CRYSTALLOGRAPHY AND SURFACE MORPHOLOGY OF Ta2O5 DOPED PbZr0.52Ti0.48O3 (PTZT) THIN FILMS

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ABSTRACT

The effect of dopant concentration of thin film of PZT grown by DC Unbalanced Magnetron Sputtering (DC UBMS) method were investigated. The films were grown at deposition temperature of 750°C for 3 hours, followed by an annealed at 700°C for 1 hour. X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) observation were employed to characterize the grown films. Tantalum (Ta)-doped PZT (PTZT) thin films show a change in crystal structure as the concentration of dopant increases. Films with 0.50 % and 1.00 % tantalum have tetragonal crystal structures, whereas those with 1.08 % tantalum have cubic structures. Further increase of dopant concentration to 1.50 % leads to a pseudo tetragonal structure. However, increases the content dopant tantalum oxide in lead zirconium titanate resulted desorption of the grown films from the surface lead to non-homogen feature of surface morphology.

Keywords: Surface morphology, PZT, thin film, DC-UBMS method, SEM

1. INTRODUCTION

A pyroelectric infrared (IR) detector has advantages of wavelength independent sensitivity and can be operated at room temperature. It is also expected to provide various thermal observations for objects at near ambient temperature. Thin films of PbTiO3 and PbZr1-xTiO3 have been used as pyroelectric IR detectors1).

PbZr1-xTiO3 films can be grown by various methods, such as sputtering2 – 8), chemical solution deposition (CSD)9 – 13), pulsed laser deposition (PLD)14, 15), and metal organic chemical vapor deposition (MOCVD)16). The varian of sputtering method, which is, the DC Unbalanced Magnetron Sputtering (DC UBMS) method is of particular interest because of its good control of stoichiometry, ease of fabrication and low or high temperature synthesis. It was reported that thin film grown by DC-UBMS has stoichiometry similar to the bulk target.

PbZr0.52Ti0.48O3 (PTZT) has been of immense interest in the use of ferroelectric thin film in pyroelectric sensor applications. In this paper we report on the fabrication of PTZT thin films by DC UBMS. The crystal structure and the surface morphology of the grown films related to the content dopant are described.

2. MATERIALS AND METHODS

A tantalum oxide doped lead zirconium titanate (PTZT) thin film was deposited on Pt (200)/SiO2/Si (100) substrates by DC Unbalanced Magnetron Sputtering methods. A 5.302 gram Lead titanate [PbTiO3, 99 %], 6.698 gram Lead zirconate [PbZrO3, 99.7 %] and 0.0600; 0.1200; 0.1296; 0.1800 gram tantalum oxide [Ta2O5, 99.9 %] were initially mixed in a bowl for 6 hours. The mixture was then pressed at 31.43 MPa for 15 minutes to form a pellet followed by a sintering at 850°C for 10 hours.

The PTZT thin film was grown on 12 mm x 12 mm Pt (200)/SiO2/Si (100) substrate using deposition parameters shown in Table 1. The film structure was analyzed by x-ray diffraction (XRD). The XRD spectra were recorded on a Diano type 2100E diffractometer using CuKα radiation at 30 KV and 30 mA (900 watt). The surface morphology and thickness of the films were examined by SEM JEOL type JSM-35C.

Table 1. DC UBMS deposition parameter

<table>
<thead>
<tr>
<th>Film</th>
<th>PTZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Pt (200)/SiO2/Si (100)</td>
</tr>
<tr>
<td>Thickness</td>
<td>150 nm</td>
</tr>
<tr>
<td>Target</td>
<td>PTZT</td>
</tr>
<tr>
<td>Temperature</td>
<td>750°C for 3 hours</td>
</tr>
<tr>
<td>Annealing</td>
<td>700°C for 1 hour</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.2 torr</td>
</tr>
<tr>
<td>Gas</td>
<td>Ar + O2 (Ar : O2 = 100 sccm : 50 sccm = 2 : 1)</td>
</tr>
<tr>
<td>DC Power</td>
<td>70 – 90 watt</td>
</tr>
<tr>
<td>Thickness</td>
<td>500 nm – 1100 nm</td>
</tr>
</tbody>
</table>
The various sets of planes in a lattice have various values of interplanar spacing. The planes of large spacing have low indices and pass through a high a density of lattice points, whereas the reverse is true for planes of small spacing. The interplanar spacing \(d_{\text{hk}l}\) is a function of both plane indices \((hkl)\) and lattice constants \((a, b, c, \alpha, \beta, \gamma)\). The relation between interplanar spacing and lattice constant for tetragonal structure is given in Equation (1)\(^{17,18}\),

\[
\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2},
\]

we use the usual Bragg Law is given in Equation (2):

\[
\lambda = 2d \sin \theta,
\]

where \(d\) = the interplanar spacing; \(a, b, c\) = lattice constants; \(h, k, l\) = the Miller indices; \(\lambda\) = wave length (for Cu target = 1.54056 Å); \(\theta\) = the diffraction angle.

