Dielectric Properties and Strain Analysis in Paraelectric ZrTiO$_4$ Thin Films Deposited by DC Magnetron Sputtering

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(Received January 24, 2000; accepted for publication April 6, 2000)

The dielectric constants and dielectric losses of ZrTiO$_4$ thin films deposited by DC magnetron reactive sputtering were investigated. The paraelectric properties were measured in the 100 kHz range, and compared with an equivalent circuit model. As the deposition temperature increased (up to 600°C), the dielectric losses (tan δ) decreased (down to 0.017 ± 0.007), while the dielectric constants (ε) were in the range of 35 ± 7. Post annealing at 800°C in oxygen for 2 h reduced tan δ down to 0.005 ± 0.001, higher than those of well-sintered bulk ZrTiO$_4$. The systematic trend of tan δ as a function of deposition temperature and post annealing showed good correlations with strains in ZrTiO$_4$ thin films deduced from the broadening of X-ray diffraction peak.

KEYWORDS: ZrTiO$_4$ thin films, paraelectric, dielectric loss, magnetron sputtering, strain analysis

1. Introduction

With a wide variety of microwave communication applications, such as mobile phones, global positioning systems (GPS), and satellite communications, the demand for monolithic microwave integrated circuit technologies (MMIC) has been increasing. For miniaturization of integrated circuitry, microwave dielectric components need improved characteristics, smaller size, and compatibility with existing circuits. ¹⁻⁴ Paraelectric materials used as resonators and filters in microwave circuits require high dielectric constants (resonator size proportional to 1/√ε), low dielectric losses (tan δ), and low temperature coefficients of resonance frequency (τε). Since inferior dielectric properties of fabricated thin films limit the application of these materials in thin film microwave devices, detailed studies on the correlations between the dielectric properties and microstructures of thin films are needed.

The bulk ZrTiO$_4$ phase has a high dielectric constant suitable for microwave devices, low dielectric losses, and good thermal stability with Sn addition.⁵⁻⁶ Single-phase ZrTiO$_4$ structure is orthorhombic with Ti and Zr ions chemically disordered in half of the eight octahedral sites in a single unit cell above 1100°C.⁷ Below this temperature, the equilibrium phase diagram shows phase separation into ZrO$_2$ and ZrTi$_2$O$_6$.⁸⁻⁹ Single-phase ZrTiO$_4$ thin films have been studied previously for the dielectric constants, leakage current, and optical index of refraction (n).¹⁰⁻¹³ The dielectric losses of these thin films in the microwave and even low frequency (~1 MHz) ranges, however, have not as yet been investigated. Therefore, in this paper, we report the effects of deposition temperature and post thermal annealing on the dielectric losses (tan δ) and dielectric constants (ε) in the low frequency (100 kHz) range. In addition the correlations between the strain in thin films and dielectric losses were investigated by analysis of the X-ray diffraction peak widths at various scattering angles.

2. Experimental Details

Thin ZrTiO$_4$ films were deposited by DC magnetron reactive sputtering using 4 inch Ti and Zr metal targets. The deposition system was arranged in a symmetric configuration with a rotating substrate holder for compositional uniformity. The base pressure of the sputtering chamber was typically $4 \times 10^{-7}$ Torr, and substrates were inserted from a load lock into the main chamber to maintain a 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. Phosphorous doped (to ~300 nm) Si (100) substrates were used as a bottom electrode. For the deposition of ZrTiO$_4$ thin films, an operating pressure of 4 mTorr was maintained during deposition. The Ar (99.999%) and O$_2$ (99.99%) flow rate ratios ranged from 83/17 to 50/50, as controlled by mass flow controllers, for stoichiometric thin films. All samples were sputtered on the Si (100) substrates at 500 W and 650 W for Zr and Ti targets, respectively, so that each film had Zr/Ti ratios in the range of 0.85 to 1.38, suitable for single phase ZrTiO$_4$.¹² The deposition temperatures were varied from room temperature up to 600°C. Before each deposition, both targets were pre-sputtered for at least 30 min, under the same conditions as the actual deposition process.

