Growth and Dielectric Properties of Pb(ScTa)\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3} (PSTT) Thin Films by MOCVD Method

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Abstract

Highly (002) textured Pb(ScTa)\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3} (PSTT) (with composition \(x = 0 - 0.3\)) thin films were deposited using metal-organic chemical vapor deposition (MOCVD) technique at temperature ranging from 600 °C to 685 °C. Dielectric properties of these PSTT thin films showed strong dependency on the growth temperature and PT content. Ti addition acted as a “Curie” temperature shifter, moving \(T_{\text{max}}\) from –10 to 120 °C with the dielectric constant peak value increasing from 1397 to 1992 (measured at 1 kHz) when composition \(x\) went from 0 to 0.3. Loss tangent values were generally below 0.025. For PSTT thin films with composition near its morphotropic boundary (\(x = 0.3\)), the room temperature dielectric constants increased from 980 to around 1600 as the growth temperature increased from 650 to 685 °C. In addition, the dielectric dispersion behaviors of films grown at different temperatures were compared.

Key Words: PSTT Relaxor Ferroelectric, MOCVD, Thin Films, Dielectric Properties

1. Introduction

Owing to their potential applications in dynamic random access memory, microelectromechanical system and integrated infrared detectors [1,4,5] relaxor ferroelectrics such as Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} (PMN), Pb(Sc\textsubscript{1/2}Ta\textsubscript{1/2})O\textsubscript{3} (PST) and their solid solutions with PbTiO\textsubscript{3} (PT) have attracted much attention of late. We were the first group to grow PST-PT(or termed as PSTT) thin films using a MOCVD technique. This article focuses on the composition and growth temperature control in connection with the phase evolution and dielectric properties PSTT thin films.

2. Experimental

We used a low pressure, horizontal, cold-wall quartz reactor with a resistive substrate heater [3]. High purity nitrogen was used as the carrier gas. The metal-organic sources were lead tetra-methyl heptanedione Pb(TMHD)\textsubscript{2}, scandium tetra-methyl heptanedione Sc(TMHD)\textsubscript{3}, titanium isopropoxide, Ti(OCH\textsubscript{3})\textsubscript{4}, tantalum trifluoroethoxide Ta(OCH\textsubscript{3}CF\textsubscript{3})\textsubscript{5} and tantalum ethoxide Ta(OCH\textsubscript{2}H\textsubscript{3})\textsubscript{5}. Substrates were platinized Si with LaNiO\textsubscript{3} bottom deposited by radio frequency magnetron sputtering at 300 °C. The LaNiO\textsubscript{3} layers were heat-treated (800 °C, 30 min) prior to the MOCVD growth of PSTT. Gold (Au) top electrodes of 200 \(\mu\)m x 200 \(\mu\)m squares
were deposited using a thermal evaporator followed by annealing at 500 °C to improve Au adhesion.

3. Results and Discussion

Several key factors were critical to PSTT film growth: (1) the use of a pre-annealed LaNiO₃ (LNO) buffered substrate, (2) control of film stoichiometry with addition of PT, and (3) optimization of precursor gas ratios and growth temperature.

Pre-annealing of the LNO buffered Si substrates before growth led to high quality PSTT films as evidenced by sharper XRP peaks of the PST phase, and columnar microstructure in the SEM image [2]. Pb control during growth is critical to the formation of perovskite phase PSTT. Figure 1 show XRD patterns of films grown using different precursor flow ratio of Pb to the B site cations (i.e. [Pb]/([Sc]+[Ta]+[Ti])). The ratio need be greater than 1.5 to obtain a pure perovskite PSTT phase. This is most likely due to PbO loss during the high temperature growth (≥650 °C) [6]. The formation of PSTT is less sensitive to the [Sc]/[Ta] ratio so long as 0.5 ≤ ([Sc]/[Ta]) ≤ 1. Outside this range Ta₂O₅-based or Sc₂O₃-based second phase was found as shown in Figure 2 (a) and (b).

