Effect of microstructures on the microwave dielectric properties of ZrTiO$_4$ thin films

Yongjo Kim, a) Jeongmin Oh, Tae-Gon Kim, and Byungwoo Park
School of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea

(Received 7 December 2000; accepted for publication 19 February 2001)

To obtain various paraelectric ZrTiO$_4$ thin-film microstructures, the films were synthesized at different deposition temperatures using rf magnetron sputtering. Both the dielectric losses ($\tan \delta$) and dielectric constants ($\varepsilon$) of the ZrTiO$_4$ thin films were measured up to 6 GHz using a circular-patch capacitor geometry. The films showed enhanced crystallinity with increasing deposition temperature, as determined from the x-ray diffraction peak widths at various scattering vectors. The microwave dielectric losses correlated very well with the level of crystallinity or strain, while the dielectric constants did not alter significantly. © 2001 American Institute of Physics.

Recently, dielectric thin films have been intensively studied for applications such as dynamic random access memory (DRAM) and wireless-communication systems. The required characteristics of such dielectric thin films are low dielectric losses ($\tan \delta$) and high dielectric constants ($\varepsilon$). Although the operating frequencies of both DRAM and wireless-communication systems range from hundreds of megahertz (MHz) to tens of gigahertz (GHz), the properties of dielectric thin films have mainly been studied in the kHz–MHz frequency range. Accordingly, the characterization of dielectric thin films in the GHz range is essential for developing devices operating at microwave frequencies.

Single-phase paraelectric ZrTiO$_4$ was chosen for this study, due to its high dielectric constant and quality factor ($Q = 1/\tan \delta$). In addition, good thermal stability with Sn addition has been observed. In this letter, the correlations between the microstructures and microwave dielectric losses are reported in ZrTiO$_4$ thin-film paraelectrics.

The ZrTiO$_4$ thin films were deposited by rf magnetron sputtering using a 5 cm ZrTiO$_4$ single target, which was made by sintering a mixture of TiO$_2$ and ZrO$_2$ powders with a 0.5/0.5 mole fraction at 1650 °C for 2 h. During deposition, the following conditions were maintained: a 10 cm distance from the substrate to the target, a flow-rate ratio of argon to oxygen of 4 to 1, an incident rf power of 200 W, and an operating pressure of 1.3 Pa. To obtain different levels of crystallinity, the deposition temperature was ranged from 300 to 800 °C. The square dots indicate deposition temperatures ranging from 300 to 800 °C. The top electrode with Au/Ag double layer was patterned by one-step photolithography. From the measured $S_{11}$ parameters in the 500 MHz–10 GHz frequency range, the dielectric losses could be deduced, and dielectric constants were obtained by measuring the capacitor dimensions (inner and outer diameters on the order of 100 $\mu$m) and the dielectric thicknesses ($\sim$250 nm).

The deposited thin films had a Zr/Ti ratio of 1.20 ±0.03, which is within the solid-solution range of the ZrTiO$_4$ phase. The composition of each sample was measured at several different points and did not vary significantly with deposition temperature. XRD confirmed that films deposited above 400 °C exhibited reasonable crystallinity (as shown in Fig. 1). As the deposition temperature increased, the films showed more intense diffraction peaks, implying a greater volume percentage of crystalline phase. The full width at half maximum (FWHM) of the $2\theta$ peaks decreased, indicating less strain and/or larger grain size.

To quantify the diffraction peak broadening, the XRD peak widths $\Delta \theta$ (FWHM) were fitted for each peak with the scattering vector $k = (4 \pi/\lambda) \sin \theta$, using a double-

![FIG. 1. X-ray diffraction patterns of orthorhombic ZrTiO$_4$ thin films deposited at temperatures ranging from 300 to 800 °C. The square dots indicate the Si diffraction peaks.](image-url)
The sensitivity of the instrument and unknown parasitic effects range from 2 to 6 GHz, which was safely chosen considering the inset, the straight dotted line was obtained from least- angular frequency graph, as shown in the inset of Fig. 3. In the real part of the impedance versus the reciprocal of the value of series resistance was obtained from the intercept of intrinsic to ZrTiO$_4$ thin films. The additional losses result from resistance in the bottom/top electrodes and contact with the CPW probe and inner/outer top electrodes. Here the series resistor represents the reduction of strain in the thin films, as shown in Fig. 2. The estimated strains from the slopes of the $\Delta k$ vs $k$ graph $[\Delta k=(0.075\pm0.007)+(0.002\pm0.0003)k]$ for a thin film deposited at 700 °C.

