The dependence of dielectric properties on the thickness of (Ba,Sr)TiO$_3$ thin films

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Abstract

In the dielectric (Ba,Sr)TiO$_3$ thin films, the correlation between the film thickness and the dielectric properties was investigated. The dielectric properties such as the dielectric constant ($\varepsilon$) and dielectric loss (tan $\delta$) were measured using the capacitor geometry. As the film thickness increased, the dielectric constant also increased due to the reduction of the interfacial dead-layer effect. However, the dielectric loss did not show a monotonous variation with the increasing film thickness. It was found that the dielectric loss correlated well with the non-uniform distribution of local strain, as analyzed by X-ray diffraction, according to the Curie–von Schweidler relaxation law.

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1. Introduction

Dielectric materials have attracted a great deal of attention for applications as microwave devices, such as phase shifters, phased array antennas, varactors, delay lines, etc. [1–4]. Among the dielectric materials, (Ba,Sr)TiO$_3$ (BST) has been intensively studied due to its high dielectric constant ($\varepsilon$), relatively low dielectric loss (tan $\delta$), and high tunability (electric-field-dependent dielectric constant) [1–3,5]. It also has a merit in that dielectric properties can be modified easily by changing the Ba to Sr ratio [5,6].

To apply dielectric thin films for microwave devices, these should have a low dielectric loss, high dielectric constant, and high tunability. It is very important to study the dielectric properties of thin films because they are usually quite different from those of the bulk [7–12]. It is well known that the dielectric constant deteriorates as the film thickness shrinks as a result of a dead-layer with a low dielectric constant [12,13]. The dead-layer is formed at the interface between the dielectric thin film and the metal electrode, because dielectric polarization is frozen at the interface adjacent to the metal electrode [9–11]. However, the dependence of the dielectric loss on the film thickness is not yet fully understood. In this paper, the possible relationships between the dielectric loss and the film thickness as well as the related loss mechanisms were investigated with the dielectric constant relaxation behavior.

2. Experimental details

BST thin films were deposited on Pt/SiO$_2$/Si (100) using a 2 in. (Ba$_{0.5}$Sr$_{0.5}$)TiO$_3$ target using magnetron sputtering [14], at the deposition temperature of 600 °C and the rf power of 100 W. During the deposition of the BST thin films, the total pressure was maintained at 40 mTorr with the Ar to O$_2$ flow-rate ratio of 9 to 1. The deposition time was varied in order to obtain the BST thin films with
different thicknesses. Pt thin films (∼100 nm) were also deposited as the top and bottom electrodes using the magnetron sputtering. To define the capacitors for measuring the dielectric properties, the Pt top electrode with a diameter of approximately 250 μm was deposited through a shadow mask. After depositing the top electrode, the samples were post-annealed at 700 °C in an oxygen-flowing environment to enhance the electrical contact between the BST and the Pt top electrode [15].

X-ray diffraction (XRD) (M18XHF-SRA, MAC Science) with Cu Kα radiation (λ = 0.15418 nm) was used to determine the thin film structure with 40 kV/200 mA in the 2θ range of 20°–115°. The composition of the thin films was analyzed by electron-probe microanalysis (EPMA) (JXA-8900 R, JEOL). BaTiO3 and SrTiO3 crystals were used as the standard samples for quantitative EPMA. The film thickness was measured by a surface profilometer. The dielectric constants and losses of BST films were measured using an impedance analyzer (HP 4194 A) in the 100 Hz–1 MHz range with 50 mV oscillation voltage.

### 3. Results and discussion

The BST film thicknesses measured using the surface profilometer ranged from 62 nm to 390 nm. The XRD patterns of the BST thin films at various thicknesses are shown in Fig. 1. (The data between 80° and 105° were omitted because there were no important peaks.) All the BST films had a good crystalline quality showing mostly a (1 1 0) texture. The XRD peak intensities became larger as the film thickness increased (shown in a log scale in Fig. 1). Despite the increase in the BST film thickness, their overall microstructures were similar.

The dielectric constants and losses of BST films were measured as a function of the frequency in the range of 100 Hz–1 MHz for the thin films with different thicknesses. To reduce the measurement errors in the dielectric properties, the data were averaged between 400 Hz and 10 kHz. Fig. 2 clearly shows that the dielectric constant increases as the film thickness is increased. The increase in the dielectric constant over the film thickness was attributed to the dead-layer effect, which was formed at the interface between the metal and dielectric film [9–13]. The thin-film capacitance can be interpreted as that of capacitors in series consisting of bulk and interfacial dead-layer capacitors as follows:

\[
\frac{1}{C} = \frac{1}{C_i} + \frac{1}{C_b}.
\]