Although the growth temperature did not affect in any substantial way the formation of the perovskite phase when it was higher than 550 °C, it did have major effects on the dielectric properties of the grown films. For PSTT films grown above 600 °C, they all showed similar morphology and crystalline orientation, as revealed by the XRD patterns and the SEM micrographs. It was also found that the grains in the PSTT layer were mostly aligned with corresponding grains in the underlying LNO layer. In conjunction with the XRD results, a grain-to-grain epitaxial relationship between LNO and PSTT is suggested. The typical lateral grain size was estimated to be 0.1-0.15 μm.

![Figure 1. XRD patterns showing the effects of excess Pb precursor gas flow on the phase evolution of PSTT thin films](image-url)
Growth and Dielectric Properties of Pb(ScTa)_{1-x}Ti_xO_3 (PSTT) Thin Films by MOCVD Method

Figure 2. XRD patterns showing the effects of Sc/Ta flow ratio on the phase evolution: (a) Sc/Ta > 1 and (b) Sc/Ta < 0.5

Figure 3 shows the variation in the (004) Bragg peak positions of PSTT films grown at 685 °C with different amounts of Ti substitution. The lattice parameter decreased approximately 0.01 Å for each 10% of PT. The addition of PT to PST also acted as a Curie-temperature shifter as seen in Table 1, moving T_{max} to higher temperature with increasing PT content. This effect is expected as PT has a Curie temperature at 490 °C.

Figure 4 (a) and (b) show the dielectric behavior of 685 °C deposited PSTT with compositions of 0% and 30% Ti. In fact, our results show that the T_{max} values were 0, 40, 80 and 120 °C for Ti contents of 0%, 10%, 20%, and 30%, respectively. The measured dielectric constants at T_{max} increased from 1397 to 1992 (1kHz) as the Ti content increased from 0% to
30%. Moreover, films typically showed low loss tangent values near $T_{\text{max}}$ (e.g. $\tan \delta \approx 0.025$ at 1 kHz), which indicates good film quality. A summary of the dielectric properties of 685 °C grown PSTT thin films is given in Table 1.

Table 1. Dielectric properties of 685 °C grown PSTT films measured at 1 kHz

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\varepsilon$ (20°C)</th>
<th>$\tan \delta$ (20°C)</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>$\varepsilon$ ($T_{\text{max}}$)</th>
<th>$\tan \delta$ ($T_{\text{max}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSTT (0% Ti)</td>
<td>1330</td>
<td>0.02</td>
<td>-10</td>
<td>1397</td>
<td>0.025</td>
</tr>
<tr>
<td>PSTT (10% Ti)</td>
<td>1500</td>
<td>0.022</td>
<td>40</td>
<td>1541</td>
<td>0.024</td>
</tr>
<tr>
<td>PSTT (20% Ti)</td>
<td>1732</td>
<td>0.019</td>
<td>80</td>
<td>1992</td>
<td>0.016</td>
</tr>
<tr>
<td>PSTT (30% Ti)</td>
<td>1630</td>
<td>0.025</td>
<td>120</td>
<td>1832</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Figure 4. Dielectric properties of 685 °C grown PSTT thin films with (a) 20% and (b) 30% Ti contents
In comparison with the 650 °C grown films, the dielectric constant values increased appreciably for the 685 °C grown films. In addition, the dielectric dispersion behavior showed the expected trend for T > T_{max} for 685 °C grown films. The improvement in dielectric properties can be attributed to the reduction in crystalline defect density, since the microstructure did not show any evident change.

The ferroelectric properties of 650 °C and 685 °C grown PSTT thin films with different Ti contents (10% and 30%) are depicted in Figure 5(a)-(d). The applied field strength was 250 kV/cm (1 kHz). It appears that the P-E behavior is not strongly dependent on the temperature of growth. The difference in P_r and P_s values for samples grown at 650 °C and 685 °C were in the range of 1-2 µC/cm², but the 650 °C grown samples did not show saturated P-E loops. The unsaturated P-E loop is generally associated with a higher dielectric loss. The lower dielectric loss indicates that the crystalline defect density was substantially reduced for samples grown at higher temperature.

![Figure 5](image1.png)

**Figure 5.** Polarization – electric filed behavior of PSTT thin films grown at (a) 650°C with Ti=10%, (b) 650°C with Ti=30%, (c) 685°C with Ti=10%, and (d) 685°C with Ti=30%

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**References**


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