### 3. RESULTS AND DISCUSSION

Figure 1 shows XRD spectra of PTZT thin films. The films are polycrystalline with preferred orientation in (100), (200) planes. This indicated that the grown film has good crystallinity if high deposition temperature (750°C). It is shown that the intensity of the (100) reflection decreases as the content dopant of Ta2O5 increases, because the high content dopant may cause desorption of the deposited layer lead to the re-orientation of the plane phases. The calculated lattice constants and \(c/a\) ratio using Equation (1) and (2) were given in Table 2. Films with 0.50 % and 1.00 % tantalum have tetragonal crystal structures, whereas those with 1.08 % tantalum have cubic structures. Further increase of dopant concentration to 1.50 % leads to a pseudo tetragonal structure. The smaller value of the \(c/a\) ratio of PTZT thin film than those of PZT thin film is possibly associated with the anti site defects of Ta dopants.

Fig. 2 show surface morphology of PTZT thin films grown at 750°C. Round with relatively homogenous features are formed at content dopant 0 % (undoped). Increases the content dopant lead to elongation the feature and become irregular columns at content dopant 1.50 %. However, the increase of content dopant resulted inhomogeneous surface morphology, probably due to desorption from the substrate surface at high temperature (750°C).

**Table 2.** The tetragonal structure and the lattice constants of PTZT thin films.

<table>
<thead>
<tr>
<th>PTZT</th>
<th>0%</th>
<th>0.5%</th>
<th>1%</th>
<th>1.08%</th>
<th>1.50%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lattice constant</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>4.056</td>
<td>4.059</td>
<td>4.051</td>
<td>4.064</td>
<td>4.069</td>
</tr>
<tr>
<td>(c) (Å)</td>
<td>4.104</td>
<td>4.072</td>
<td>4.059</td>
<td>4.003</td>
<td></td>
</tr>
<tr>
<td>(c/a) ratio</td>
<td>1.012</td>
<td>1.003</td>
<td>1.002</td>
<td>1.000</td>
<td>0.984</td>
</tr>
</tbody>
</table>

| **Lattice constants in literature**\(^{19}\) |     |      |      |       |       |
| \(a\) (Å)             | 4.036 |      |      |       |       |
| \(c\) (Å)             | 4.146 |      |      |       |       |
| \(c/a\) ratio         | 1.027 |      |      |       |       |

| **Lattice constants in literature**\(^{20}\) |     |      |      |       |       |
| \(a\) (Å)             | 4.131 |      |      |       |       |
| \(c\) (Å)             | 4.041 |      |      |       |       |
| \(c/a\) ratio         | 1.022 |      |      |       |       |

Fig. 1. XRD spectra of PTZT thin films on Pt (200)/SiO2/ Si (100) substrate at various content dopant
(a) PZT (tetragonal)
(b) PTZT (0.50/52.00/48.00)(tetragonal),
(c) PTZT (1.00/52.00/48.00) (tetragonal),
(d) PTZT (1.08/52.00/48.00) (cubic)
(e) PTZT (1.50/52.00/48.00) (pseudo tetragonal).

The film thicknesses were measured by means of cross section SEM measurement. Fig. 3 shows the cross section SEM images of the films. Although the deposition time is the same for all deposition temperatures, the film thickness and the growth rate depend on the dopant content. At dopant content of 0 %, 0.50 %, 1.00 %, 1.08 %, and 1.50 %, the film thicknesses are 1100 nm, 750 nm, 650 nm, 550 nm and 500 nm, respectively. At dopant content of 0 %, the film thickness and the growth rate are the highest. Increasing the content dopant leads to a reduction of the film thickness and the growth rate. This presumably is caused by the desorption of the grown film due to the high dopant concentration.
Fig. 2. Surface morphology of PTZT thin films on Pt (200)/SiO₂/Si (100) substrate at 20000x magnification by SEM at various content dopant (a) 0 % (b) 0.50 % (c) 1.00 % (d) 1.08 % (e) 1.50 %

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4. CONCLUSIONS

We have investigated the dependence of content dopant on crystallography and the surface morphology of PTZT (Ta-doped PZT) thin films. The films were grown at temperature of 750°C for 3 hours followed by an annealed at 700°C for 1 hour by DC UBMS method. The films are polycrystall with preferred orientation in (100), (200) planes, and the crystalline quality of the grown films significantly depend on the content dopant. At content dopant 0 % (undoped) relatively homogen surface are formed. Increasing the content dopant lead to inhomogeneous surface morphology presumably due desorption of the grown layer resulted re-sputtering at high temperature (750°C).

ACKNOWLEDGEMENT

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Fig. 3. The cross section of PTZT thin films on Pt (200)/SiO$_2$/Si (100) substrate at 20000x magnification by SEM at various content dopant (a) 0 % (b) 0.50 % (c) 1.00 % (d) 1.08 % (e) 1.50 %

REFERENCES


