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Dielectric properties of $ZrTiO_4$ thin films deposited by DC magnetron reactive sputtering

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Abstract — Paraelectric $ZrTiO_4$ thin films were synthesized on a Si (100) substrate using DC magnetron reactive sputtering. Films deposited above 400°C exhibited crystalline characteristics. The dielectric constants (ε) and dielectric losses (tan δ) of as-deposited and annealed films were measured in the 1 MHz range using a Pt upper electrode and a phosphorous-doped Si bottom electrode. Preliminary data showed that as the deposition temperature increased, the dielectric losses decreased while the dielectric constants did not change significantly. Similar trends for dielectric losses were observed when the as-deposited samples were annealed at 800°C. The reduction of dielectric losses at high-deposition temperatures and post annealing correlated well with the x-ray diffraction peak widths.

I. Introduction

Recently, demand for monolithic microwave integrated circuit technologies (MMIC) is increasing with wide 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 [1-4]. Generally, dielectric materials used for resonators and filters in microwave circuits must exhibit high dielectric constants (because the resonator size is proportional to $\sqrt{\varepsilon}$), low dielectric losses (tan $\delta = 1/Q$, where Q is the dielectric quality factor), and temperature coefficients of resonance frequency (τ_f) [5].

It has been reported that the bulk $ZrTiO_4$ phase has a high dielectric constant suitable for microwave devices, low dielectric losses, and good thermal stability with Sn addition [6-8]. The single phase $ZrTiO_4$ structure is α-PbO_2 orthorhombic where Ti and Zr ions are chemically disordered in half of the eight octahedral sites in a sigle unit cell above 1100°C [9-12].

Thin films of $ZrTiO_4$ have been synthesized by several researchers [13-16]. However, the dielectric losses of these thin films in the microwave and MHz ranges have not been investigated yet. In this paper, the synthesis of $ZrTiO_4$ thin films using DC magnetron reactive sputtering, with the effects of deposition temperature and post thermal annealing on the dielectric losses (tan δ) and dielectric constants (ε) in the 1 MHz range, is reported.

II. Experimental Details

Thin films of $ZrTiO_4$ were deposited by DC magnetron reactive sputtering using 4 inch 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 4×10^{-7} Torr. After heating to the desired deposition temperature, the targets were pre-sputtered for at least 30 minutes in the same condition as the actual deposition process. Substrates were loaded from a load lock into the main chamber to maintain low base pressure. A SiC coated graphite block was used for heating, and the substrate temperature was calibrated with a thermocouple located between the substrate and heating block. An operating pressure of 4 mTorr was maintained during deposition by a throttle valve. The Ar (99.9999%) and O_2 (99.99%) flow rate ratios were in the range of 83/17 to 50/50, as controlled by mass flow controllers. All the films were sputtered at 500 W and 700 W for Zr and Ti

targets, respectively. For electrical measurements, 200 μm diameter platinum upper electrodes were sputtered using a shadow hard mask. The phosphorous-doped Si (100) substrate had a resistivity of 6.1×10^{-4} Ω·cm. This made it possible to measure the electric characteristics without a separate bottom electrode. Thin film samples deposited at temperatures between room temperature and 600°C were annealed at 800°C in an oxygen atmosphere for 2 hours to investigate the effects of post annealing.

The crystal structure and film texture were characterized by x-ray diffraction (XRD) using Cu K_α radiation. Film compositions were measured by electron probe micro-analysis (EPMA) on several areas for each sample. The film thickness was measured with field-emission scanning electron microscopy (FE-SEM) and α-step. The typical film thickness was found to be 400 nm. The film capacitances and dielectric losses were measured using a HP4194A impedance analyzer in the 1 MHz range with a 0.04 volt r.m.s. oscillation voltage. Using the measured capacitances, the dielectric constants were calculated with film thickness, and upper electrode area.

III. Results and Discussion

The XRD patterns for the as-deposited and post-annealed thin films are shown in Figs. 1 and 2, respectively. The XRD patterns of films deposited at room temperature exhibited amorphous characteristics with only substrate peaks showing. Above 400°C, the films show polycrystalline $ZrTiO_4$ peaks. After annealing in an oxygen atmosphere, the films show more crystalline characteristics as shown in Fig. 2. To qualitatively estimate the effective grain size of deposited $ZrTiO_4$, XRD peak widths (Δk) were fitted at various stages where Δk is full width at half maximum (FWHM) for the (111) peak with the scattering vector $k = (4\pi / \lambda)\sin\theta$. Figure 3 clearly shows a reduction of the (111) peak widths after annealing at 800°C. The peak positions were found to shift slightly from a bulk value (~1% larger lattice constant for deposition at 400°C). This shift was reduced at higher deposition temperatures and after the post-annealing process, indicating some structural relaxation in thin films.

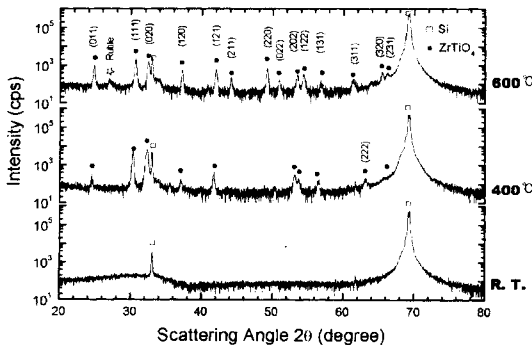

Fig. 1. X-ray diffraction pattern of the as-deposited $ZrTiO_4$ thin films at room temperature, 400°C, and 600°C. Diffraction peaks are indexed from the high-temperature phase $ZrTiO_4$.