Here, \(C_i\) and \(C_b\) represent the capacitance of the interfacial and bulk layer, respectively. Therefore, the dielectric constant can be described as

\[
\frac{d}{\varepsilon} = \frac{d_i}{\varepsilon_i} + \frac{d - d_i}{\varepsilon_b} \approx \frac{d_i}{\varepsilon_i} + \frac{d}{\varepsilon_b}
\]

where \(d_i\) is the interfacial dead-layer thickness, \(\varepsilon_i\) is the dielectric constant of the interfacial dead-layer, and \(\varepsilon_b\) is the dielectric constant of the bulk layer. The last term of Eq. (2) is valid because the total film thickness \(d\) is much larger than the interfacial dead-layer thickness \(d_i\) [12,15,16]. After performing a least-square fit (solid line) for the \(d/\varepsilon\) vs. \(d\) data, as seen in the inset of Fig. 2, \(\varepsilon_b\) and \(d_i/\varepsilon_i\) were obtained from the reciprocal of the slope and the \(y\)-intercept, yielding \(\varepsilon_b = 340 \pm 6\) and \(d_i/\varepsilon_i = 0.285 \pm 0.007\) nm. The relatively small dielectric constant \(\varepsilon_b\) of the bulk layer may originate from the off-stoichiometry of Ti [1,17]. The \(d_i/\varepsilon_i\) value is in the same order of magnitude as other reported data of \(d_i/\varepsilon_i \sim 0.1–0.2\) nm [15,18,19].

The behavior of the dielectric loss (solid squares) appeared to be different from that of the dielectric constant, as shown in Fig. 3. As the film thickness increased, the dielectric loss increased to a maximum and then

Fig. 1. X-ray diffraction patterns of the BST thin films deposited with thicknesses ranging from 62 to 390 nm.

Fig. 2. The dielectric constants (averaged between 400 Hz and 10 kHz) of the BST thin films at various film thicknesses. The inset shows variations in \(d/\varepsilon\) over the film thickness. The solid line was obtained from a least-square fit, and the dotted line is a guide to the eyes.
decreased. To address the reasons for this non-monotonic variation in the dielectric loss, the relaxation of the dielectric constant was measured as a function of the frequency (see Fig. 4). According to the Curie–von Schweidler relaxation law, which describes a power-law dependence of the dielectric constant on frequency ($\varepsilon \propto f^{-n}$ with $0 \leq n \leq 1$), the dielectric loss is determined by the degree of the relaxation in the dielectric constant ($\tan \delta \propto \cot(n\pi/2)$) [3,20–26]. That is, the dielectric loss of the BST thin film increases as the value of the exponent ($n$) deviates from 1. The Curie–von Schweidler relaxation is believed to originate from the inhomogeneity or many-body interactions [21–23,27]. The value of the exponent (solid squares) was obtained from a least-square fit (solid line) of the dielectric constant to the frequency, as shown in the inset of Fig. 4. In Fig. 3, the measured dielectric losses and the dielectric losses obtained from the exponent were represented, respectively, by the solid and open squares. In Fig. 4, the values of the exponent obtained from the least-square fit of the dielectric constant and from the measured dielectric losses were represented, respectively, by the solid and open squares. Figs. 3 and 4 both show that the dielectric loss correlates well with the value of the exponent.

Considering that the crystallinity of the dielectric thin film is the main factor for the Curie–von Schweidler relaxation, a non-uniform distribution of local strain was obtained from XRD as a measure for the level of crystallinity. To estimate the local strain, which is possibly due to point defects, off-stoichiometry, stacking faults, dislocations, etc. [28–30], the XRD peak widths $\Delta k$ (full width at half maximum) were fitted to each peak (with the scattering vector $k = (4\pi/\lambda)\sin\theta$), using a double-peak Lorentzian function [31–33]. The instrumental broadening effect was then subtracted using the resolution function [$D_{\text{res}} = (0.084 \pm 0.008) + (-0.00052 \pm 0.00002)k$ (nm$^{-1}$)], which was estimated from the diffraction pattern for standard silicon powders. The local strain in the thin films was estimated from the slope of $\Delta k$ vs. $k$, as shown in the inset of Fig. 5. As the texture of the (110) grains was dominant, the peak widths from the (110) grains were used to obtain the local strain.

Figs. 4 and 5 show that the exponent ($n$) in the Curie–von Schweidler relaxation law is dependent on the degree of local strain, with $n$ being closer to one for films with less local strain. This shows that the dielectric loss correlates well with the local strain. The increase in the local strain with the film thickness up to a certain value might be due to the off-stoichiometry of (Ba + Sr) to Ti ratio. The local strain decreased as the film thickness increased further, which has been reported generally [34–36].
The dielectric constant is determined by the relative position of the ions when an electric field is applied, while the dielectric loss originates from the phase difference between the motion of ions and the electric field. These results show that the local strain in BST thin films mainly affects the phase difference and not the relative position of the ions. Similar observations have been made for paraelectric ZrTiO$_4$ thin films [31,32]. It should be noted that the increase in the dielectric constant with the film thickness resulted from the reduced relative fraction of the dead-layer, and the bulk-layer dielectric constant $\varepsilon_b$ in the thin film did not change much for the different thicknesses, as confirmed in Fig. 2. In addition, the dielectric loss appears to be influenced by the local strain quite sensitively. In this context, the existence of the dead-layer does not have a major effect on the dielectric loss. Further studies are needed to clarify these various structural effects on the dielectric properties.

4. Conclusions

The effect of film thickness on the dielectric properties of the BST thin films was investigated. The dielectric constant increased with the increasing film thickness, while the dielectric loss showed a non-monotonous variation. The change in the dielectric constant was attributed to the dead-layer effect. On the other hand, the dielectric loss of the BST thin films correlated well with the local strain according to the Curie–von Schweidler relaxation law.

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References