Thin film samples deposited at temperatures between room temperature and 600°C were then annealed at 800°C in an oxygen atmosphere for 2 h in order to investigate the effects of post annealing. During the post annealing process, oxygen gas flowed continuously through the quartz tube where the pressure was 200 mTorr, to reduce oxygen out-gassing from the fabricated thin films.

The crystal structure and strain in the thin films were characterized by X-ray diffraction (M18XHF-SRA, MAC Science) using Cu Kα radiation ($λ = 1.54050$ Å) with 40 kV/200 mA, sampling width of 0.02°, and scan speed of 5°/min in the 2θ range of 20°–80°. Film compositions were measured by electron probe micro-analysis (EPMA) on several areas for each sample. The diameter of the probing area was fixed at 10 μm, and the standard samples for the quantitative analysis were ZrO$_2$ and TiO$_2$ (rutile) single crystals. The film thicknesses were measured with a step-scanner, and were typically around 400 nm.

For electrical measurements, 200 μm diameter platinum upper electrodes were sputtered to ~200 nm using a shadow mask. The Si (100) substrate had resistivity of 6.1 × 10⁻⁴ Ω·cm (40.7 times higher than Pt), which is suitable for use as a bottom electrode. The film capacitances and dielec-
tric losses were measured using a HP 4194A impedance analyzer in the 1 kHz–10 MHz range with 0.04 V ms oscillation voltage. Compensation using open and short circuit modes was applied for all the measurements. Using the measured capacitances, the dielectric constants were calculated with each measured film thickness and upper electrode area.

3. Results and Discussion

X-ray diffraction patterns for the as-deposited and post-annealed thin films are shown in Figs. 1(a) and 1(b), respectively. X-ray diffraction data for thin films correspond well with the JCPDS card of single phase ZrTiO$_4$. The compositions of thin films are Zr$_{0.83}$TiO$_{4.19}$ (deposited at room temperature), Zr$_{0.95}$TiO$_{4.80}$ (200°C), Zr$_{0.95}$TiO$_{4.64}$ (300°C), Zr$_{0.76}$TiO$_{4.76}$ (400°C), and Zr$_{0.63}$TiO$_{5.96}$ (600°C). These compositions remained unchanged after the annealing process. Although the compositions of some samples are out of range of stable ZrTiO$_4$ composition, it is convinced that these samples are also single phase ZrTiO$_4$, based on the X-ray diffraction data. Films deposited at room temperature exhibited amorphous characteristics with only the Si substrate peaks. Above 200°C, polycrystalline ZrTiO$_4$ peaks appeared in the films. After annealing in an oxygen atmosphere, the films showed more crystalline characteristics, as shown in Fig. 1(b).

The dielectric properties of bulk ZrTiO$_4$ were reported to be $\varepsilon = 42$, $\tan \delta = 2.13 \times 10^{-4}$ ($Q = 4700$) at 7 GHz, and $\tau_f = 58$ ppm/$^\circ$C,$^{14}$ and have almost the same dielectric constant in the MHz range. The change in dielectric losses as a function of deposition temperature is shown in Fig. 2(a). The data in Fig. 2 are average values from at least five different platinum upper electrodes for reliable dielectric property values. Hence, the scattering of the data results from the standard deviations of $\tan \delta$ and dielectric constant, with estimated errors in the measurement of the electrode radius. The dielectric losses (0.017–0.038) at 100 kHz were two-orders-of-magnitude higher than observed with bulk ZrTiO$_4$ ($\sim 10^{-5}$).$^{14}$ A higher deposition temperature and post annealing reduced the dielectric losses (0.005–0.034). This decrease in dielectric losses correlated well with the reduction of strain in the thin films described below.

