Correlation between strain and dielectric properties in ZrTiO$_4$ thin films

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Single-phase paraelectric ZrTiO$_4$ thin films were synthesized at various temperatures using direct-current magnetron reactive sputtering. The dielectric constants ($\varepsilon$) and dielectric losses ($\tan \delta$) of as-deposited and annealed films were measured in the 100 kHz range using a Pt upper electrode and a phosphorous-doped Si (100) bottom electrode. Data showed that as the deposition temperature increased, the dielectric losses decreased, while the dielectric constants did not change much. Similar trends for dielectric losses were observed after annealing at 800 °C. These results of dielectric losses correlated well with strains in ZrTiO$_4$ thin films, analyzed from x-ray diffraction peak widths at various scattering angles. © 2000 American Institute of Physics.

Recently, demand for monolithic microwave integrated circuit technologies (MMIC) has increased with a wide variety of microwave communication applications, such as mobile phones, global positioning systems (GPS), and satellite communications. Continued miniaturization of integrated circuitry requires microwave components with improved characteristics, smaller size, and compatibility with existing circuits. Generally, dielectric materials used for resonators and filters in microwave circuits must exhibit high dielectric constants (because the resonator size is proportional to $1/\sqrt{\varepsilon}$), low dielectric losses ($\tan \delta = 1/Q$, where $Q$ is the dielectric quality factor), and low temperature coefficients of resonance frequency ($\gamma_r$).

It has been reported that the bulk ZrTiO$_4$ phase has a high dielectric constant suitable for microwave devices, a low dielectric loss, and good thermal stability with Sn addition. The single-phase ZrTiO$_4$ structure is $\alpha$-PbO$_2$ orthorhombic where Ti and Zr ions are chemically disordered in half of the eight octahedral sites in a single unit cell above 1100 °C. But the metastable room temperature structure of ZrTiO$_4$ is of interest.

Thin films of single-phase ZrTiO$_4$ have been synthesized by several researchers. However, the dielectric losses of these thin films in the microwave and low frequency (1 MHz) ranges have not yet been investigated. In this letter, the effect of strain in ZrTiO$_4$ thin films on the dielectric losses ($\tan \delta$) and dielectric constants ($\varepsilon$) in the 100 kHz range is reported.

Thin films of ZrTiO$_4$ were deposited by direct-current (dc) magnetron reactive sputtering using 4 in. Ti and Zr metal targets on a phosphorous-doped Si (100) substrate. The deposition system was arranged in a symmetric configuration with a rotating substrate holder for composition uniformity. The base pressure of the sputtering chamber was typically 5 $\times$ 10$^{-5}$ Pa, and an operating pressure of 4 mTorr was maintained during deposition. The flow rate ratio of Ar (99.99999%) and O$_2$ (99.99%) was 17.0/3.5, as controlled by mass flow controllers. All the films were sputtered at 500 and 650 W for Zr and Ti targets, respectively. For electrical measurements, 200-µm-diam platinum upper electrodes were deposited using a shadow mask. The phosphorous-doped Si (100) substrate had a resistivity of 6.1 $\times$ 10$^{-4}$ Ω cm. This made it possible to measure the electric characteristics without a separate metal bottom electrode. Thin film samples deposited at temperatures between 25 and 600 °C were annealed at 800 °C in an oxygen atmosphere for 2 h to investigate the effects of postannealing.

The crystal structure and film texture were characterized by x-ray diffraction using Cu K$\alpha$ radiation. Film compositions were confirmed by electron probe microanalysis (EPMA) on several areas for each sample. The film thicknesses were measured with an $\alpha$ step, and the typical film thicknesses were around 400 nm. The film capacitances and dielectric losses were measured using an impedance analyzer (HP 4194A) in the 1 kHz-10 MHz range with a 0.04 V root-mean-square (rms) oscillation voltage. Using the measured capacitances, the dielectric constants were calculated with the measured film thickness and upper electrode area.

From the quantitative analysis by EPMA, the compositions of the as-deposited thin films were found to be in the solid solution range of the ZrTiO$_4$ phase. The x-ray diffraction patterns of films deposited at room temperature exhibited amorphous characteristics with only substrate peaks. Above 200 °C, the films started to show polycrystalline ZrTiO$_4$ peaks, and after annealing in an oxygen atmosphere, the films showed more crystalline characteristics, as shown in Fig. 1. To qualitatively estimate strain and effective grain size of the deposited ZrTiO$_4$, x-ray diffraction peak width $\Delta k$ (full width at half maximum) were fitted at various stages for each peak with the scattering vector $k = (4 \pi/\lambda) \sin \theta$, using double-peak Lorentzian function. To consider the instrumental broadening effect, a resolution function ($\Delta k = 0.046 + 0.00004k$ for K$\alpha_1$) estimated from the silicon substrate was subtracted after fitting for each peak. Figure 2 shows the strain in the thin films deduced from the slope of the $\Delta k$ vs $k$ graph, as shown in the inset as an example. It is known that a simple expression can be used to describe $\Delta k$ vs $k$:

$$\Delta k = 2 \pi/D + (\Delta d/d)k,$$

where $D$ is the grain size, $\Delta d$ is the lattice parameter change, and $k$ is the scattering vector.

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where $D$ is the effective grain size suggested by Scherrer, and $\Delta d/d$ is the strain derived from the Bragg relation. The effective grain sizes in the films could not be estimated reliably from our samples due to large error range in the fitting process, and the peak positions were found to shift insignificantly from a bulk value.

The change in dielectric losses ($\tan \delta$) as a function of deposition temperature is shown in Fig. 3. The dielectric losses (0.017–0.038) at 100 kHz were much higher than those from the well-sintered bulk ZrTiO$_4$ ($\sim 10^{-4}$). Higher deposition temperature and postannealing reduced the dielectric losses (0.005–0.034). This decrease in dielectric losses correlated well with the reduction of strain in thin films, as shown in Fig. 2. We could not, however, observe any systematic variations in the dielectric constants of thin films ($\varepsilon \approx 35 \pm 7$) for various processing conditions. Different processing conditions may cause variations in microstructures, such as strain, stoichiometry, oxygen vacancies, etc., which may reflect on different dielectric constants.

Figure 4 shows the dielectric constants and dielectric losses as a function of frequency, for the ZrTiO$_4$ film deposited at room temperature and annealed at 800 °C for 2 h. The resonance behavior induced by an appreciable resistance which may have arisen from contacts, electrodes and dielectric itself, and stray inductance of the contacts and wires, was observed as shown in Fig. 4. Therefore, all the dielectric measurements were conducted at frequencies much lower than this resonance frequency. The dotted lines represent dielectric constants and losses calculated from an equivalent-circuit model with parallel resistor/capacitor and series resistor/inductor.

In conclusion, the effects of strain on the dielectric properties of the near-stoichiometric ZrTiO$_4$ thin films that exist in a metastable high-temperature disordered phase have been investigated for various deposition temperatures and postannealing processes. As deposition temperature increased, the dielectric losses decreased while the dielectric constants were not observed to change significantly. Similar trends for dielectric losses were observed after the as-deposited samples were annealed at 800 °C. The strain in thin films were analyzed from the diffraction peak widths, and correlated well with the decrease of the dielectric losses. However, dielectric losses in thin films were much higher than the published bulk values. Further studies are required to corre-
late the dielectric properties with thin film microstructures, including stoichiometry, vacancy, grain-boundary segregation, texture, etc.

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