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Microwave dielectric properties of magnesium calcium titanate thin films

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Abstract

The microwave dielectric properties of $CaTiO_3$ (CT), $MgTiO_3$ (MT) and $(Mg_{0.93}Ca_{0.07})TiO_3$ (MCT) thin films prepared by the metalorganic solution deposition technique were investigated. The well-crystallized CT, MT and MCT thin films were annealed at 800 °C. The microwave dielectric properties of the thin films were measured using a circular-patch capacitor geometry with a network analyzer. The dielectric constant (K), dielectric loss (tan δ) and temperature coefficient of dielectric constant (TCK) of CT films measured up to 6 GHz were 160 ± 3, 0.003 ± 0.0003 and -1340 ppm/°C, respectively. In contrast, the MT films showed $K \sim 16 \pm 1$, tan $\delta \sim 0.0008 \pm 0.0001$ and TCK ~ +260 ppm/°C. MCT films exhibited microwave dielectric properties of $K \sim 22 \pm 1$, tan $\delta \sim 0.0012 \pm 0002$ and TCK ~ +10 ppm/°C.
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Keywords: CT; MT; MCT; Film; Microwave; Dielectric constant; Dielectric loss; Temperature coefficient of dielectric constant

1. Introduction

As communication technologies such as wireless-communication systems rapidly develop, much attention is focused on microwave dielectric materials [1,2]. Among the microwave dielectrics, $MgTiO_3$- and $CaTiO_3$-based ceramics have wide applications as resonators, filters and antennas for communication, radar and global positioning systems operating at microwave frequencies [3,4]. $MgTiO_3$ and $CaTiO_3$ bulk ceramics exhibit dielectric constants ~17 and 170, quality factor ($Q \approx 1/\tan\delta$) ~ 160,000 and 3600 at 7 GHz and temperature coefficient of the resonant frequency (TCF) ~ −50 ppm/°C and +800 ppm/°C, respectively [5,6]. Recent advances in microwave-integrated systems for wireless communications demand for the development of small size, low power loss, and temperature stable microwave components. Therefore, microwave dielectric materials require a high dielectric constant, a low dielectric loss, and a near-zero temperature coefficient of the resonant frequency. $CaTiO_3$ with positive TCF has been controlled by many materials with negative TCF to obtain near-zero TCF [7,8]. Especially, $(Mg_{0.93}Ca_{0.07})TiO_3$ ceramics, a solid solution of $CaTiO_3$ with $MgTiO_3$ which has a negative TCF (−50 ppm/°C), exhibit excellent microwave dielectric properties, i.e. $K \sim 22$, $Q \sim 22{,}000$ at 5 GHz and TCF ~ 5 ppm/°C [4,5].

The progress in microwave communication applications and continuing miniaturization of integrated circuitry has resulted in a demand for microwave dielectric thin films. Thin films may have the advantages of lower crystallization temperatures and smaller device size than bulk ceramics and can be integrated in microelectronic devices. However, CT, MT and MCT thin films have been studied around the MHz-frequency range instead of frequencies for microwave devices because of measurement difficulty [9,10]. In this work, the dielectric properties of CT, MT and MCT thin films prepared by a metalorganic solution deposition technique were investigated up to the microwave frequency range.

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2. Experimental procedures

CT, MT and MCT thin films were prepared by a metalorganic solution deposition technique (MOSD). MOSD processing has been extensively used in thin film technology because of the advantages of low processing temperature, precise composition control, low equipment cost, and uniform deposition over large area substrates. Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$), and titanium iso-propoxide ($Ti(O\text{-}iC_3H_7)_4$) were used as starting materials, and 2-methoxyethanol as a solvent. Calcium nitrate tetrahydrate and magnesium nitrate hexahydrate were dissolved in excess 2-methoxyethanol and then distilled to remove reaction products and the excess solvent. After adding titanium iso-propoxide, these solutions were reacted and concentrated to final concentration of 0.4 M by distillation. 0.4 M solutions were spin-coated on the Pt(1 1 1)/Ti/SiO_2/Si substrate. The thin films were pyrolyzed at 400 °C for 5 min, and crystallized at 800 °C for 30 min. The thickness of thin films was 0.4 μm. The crystallization behavior of the films was studied using by XRD (290621A, Rigaku), and the microstructures were analyzed using by atomic force microscopy (Autoprobe CP, PSIA). The microwave dielectric properties were measured using a circular-patch capacitor geometry with a network analyzer (HP8753ES, Agilent) and coplanar wave guide probe [11,12]. The two top electrodes of molybdenum shaped in a circular-patch capacitor structure with the same outer diameters (150 μm) and different inner diameters (50 and 80 μm) were patterned by photolithography.