Figure 2(b) shows the dielectric constants ($\varepsilon$) measured at 100 kHz for thin films at various deposition temperatures and after post annealing. The figure shows no systematic variations in the dielectric constants, even though an increase in the dielectric constant is expected with increasing crystallinity. It has been reported that different processing conditions may cause variations in stoichiometry and oxygen vacancies, resulting different dielectric constants.$^{15}$ Although the compositions of thin films vary, correlations between the composition and dielectric properties are not observed from many different samples we prepared. However, the effect of com-

![Fig. 1](image1.png)  
Fig. 1. X-ray diffraction patterns of the (a) as-deposited and (b) post-annealed ZrTiO$_4$ thin films. The deposition temperatures were room temperature, 200°C, 400°C, and 600°C. Post annealing was conducted at 800°C in oxygen for 2 h.

![Fig. 2](image2.png)  
Fig. 2. (a) Dielectric losses and (b) dielectric constants for as-deposited and post-annealed ZrTiO$_4$ thin films. Post annealing was conducted at 800°C in oxygen for 2 h.
position needs to be clearly elucidated.

The apparent (measured) dielectric constants of the thin films dropped as the frequency increased, as shown in Fig. 3(a). Around the MHz frequency range, the dielectric loss (\(\tan \delta\)) showed a very strong increase. In the measurement of dielectric properties, an appreciable resistance and inductance may arise from extrinsic sources. This can affect the dielectric response at relatively higher frequencies.\(^{16, 17}\)

Because the dielectric relaxation in paraelectric materials appears in the optical frequency range, the resonance behavior in our measurement may be caused by extrinsic sources. The capacitance \((C)\) and dielectric loss \((\tan \delta)\) are usually measured by a capacitor type test fixture. The measuring equipment is usually designed to read the complex impedance from the device under test, and calculate the capacitance and phase shift (dielectric loss) from the impedance assuming an equivalent circuit including only a parallel resistor/capacitor.\(^{16}\)

Thus, depending on the frequency range, there is a deviation between the apparent and true dielectric properties of specific materials. To separate this effect, we designed an equivalent circuit as shown in Fig. 3(b). From the definition, the measured dielectric loss \((\tan \delta_m)\) may be written as

\[
\tan \delta_m = \frac{\text{Re}(Z)}{\text{Im}(Z)} = \left( R_s + \frac{R_p}{1 + \omega^2 C_p^2 R_p^2} \right) \left( \frac{\omega C_p R_p^2}{1 + \omega^2 C_p^2 R_p^2} - \omega L \right)
\]

(1)

where \(Z\) is the impedance, \(\omega\) is the measuring frequency, \(C_p\) is the parallel capacitance, \(L\) is the inductance, and \(R_s\) and \(R_p\) are the series and parallel resistances, respectively. The term \(\tan \delta = 1/\omega C_p R_p^2\) is the true dielectric loss, which is so small that the approximation \(\omega^2 C_p^2 R_p^2 \gg 1\) is reasonable. Through a similar process, the measured capacitance \((C_m)\) can be also estimated:

\[
C_m \approx \frac{C_p}{(1 - \omega^2 C_p L)(1 + \tan^2 \delta_m)}.
\]

(2)

The dotted lines in Fig. 3(a) show the calculated dielectric losses and dielectric constants as a function of frequency for a ZrTiO₄ thin film deposited at room temperature and annealed at 800°C in oxygen for 2 h. Note that the dotted lines show calculated \(\tan \delta\) and dielectric constant from the equivalent circuit model.

The equivalent circuit model composed of parallel capacitor/resistor and series resistor/inductor.

Fig. 3. (a) Measured dielectric losses and dielectric constants as a function of frequency for a ZrTiO₄ thin film deposited at room temperature and annealed at 800°C in oxygen for 2 h. Note that the dotted lines show calculated \(\tan \delta\) and dielectric constant from the equivalent circuit model. (b) The equivalent circuit model composed of parallel capacitor/resistor and series resistor/inductor.

