Thickness dependence of the ferroelectric PbTiO$_3$ thin films on the dipolar relaxation in the microwave-frequency range

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The effects of film thickness on the dipolar relaxation of ferroelectric PbTiO$_3$ thin films were investigated in the microwave-frequency range. The real and imaginary dielectric constants ($\varepsilon' - i\varepsilon''$) were measured up to 30 GHz using interdigital capacitors on high-quality SiO$_2$. As the polycrystalline PbTiO$_3$ film thickness increased from 42 to 407 nm, the dipolar-relaxation frequency reduced with increasing grain size. The observed relaxation behavior for $\varepsilon' - i\varepsilon''$ was explained in terms of the convolution of Debye relaxation. The relaxation frequency in the thin films was higher than the previous values reported in bulk PbTiO$_3$ due to the smaller grain size of the thin films. © 2004 American Institute of Physics. [DOI: 10.1063/1.1794865]

Ferroelectric materials have been widely studied for nonvolatile memory devices and rf-circuit elements, and some devices operate at microwave-frequency range. Therefore, for reliable performance of the devices, ferroelectric thin films require frequency-stable permittivity and low dielectric loss in the microwave-frequency range. However, ferroelectric materials undergo dipolar relaxation in the microwave-frequency range, mainly due to the existence of domain structures. Powles and Jackson and Von Hippel reported that the dielectric constant of polycrystalline bulk titanate relaxes, and the center of the relaxation spectrum appears to be a few GHz.

Despite the progressive results for the high-frequency dispersion of bulk ceramics, there are few reports on thin-film ferroelectrics. The difficulty is obtaining the intrinsic dielectric properties of thin films without any parasitic effects in the microwave-frequency range.

In this study, the dielectric properties of PbTiO$_3$ thin films were investigated up to 30 GHz ($K_a$ band) using interdigital capacitors. The parasitic effects were eliminated using a reference capacitor with an equivalent circuit model. The intrinsic dielectric properties of the PbTiO$_3$ thin films show a clear relaxation behavior at a relatively higher frequency (about tens of GHz) than that of the bulk ceramics.

Polycrystalline PbTiO$_3$ thin films with thicknesses varying from 42 to 407 nm were prepared by rf magnetron sputtering. An approximately 10 wt % PbO-excess PbTiO$_3$ target was used to compensate for Pb loss during the sputtering and annealing processes. The substrate was high-quality amorphous SiO$_2$ to measure the dielectric properties of the thin films by interdigital capacitors. The SiO$_2$ substrate was pre-annealed at 200°C in the chamber to remove water vapor or any organic residue, and the typical deposition rate was ~3 nm/min. The as-deposited amorphous films were post-annealed to crystallize into the perovskite structure.

The thin-film microstructures were analyzed by x-ray diffraction (XRD), and the stoichiometry of the thin films was confirmed by electron probe micro-analysis (EPMA). The grain size of the films was investigated by XRD and transmission electron microscopy (TEM). For the dielectric-property measurements in the microwave-frequency region, a vector network analyzer (HP 8510C) was used with a Be–Cu coplanar-wave-guide probe. Interdigital capacitors with 700 nm Au electrodes were patterned on the film surface by photolithography. The dimensions of the interdigital capacitors (finger length =80 μm, finger width =4 μm, and finger gap =2 μm) were determined by simulation to optimize the sensitivity for the variation of the dielectric properties in ferroelectric thin films.

Figure 1 shows the XRD pattern of the PbTiO$_3$ thin films as a function of the different thicknesses. It reveals splitting of the (hk0) peaks, confirming the tetragonal perovskite PbTiO$_3$ phase, and the crystallinity was enhanced with increasing film thickness. The background peak at a low angle originates from the amorphous SiO$_2$. XRD did not show any trace of pyrochlore phase, and exhibited negligible texture. As the film thickness decreases, the cell volume and $c/a$ ratio were gradually reduced from the value of bulk PbTiO$_3$ due to the ferroelectricity weakening. EPMA confirmed the Pb/Ti ratio of the deposited thin films ranging from 0.940±0.005 (42 nm thickness) to 1.056±0.002 (407 nm thickness).

