with bigger ones concentrated at the PST grain boundaries. Occasionally, very large voids or small areas of pyrochlore (as marked by arrow-heads) were observed. There was no sign of materials diffusion during the deposition or the RTA annealing. Chemical analysis by scanning electron microscope showed that the composition was Sc:Ta:Pb = 1:0.9:2.47,

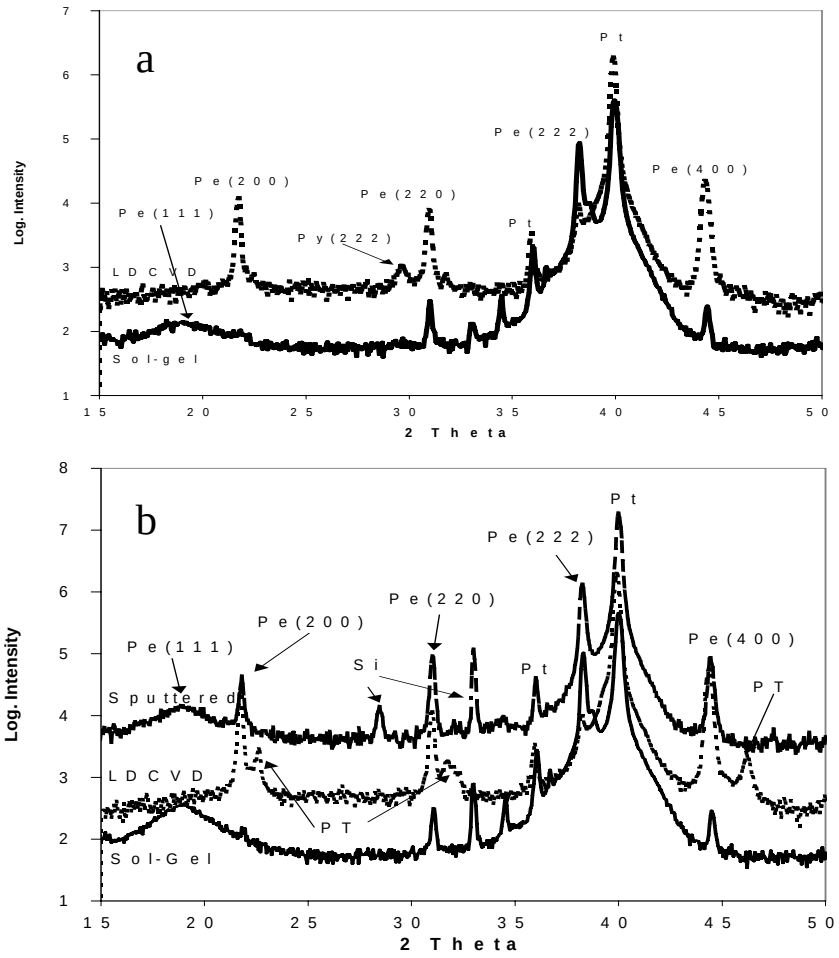


Figure 1 XRD patterns for the (a) as-deposited and (b) RTA annealed PST thin films as prepared by different techniques.

indicating a high level of excess lead. Unlike the sol-gel film, the LDCVD film surface was rough, with peak to trough about a third of the film thickness. The film appeared to be fully perovskite and had good crystallinity with grain size of about 0.5 μm. For the sputtered film, there were many voids in the PST and the film surface was relatively

smooth. Some PST grains were a few microns in diameter. Pyrochlore (marked by the arrow-head) was seen occasionally at the bottom of the PST and immediately above the Pt layer.