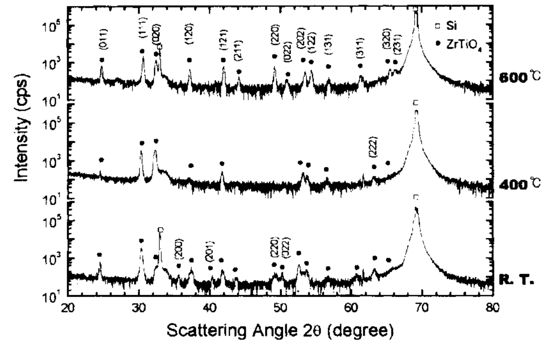

Fig. 2. X-ray diffraction pattern of $ZrTiO_4$ thin films annealed at 800°C in oxygen for 2 hours.

Figure 4 shows the dielectric constants (ε) measured at 1 MHz for films at various deposition temperatures. The dielectric properties of bulk $ZrTiO_4$

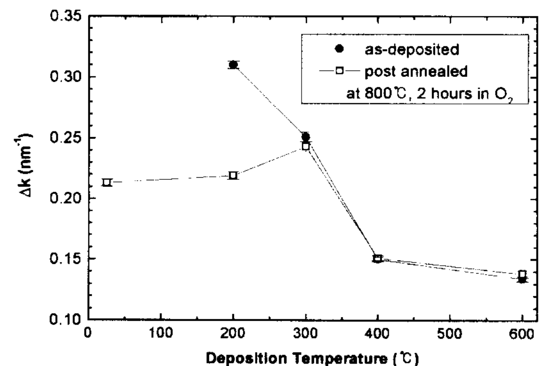

Fig. 3. $ZrTiO_4$ (111) peak widths (Δk), as a function of deposition temperature.

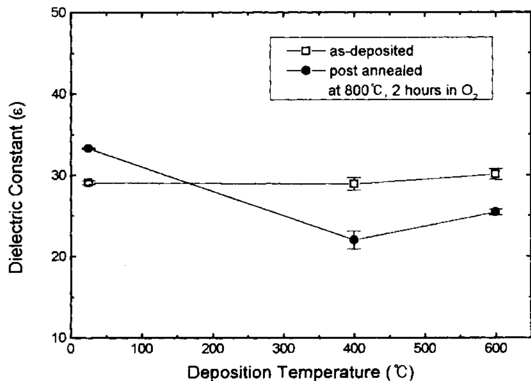

Fig. 4. Dielectric constants for as-deposited and post-annealed $ZrTiO_4$ thin films.

were reported to be $\varepsilon = 42$, $\tan\delta = 2.13\times10^{-4}$ (Q = 4700) at 7 GHz, and $\tau_f = 58$ ppm / °C [17]. There was no systematic variation observed in the dielectric constants of the as-deposited samples as a function of deposition temperature. An increase in ε was expected with increasing crystallinity. It has been reported that different processing conditions may cause variations in stoichiometry and oxygen vacancies, which may result in different dielectric constants [18]. Ramakrishinan *et al.* [19] claim that the decrease in ε for $ZrTiO_4$ after annealing may be due to the formation of a low dielectric interfacial layer between films and substrates, for example SiO_2. However, these claims should be investigated further.

The change in dielectric losses (tan δ) as a function of deposition temperature is shown in Figure 5. The dielectric losses at 1 MHz were much higher than observed with bulk $ZrTiO_4$, but a decrease with

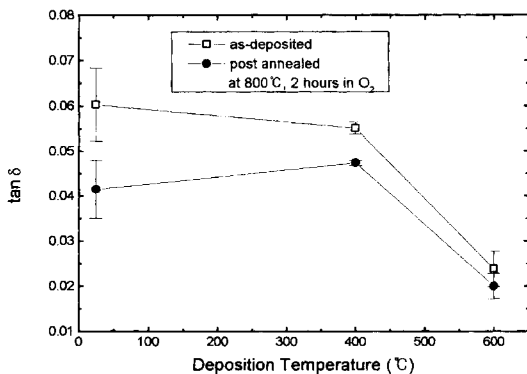

Fig. 5. Dielectric losses for as-deposited and post-annealed $ZrTiO_4$ thin films.

higher deposition temperature and post annealing was seen, as expected. The decrease in dielectric losses correlated with the diffraction peak widths (Figs. 3 and 5). However, it is not yet clear why $ZrTiO_4$ thin films have higher dielectric losses compared to the sintered bulk phase.

IV. Conclusions

The effects of deposition temperature and post annealing on the dielectric properties and crystallinity of $ZrTiO_4$ thin films have been investigated. Near-stoichiometric $ZrTiO_4$ thin films that exist in a metastable high-temperature disordered phase were successfully synthesized. 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. However, dielectric losses in thin films were much higher than the published bulk values. Further studies are required to correlate the dielectric properties with thin film microstructures, including grain size, stoichiometry, vacancy, grain-boundary segregation, and texture.

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