3. Results and discussion

The XRD patterns of CT, MCT and MT thin films annealed at 800 °C are shown in Fig. 1(a–c). A well-crystallized perovskite CT films without secondary phases could be obtained at 800 °C, Fig. 1(a). The lattice constants a, b and c, calculated using the XRD data, were 5.432, 7.668 and 5.396 Å, respectively. Also, it was found that the intensities of the main peak (1 0 4) and the relatively weaker peaks (1 1 0), (0 1 2), (0 2 4) and (1 1 6) of MT films with ilmenite structure strengthened with increasing annealing temperature. MT ceramics could not form the perovskite structure due to the magnesium ion with smaller ionic radius than calcium ion [13].

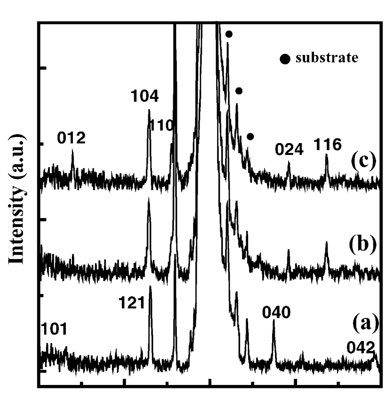

Fig. 1. XRD patterns of (a) CT, (b) MCT and (c) MT thin films.

The AFM images of CT, MCT and MT thin films annealed at 800 °C are shown in Fig. 2. It was observed that the grain size of CT film was larger than for MCT and MT films. In addition, the surface roughness of CT films calculated from the AFM data was about 6.1 nm at an annealing temperature of 800 °C, while for MCT and MT were about 2.8 and 2.2, respectively.

The dielectric constants of CT, MCT and MT films annealed at 800 °C in the frequency range of 100 MH–6 GHz are shown in Fig. 3. CT and MT films exhibited dielectric constants of about 160 ± 3 and 16 ± 1, respectively. This result is consistent with MT having lower dielectric constant than CT due to the isolation of the TiO_6 octahedron [14]. Also, it was found the dielectric constants of CT and MT thin films to be similar to bulk CT and MT with dielectric constants 170 and 17, respectively. MCT films showed dielectric constant of about 22 ± 1 according to the dielectric mixing rule. The dielectric constants of the films showed no appreciable dispersion with frequency up to about 6 GHz, as shown in Fig. 3. To obtain the dielectric constants of the films at the microwave region, the impedances of two test structures with the same outer diameter (150 μm) but different inner diameters (50 and 80 μm) were measured by a network analyzer, and then subtracted to remove the effect of the outer ground. Given the two inner diameter values of a_1 and a_2, the impedance difference is [11,15]

$$Z = Z_1 - Z_2 = \frac{R_s}{2\pi}\ln\left(\frac{a_2}{a_1}\right) + \frac{t}{i\omega\pi\varepsilon_0 K}\left(\frac{1}{a_1^2} - \frac{1}{a_2^2}\right) \quad (1)$$

$$C = -\frac{1}{\omega} \times (\text{imaginary component of } Z) \quad (2)$$

where Z is the impedance of test structure, which can be converted from the complex reflection coefficient (=S_{11}), ε_0 is the permitivity of free space (=8.854×10^{-12} F/m), t is the thickness of the film, R_s is the resistance per square of bottom electrode and ω is the angular frequency (=$2\pi f$). The relative dielectric constants (K) of films could be obtained from above Eqs. (1) and (2) in the GHz region.