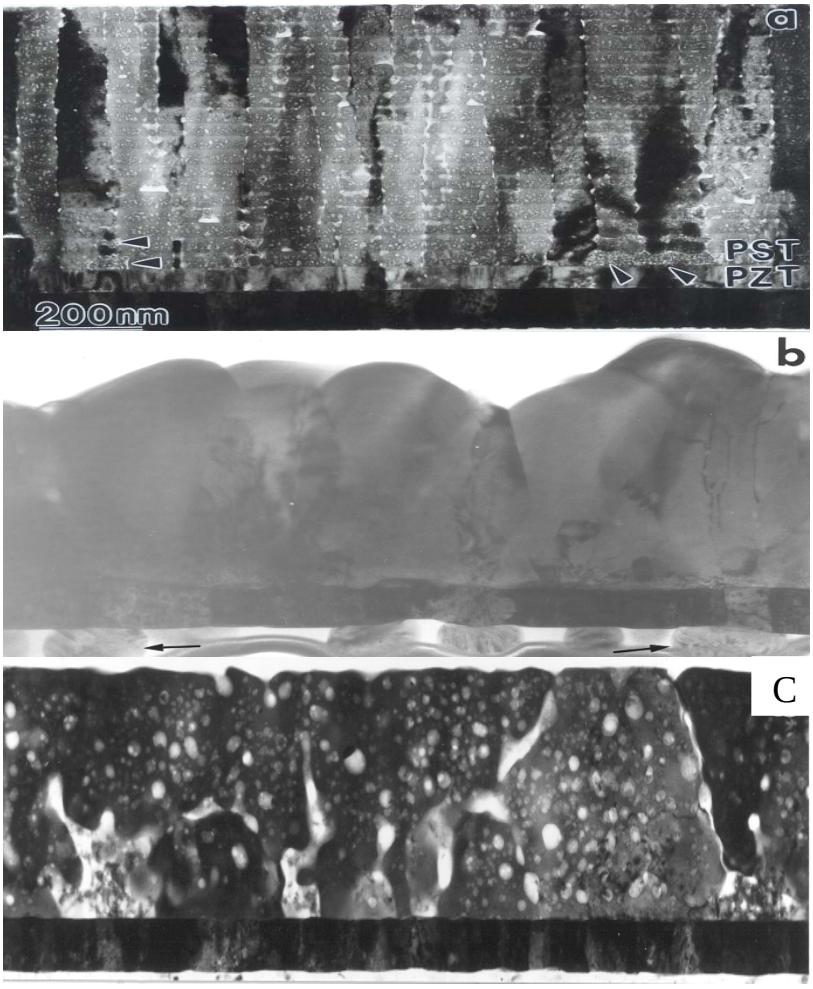


Figure 2 Transmission electron microscope images for the cross-section of RTA treated thin films deposited by (a) sol-gel; (b) LDCVD and (c) sputtering techniques.

The as-deposited LDCVD films had very high loss and low resistance. Several as-deposited films had been tested and they all had small breakdown field, the highest breakdown field for the as-deposited films was measured to be 3 V/μm, this lead to a merit figure F_d of about $1\times10^{-}$

^{5} $Pa^{-1/2}$. For sol-gel films, RTA annealing in O_2 resulted in blistering to the extend that no electrical measurements were carried out for the RTA treated films. The sputtering as-deposited films contained no perovskite phase and no electrical measurement was attempted.

The relative permittivity ε_r and dielectric loss tanδ at 50 °C as functions of applied field at 120Hz for the as deposited sol-gel, RTA annealed LDCVD and sputtered films are shown in figure 3. The as-deposited sol-gel film showed very low permittivity ε_r and high dielectric loss tanδ.
For the LDCVD and sputtered films, as is expected for a relaxor like PST, relative permittivity ε_r and dielectric loss tanδ decrease with increasing applied field. However, for sol-gel films, the decrease was much more moderate and there was no significant frequency dependence of the ε_r and tanδ.

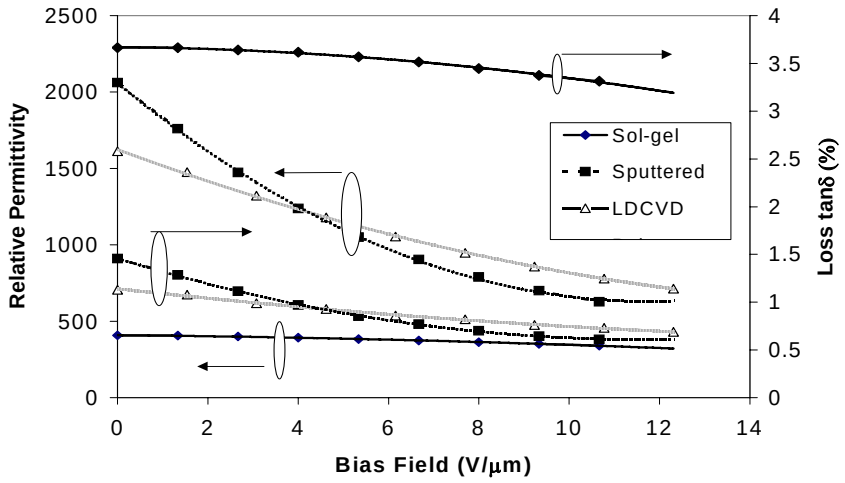


Figure 3 The relative permittivity ε_r and dielectric loss tanδ as Functions of dc bias at 120Hz for the PST films.

The pyroelectric coefficient p and materials merit figure F_d (50 °C, 120Hz) at temperature of 50 °C for the above films are shown in figure 4. For the as-deposited sol-gel films, a reasonable maximum pyroelectric coefficient of 269 $\mu Cm^{-2}K^{-1}$, and a merit figure F_d of 1.0×10^{-5} $Pa^{-1/2}$ was achieved at an applied field of 10.7 V/μm. Unusualy for PST thin films the zero field pyroelectric coefficient was small and indeed there was evidence for a small internal bias field antiparallel to the applied field (top electrode positive). The LDCVD film has shown

pyroelectric coefficients under field up to 576 $\mu Cm^{-2}K^{-1}$, and a merit figure of 3.2×10^{-5} $Pa^{-1/2}$. The sputtered films gave the highest pyroelectric coefficient, and reached 743 $\mu Cm^{-2}K^{-1}$ at the applied field of 7 V/μm. Upon further increase of the field, the pyroelectric coefficient showed little change. A merit figure F_d of 4.6×10^{-5} $Pa^{-1/2}$ was achieved at an applied field of 13.3 V/μm.