To qualitatively estimate the strain and effective grain size of the deposited ZrTiO₄, the X-ray diffraction peak widths \(\Delta k\) (full width at half maximum: FWHM) were fitted at various stages for each peak (scattering vector \(k = (4\pi/l) \sin \theta\)). To consider unresolved \(K\alpha_1\) and \(K\alpha_2\) peaks with the instrumental broadening effect, the following fitting process was used in obtaining the true peak widths \(\Delta k\). A double-peak Lorentzian function, \(f(x)\), was used to separate the \(K\alpha_1\) and \(K\alpha_2\) peaks, as shown in Fig. 4.

\[
f(x) = \frac{I w}{4(x - x_0)^2 + w^2} + \frac{0.5 I w}{4(x - x_0)^2 + w^2} + b.
\]

(3)

Fig. 4. Double-peak Lorentzian fitting using \(f(x)\) as a fitting function \((I:\) peak intensity, \(w:\) full width at half maximum, \(x_0: K\alpha_1\) peak position, \(b:\) background). The X-ray diffraction pattern is from the sample deposited at room temperature and annealed at 800°C for 2 h.
where 

\[ I : \text{intensity,} \]
\[ w : \text{full width at half maximum,} \]
\[ x_0 : \text{peak position for } K\alpha_1, \]
\[ x'_0 : \text{peak position for } K\alpha_2, \]
\[ b : \text{background,} \]

assuming that the FWHM \((w)\) of each peak due to \(K\alpha_1\) and \(K\alpha_2\) have the same value. The instrument broadening effect is then subtracted using the resolution function estimated from the diffraction pattern of a single and poly-crystalline silicon substrate.\(^{18}\)

In addition \(\Delta k\) is known to have a relation with strain and grain size as follows:

\[ \Delta k = \frac{\Delta d}{d} k + K \frac{2\pi}{D}, \]

where \(\Delta d/d\) is the strain in the thin films and \(D\) is the effective grain size suggested by Scherrer,\(^{19}\) with the shape factor \(K\). Using this relation, the strain in thin films can be estimated from the slope of the plot of \(\Delta k\) versus \(k\) after correction by the resolution function \((\Delta k_{\text{resolution}} = 0.046 + 0.00004k)\), as shown in Fig. 5 as an example. The error ranges in Fig. 5 are from the double-peak Lorentzian fitting for the X-ray diffraction peaks.

Figure 6 shows that at higher deposition temperatures and after the post annealing process, there is appreciable reduction of strain in the thin films (from 7.2% to 0.04%), clearly reflecting some sort of structural relaxation in the thin crystalline films. This result of strain reduction in the films correlates well with the decrease in dielectric losses in the annealed films [shown in Fig. 2(a)]. In Fig. 6, the scattering occurred from \(\Delta k - k\) linear fitting processes. The grain sizes estimated from \(\Delta k\) vs \(k\) graphs, however, had fitting errors that were too large to give any reasonable meaning about the microstructures of the thin films. The volume of the orthorhombic unit cell of the thin films estimated from the diffraction peak positions became closer to the bulk \(\text{ZrTiO}_3\) values at higher deposition temperatures (Fig. 7) showing similar trends with dielectric losses [Fig. 2(a)] and strain (Fig. 6). The scattering of data in Fig. 7 resulted from the uncertainty of the X-ray peak position during the X-ray data fitting processes.

4. Conclusions

The effects of deposition temperature and post annealing on the dielectric properties and crystallinity of \(\text{ZrTiO}_3\) thin films have been investigated with \(\text{ZrTiO}_3\) thin films existing in a high-temperature disordered phase. As deposition temperature increased, the dielectric losses decreased, while the dielectric constants did not change significantly. Similar trends for dielectric losses were observed after the as-deposited samples when annealed at 800°C. The strain in the thin films were analyzed from the diffraction peak widths, and correlated with the decrease in dielectric losses. However, dielectric losses in sputtered \(\text{ZrTiO}_3\) thin films were at least an order-of-magnitude higher than the values from well-sintered bulk samples. Further investigation is required in order to correlate the dielectric properties with thin film microstructures, including stoichiometry, vacancy, grain-boundary segregation, and texture, in addition to studying the microwave dielectric properties of thin films.
Acknowledgments

The authors thank Euijoon Yoon for providing the sputtering system. This work was supported by the Center for Iron and Steel Research at Seoul National University and by the Share-ISRC program through Inter-University Semiconductor Research Center in the year of 2000.

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