The instrumental broadening effect $[\Delta k_{\text{res}}=0.046+0.0004 k\ (\text{nm}^{-1})$ for $K_\alpha_1]$ was obtained using silicon crystals. The strain in the crystalline thin films was deduced from the slope of the $\Delta k$ vs $k$ graph, as shown in Fig. 2, indicating a nonuniform distribution of local strain, possibly due to point defects, off-stoichiometry, stacking faults, dislocations, etc.$^{11-14}$ The error bars result from the least-square fitting processes for the peak width and strain. The effective grain size estimated from the intercept at $k=0$ did not show any systematic changes due to the large error range in the fitting process. Figure 2 shows significantly reduced strain at higher-deposition temperatures. The strain was estimated to be $5.67\%\pm1.70\%$ at 400 °C deposition, while it decreased to $0.01\%\pm0.04\%$ at 800 °C, clearly reflecting structural relaxation in the ZrTiO$_4$ thin films.

For effective measurement of microwave dielectric properties in thin films, the circular-patch capacitor geometry was used, consisting of a disk-shape capacitor and an outer capacitor surrounding it.$^{10}$ To remove the effect of outer capacitor, the impedances of two capacitor structures, having different inner diameters with the same outer diameters, were subtracted. In Fig. 3, the upper solid line, obtained from a simple ratio of the real and imaginary parts of the subtracted impedance, still incorporates additional dielectric losses, not intrinsic to ZrTiO$_4$ thin films. The additional losses result from resistance in the bottom/top electrodes and contact with the CPW (between the CPW probe and inner/outer top electrodes).

To determine the intrinsic dielectric loss, an equivalent-circuit model was designed with a parallel resistor/capacitor and series resistor. Here the series resistor represents the resistance from the electrodes and contact resistance.$^{15}$ The value of series resistance was obtained from the intercept of the real part of the impedance versus the reciprocal of the angular frequency graph, as shown in the inset of Fig. 3. In the inset, the straight dotted line was obtained from least-square fitting of the measured values over the frequency range from 2 to 6 GHz, which was safely chosen considering the sensitivity of the instrument and unknown parasitic effects. The lower line in Fig. 3 is the corrected (intrinsic) dielectric loss that excludes the series-resistance effect. The frequency dependence of $\tan \delta$ is clearly minimal between 2 and 6 GHz (Fig. 4). With a simple circular-patch capacitor and equivalent-circuit model, the parasitic effect is effectively removed below 6 GHz. Figure 4 shows the corrected dielectric losses as a function of frequency with various deposition temperatures. The frequency dependence above 6 GHz or below 1 GHz, which was caused by the sensitivity of the instrument and any uncompensated parasitic effect, does not necessarily indicate dielectric relaxation.$^{10,16}$ It is, however, a task to effectively separate the parasitic effect and potential dielectric relaxation in thin films at the higher frequency ranges.

A strong dependence of the dielectric losses ($\tan \delta$) on the deposition temperature was found (Fig. 5), with the error bars from standard deviation of $\tan \delta$ from 2 to 6 GHz. The dielectric losses were $0.0131\pm0.0005$ at 300 °C deposition, which decreased dramatically to $0.0009\pm0.0008$ at 800 °C. (It is still higher than that of the well-sintered bulk ZrTiO$_4$ ($2.3\times10^{-4}$).$^{17}$) This decrease in dielectric losses correlates very well with the reduction of strain in the thin films, as shown in Fig. 2. The estimated strains from the slopes of the $\Delta k$ vs $k$ graph $[\Delta k=(0.075\pm0.007)+(0.002\pm0.0003)k]$ for a thin film deposited at 700 °C.

The estimated strains from the slopes of the $\Delta k$ vs $k$ graph $[\Delta k=(0.075\pm0.007)+(0.002\pm0.0003)k]$ for a thin film deposited at 700 °C.
shown in Figs. 2 and 5. Crystalline defects represented by local strain cause anharmonic lattice motion for the imposed high-frequency electric field, leading to high dielectric losses. However, in this experiment, no systematic variations in the dielectric constants \( \varepsilon \equiv 34.7 \pm 2.3 \) for the various processing conditions could be observed.

In conclusion, correlations between the microstructures and microwave dielectric losses were investigated in ZrTiO\(_4\) thin films at frequencies up to 6 GHz. As the deposition temperature increased, the microwave dielectric losses decreased. The crystallinity or strain in the thin films was analyzed from the diffraction-peak widths, and correlated well with the decrease in the microwave dielectric losses. From the measured apparent dielectric losses using a simple circular-patch capacitor and equivalent-circuit model, it is evident that dielectric relaxation does not appear up to 6 GHz in ZrTiO\(_4\) thin-film paraelectrics. However, the dielectric losses (\( \tan \delta \)) of these thin films were higher than those of the bulk values (approximately by a factor of 4). Further studies are necessary to systematically correlate the dielectric properties with thin-film microstructures, such as point/linear/planar defects, stoichiometry, and crystalline orientation, to develop thin films having \( \tan \delta \) equivalent to the bulk values, at the tens of GHz frequency ranges.

The authors gratefully acknowledge the contributions of Sangwook Nam, Jungwon Lee, Seong-Hun Kim, Sung Hoon Kang, and Taeseok Kim for the high-frequency measurements. This work was supported by the National Program for Tera-level Nanodevices of the Ministry of Science and Technology as one of the 21st-century Frontier Program.

---