The dielectric properties of the PbTiO$_3$ thin films were investigated as a function of frequency up to 30 GHz. The conductor loss was known as the major parasitic component in the entire frequency region. It can be interpreted as the

![FIG. 1. X-ray diffraction patterns of the PbTiO$_3$ thin films as a function of the film thicknesses. The ideal peak positions and intensities are marked for PbTiO$_3$ (JCPDS #06-0452).](image-url)
series resistance in the equivalent circuit, To measure the resistance of metal, the interdigital pattern on bare SiO₂ was used as a reference. The series resistance \( R_s \) was obtained by a least-squares fitting of the measured dielectric loss of the bare substrate over the frequency range from 500 MHz up to 30 GHz, and it did not show frequency-dependence characteristics in this frequency range. The real and imaginary parts of the dielectric constants of SiO₂ were found to be consistent with the low-frequency measurement, the intrinsic dielectric properties of the thin films.

The dielectric loss of the bare substrate over the frequency range from 1 MHz to 0.024± 0.002 at 407 nm. The dielectric spectra of the PbTiO₃ thin films are comprised of substantially single-domain structures.

The XRD peak widths, \( \Delta k \) (full width at half maximum), were fitted for each peak with the scattering vector \( k = (4 \pi / \lambda) \sin \theta \). The average grain size increases with increasing film thickness, as shown in Table I. The cross-section TEM images of the PbTiO₃ confirm that the grain size increases gradually from the bottom to the top of the films. Figure 4 from a thickness of 407 nm shows a grain-size ranging from ~20 up to ~50 nm. At a sufficiently small grain size, it was proposed that the ferroelectric ceramics are comprised of substantially single-domain structures.

Therefore, the domain width can be approximated by the grain size.

**TABLE I.** Correlation between the relaxation frequency and the film thickness.

<table>
<thead>
<tr>
<th>Film thickness (nm)</th>
<th>Average grain size (d) (nm)</th>
<th>Calculated ( f_r = \sqrt{c_{55}^p / \pi d} ) (GHz)</th>
<th>Measured ( f_r = (1/2 \pi \tau_0) ) (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>...</td>
<td>...</td>
<td>45.2±16.4</td>
</tr>
<tr>
<td>168</td>
<td>26.3±8.7</td>
<td>45.1±14.9</td>
<td>32.7±1.9</td>
</tr>
<tr>
<td>210</td>
<td>28.9±6.8</td>
<td>41.0±9.7</td>
<td>29.2±0.8</td>
</tr>
<tr>
<td>407</td>
<td>36.7±9.8</td>
<td>32.3±8.6</td>
<td>26.8±0.2</td>
</tr>
</tbody>
</table>

**FIG. 2.** Dielectric constants (real part) of the PbTiO₃ thin films as a function of frequency. The solid line is a fit by the convolution of Debye relaxation, and the inset denotes the dielectric constant of bare SiO₂.

**FIG. 3.** Imaginary part of dielectric constants for PbTiO₃ thin films. The inset data are from bare SiO₂. The solid line is from the same fit as shown in Fig. 2, and the arrows indicate that the relaxation frequency shifts toward lower frequency as the film thickness increases.
TEM) with $c_s=111 \text{ GPa}$ and $\rho=7.97 \text{ g/cm}^3$, $f_r$ is 23.7 GHz. This confirms that the relaxation frequency in the thin films is higher than the reported values for the bulk ceramics. The relaxation frequencies from the grain size of thin films are listed in Table I, yielding reasonably consistent values with the measured $f_r$ from curve fitting.

The relaxation phenomena in the thin films are characterized by a broadening of the relaxation frequency. The value, $\Delta(\ln \tau_0)$, from the polydispersive Debye-relaxation fitting was approximately 0.5–1, which was larger than the reported values in the bulk ceramics, due to the spread in grain size and imperfect crystallinity in the thin films. The small variation in stoichiometry may induce changes in the vacancy concentration. If there exist any systematic oxygen-vacancy variations as a function of film thickness, it may play an important role in the low-frequency dielectric relaxation, since the segregation of defects in the grain boundary results in the space charge at the charged defective region. Further experiments are clearly needed to evaluate the effect of defects (such as oxygen vacancies, stoichiometry, local strains, etc.) on the dipolar relaxation.

In conclusion, the thickness effects on the dipolar relaxation of PbTiO$_3$ thin films were investigated as a function of frequency up to 30 GHz. The relaxation frequency decreased, as the film thickness increased. The shift in the relaxation frequency with different film thickness was explained by the convolution of Debye relaxation. In addition, the dipolar-relaxation frequency of the thin films was higher than that of the bulk ceramics.

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