Fig. 4 shows the temperature coefficient of dielectric constants (TCK) of CT, MCT and MT thin films measured in the temperature range 30–130 °C. The TCK was determined as follows:

$$\text{TCK} = \frac{\Delta K}{K_0\,\Delta T} \times 10^6 (\text{ppm/°C}) \quad (3)$$

where ΔK is the change in dielectric constant relative to dielectric constant K_0 at 30 °C and ΔT is the change in temperature relative to 30 °C. The CT films exhibited a

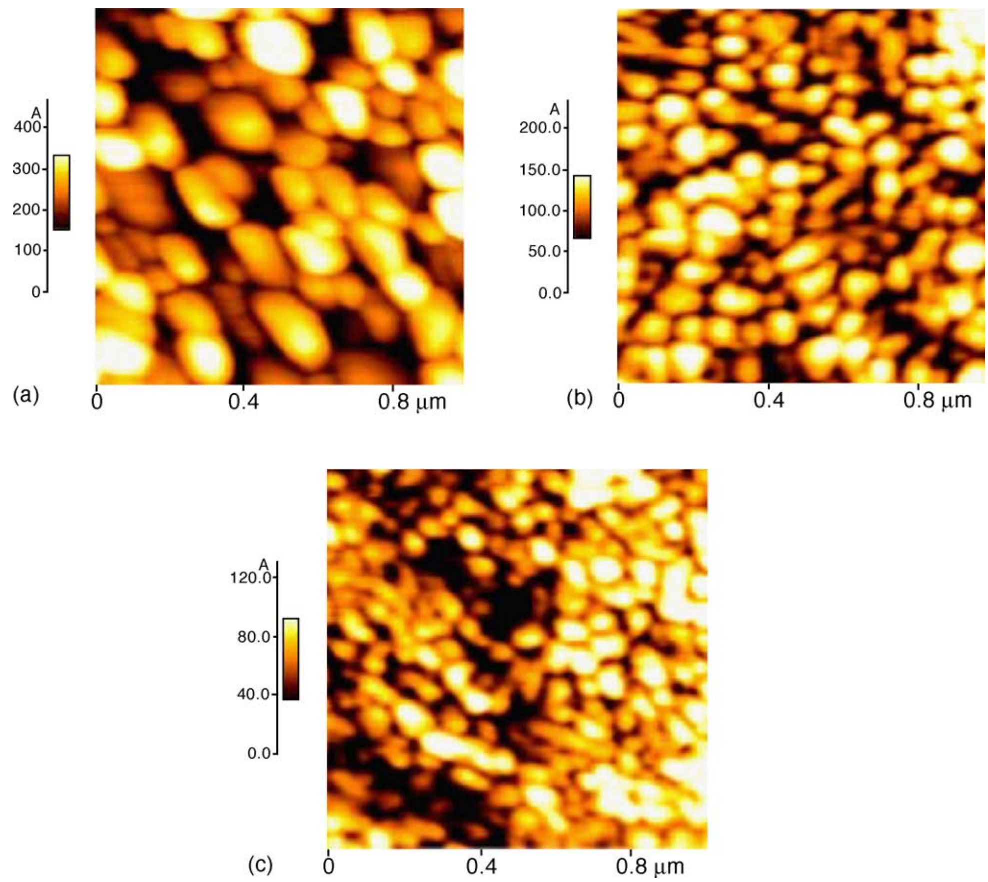

Fig. 2. AFM images of (a) CT, (b) MCT and (c) MT thin films.

negative TCK of −1340 ppm/°C, while the MT films showed a positive TCK of +260 ppm/°C at 6 GHz. MCT films showed a TCK of +10 ppm/°C indicating good temperature stability. Also, TCF (≈5 ppm/°C) of MCT bulk ceramics was converted to TCK as follows.

$$\mathrm{TCF} = -\frac{1}{2} \times \mathrm{TCK} - \alpha \quad (4)$$

where α is the thermal expansion coefficient. α does not deviate significantly from a value of 8×10^{-6} to $8 \times 10^{-5}\ \mathrm{K}^{-1}$ over a broad temperature range for common ceramic dielectric materials. Therefore, it was found that TCK of MCT thin films was similar to that of MCT bulk ceramics.