The temperature dependence of the relative permittivity ε_r and dielectric loss tanδ at 120Hz for the above films are shown in figure 5. The LDCVD and sputtered films behaved like a relaxor, namely, ε_r peaked just under 20 °C and loss tanδ peaked at a temperature below 20 °C. However, for the sol-gel film, there was little temperature dependence of ε_r and the dielectric loss increased with increasing temperature until the highest temperature 80 °C. In this sense, the as-deposited sol-gel film did not behave like a relaxor. This was probably due to a dc leakage for this film.

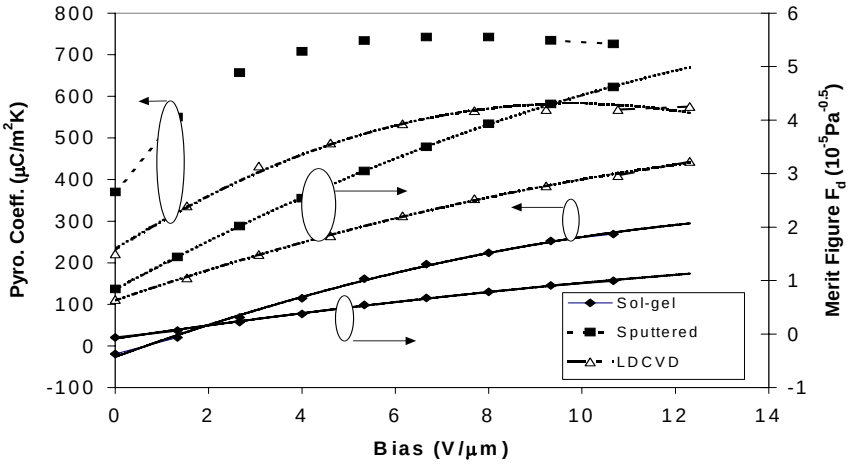


Figure 4 The pyroelectric coefficient p and merit figure F_d as functions of dc bias at 120Hz for the PST films.

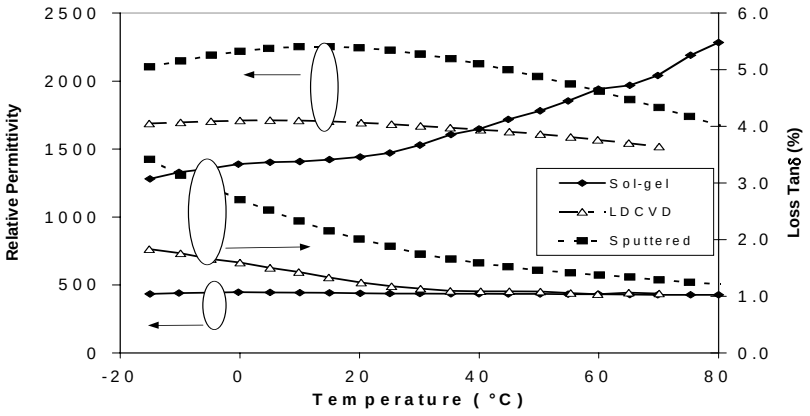


Figure 5 The temperature dependence of the relative permittivity ε_r and dielectric loss tanδ at 120Hz for the PST films

The above results indicate that it is necessary to anneal the PST films at high temperature (800 °C and above) in order to obtain excellent electrical properties such as high pyroelectric coefficient and low dielectric loss. Nevertheless it is a surprise to observe that the as-deposited LDCVD films had very low breakdown strength and low resistivity whilst post-annealed LDCVD films showed good electrical properties, although both XRD and TEM did not reveal significant structural changes. The surface roughness is unlikely to be responsible for the low breakdown field since this is the same before and after the RTP annealing. There must be something else which had be changed dramatically during the RTA annealing but cannot be revealed either by XRD or TEM techniques. Such effects including oxygen vacancy, excess Pb level, interface effect, etc. Further study in this direction is in progress.

The surface roughness of the LDCVD films could be improved if these films were subjected to further sol-gel coating.

3. CONCLUSIONS

Lead scandium tantalate thin films for pyroelectric applications have been deposited by using liquid delivery chemical vaporise deposition, sputtering and sol-gel techniques. These films were rapid thermal annealed to improve their electrical properties. Their microstructure was investigated by using x-ray diffraction and transmission electron microscopy and their electrical properties such as permittivity ε_r, dielectric loss tanδ, pryoelectric coefficient p, and thermal detection figure of merit F_d were measured. A comparison of microstructure and electrical property between different films suggest that there is no simple relationship between the microstructure and its electrical properties. Sol-gel and LDCVD produce very ‘good looking’ as-deposited PST films in terms of XRD spectra and TEM micrograph but these films show poor dielectric loss and figure of merit. On the other hand, the sputtered and then RTP annealed films had lots of voids but gave rather good electrical properties. It is suggested that the best strategy to prepare high quality PST thin films should be to use a

combination of methods to deposit the films and then apply the RTA technique.

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