Fig. 5(a) shows dielectric losses obtained by subtracting the impedances of two capacitor structures and corrected by removing the parasitic resistance (R_s) of MCT films. To obtain R_s with top/bottom electrodes resistance and contact resistance between probe and top electrode, an equivalent circuit composed of true capacitance of the film, resistance

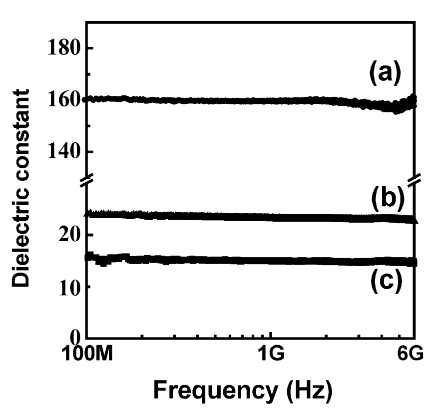

Fig. 3. Dielectric constants of (a) CT, (b) MCT and (c) MT thin films as a function of frequency.

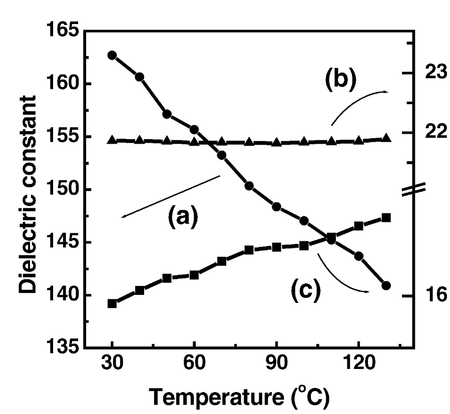

Fig. 4. Dielectric constants vs. measured temperature of (a) CT, (b) MCT and (c) MT thin films at 6 GHz.

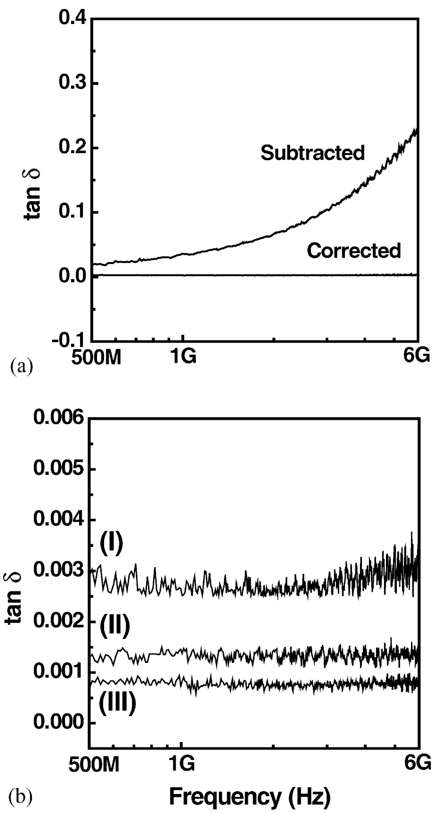

Fig. 5. (a) Dielectric losses obtained by subtracting the impedances of two capacitor structures and corrected by removing the parasitic resistance (R_s) of MCT films, (b) dielectric losses of (I) CT, (II) MCT and (III) MT thin films.

of the film and parasitic resistance was modeled [16] and evaluated by the following equation [12].

$$Z = R_s + \frac{R}{\omega}(\tan\delta)^2 - i\frac{1}{\omega C} \quad (5)$$

R_s was measured from the intercept of the real part of impedance (Z) and the angular frequency ($\omega = 2\pi f$). After R_s was removed, tan δ, i.e. the ratio of real and imaginary parts of impedances, was obtained. Fig. 5(b) shows the dielectric losses of CT, MCT and MT films in the frequency range 500 MHz–6 GHz. The dielectric loss (0.003 ± 0.0003) of CT film was higher than for MT (0.0008 ± 0.0001) and MCT (0.0012 ± 0.0002) films in the GHz region. This results is consistent with the fact that the Qf values of bulk CT are lower than for bulk MT and MCT.

4. Conclusions

The microwave dielectric properties of CT, MCT and MT films prepared by MOSD were investigated. K, tan δ and TCK of CT films were about 160, 0.003 ± 0.0003 and −1340 ppm/°C up to 6 GHz. MT films showed values of K ~ 16, tan δ ~ 0.0008 ± 0.0001 and TCK ~ +260 ppm/°C. MCT films with controlled Mg to Ca ratio to obtain temperature stability exhibited K ~ 21, tan δ ~ 0.0012 ± 0.0002 and TCK ~ +10 ppm/°C.

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