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Comparison of dielectric properties between Ag(Ta,Nb)O₃ bulk ceramics and thick films on alumina substrate

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Comparative analyses for the $Ag(Ta,Nb)O_3$ bulk ceramics and thick films were performed. Screen printing method was employed to prepare the $Ag(Ta,Nb)O_3$ thick films. For the microwave applications, crystalline and electrical properties were investigated by X-ray diffraction analysis and current-voltage characteristics, respectively. Scanning electron microscopy was also performed to evaluate the surface morphology. Dielectric permittivity of $Ag(Ta,Nb)O_3$ thick films was lower than that of bulk ceramics, while the loss tangent of thick films was higher compared with that of bulk ceramic. Frequency-dependent dielectric permittivity showed that $Ag(Ta,Nb)O_3$ thick film interdigital capacitors have very weak frequency dispersion with low a loss tangent. From the current-voltage characteristics, it was found that the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics and thick films had NTCR properties.

Key words: Ag(Ta,Nb)O₃, Bulk ceramics, Thick films, NTCR.

Introduction

High-dielectric and low loss paraelectric materials have attracted attention for frequency applications. Such functional materials can be employed for microwave applications due to their low energy consumption. Perovskite (Ba,Sr)TiO₃ (BST) [1-4], incipient ferroelectric SrTiO₃ (STO) [1, 5], and KTaO₃ [6] films have been considered as candidates for high-frequency applications. Among them BST is one of the most attractive materials for room-temperature applications due to its high permittivity and low loss tangent for the planner capacitive cell structure [1]. However, there are some unsolved problems with using BST materials for microwave applications. For example, the pyroelectric properties of BST materials are serious problems for device application [7].

As an alternative, Ag(Ta,Nb)O₃ (hereafter ATN) material can replace the BST materials for the microwave applications due to their low loss tangent around 3×10^{-3} from the kHz to GHz range [8]. Also it shows negligible pyroelectric properties from 100 K to 900 K. As a thick film form, ATN was investigated by employing the interdigital capacitors on the alumina substrates, ATN thick films showed very low loss tangent of 0.09 % at 1 kHz. [9, 10]

ATN materials show interesting dependence of its physical properties such as phase transition sequence and dielectric permittivity on the function of tantalum composition. ATN ceramics undergo successively monoclinic (M_1) - monoclinic (M_2) - monoclinic (M_3) orthorhombic (O) - tetragonal (T) - cubic (C) transition at temperature about 180, 370, 589, 674, and 833 K, respectively [8]. At 180 K, a phase transition occurs from the ferro- to the antiferro- electric phase and this phase is stable until 370 K. Due to such complicated phase transition, ATN material show very stable temperature dependent dielectric properties. Dielectric thermal stability, which can be determined by a temperature coefficient of permittivity TCP = $[e_{max} - e_{ref}] / [(e_{ref}(T_{max} - T_{ref})]]$ where emax represents the maximum value of er within a temperature range of interest, T_{max} is the temperature point corresponding to emax, eref is the er value at the reference temperature point T_{ref}, respectively [11, 12]. Therefore, broader dielectric peaks and the shift of T_c which can improve the dielectric thermal stability. Since ATN system experience multiple phase transition at wide temperature range, it bring similar effects of peak broading of Tc. Therefore, ATN system has dielectric thermal stability.

In this paper, the frequency and temperature dependent dielectric properties and temperature dependent leakage current behavior was investigated for the microwave applications.

Experimental

The Ag₂O, Ta₂O₅, and Nb₂O₅ powders were employed to prepare Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics and thick films with stoichiometric compositions. After being ball milled for 24 h with ZrO₂ balls and then dried, the Ag(Ta_{0.5}Nb_{0.5})O₃ powders were calcined at 1000 °C for 2 h. These powders were sieved to 100-mesh and were

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pressed at 100 MPa. After pressing, the Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics were sintered at 1200 °C for 2 h. To prepare thick films on the alumina substrates, MEK (methyl-ethyl-ketone) and alcohol (4:6) in a bottle were mixed with ball-milled Ag(Ta_{0.5}Nb_{0.5})O₃ powders. A dispersant of ceraperse 111 (1 wt%), a bonding agent of polyvinyl butyral (6 wt%), and a plasticizer of di-nbutyl phthalate were added to this slurry in turn and the resultant slurry was then ball milled. To remove the pores and improve the viscosity, a deaerator was used for 15 min. The thick films were fabricated on alumina substrates by employing the screen printing method and were sintered at 1150 °C for 2 h. The sintering temperature of thick film is 50 °C lower than that of bulk ceramic. [13] Because thick films have quite high level of porosities, which can be formed during the sintering process. Thick film process is based on the liquid screen printing or tape casting process. Therefore, porosities were formed and enhanced the sintering process more easily.

Silver interdigital capacitors (IDC) were patterned through a mask by using a manual screen printer. The IDCs were composed of five pairs of fingers separated by 50 μ m gap and were 100 μ m in width and 200 μ m in length. By using the α -step, We measured the thickness of Ag(Ta_{0.5}Nb_{0.5})O₃ thick films. Consequently, thickness of sample was about 6 um.

The crystalline structures of the Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics and thick films were investigated by employing X-ray diffraction (XRD) analysis (θ -2 θ scans with Cu-*K* α source). The electrical properties of the devices were characterized employing a Cascade Rel 4500 probe station connected to a HP 4284 precision LCR meter and to a Keithley 6517A electrometer / high resistance meter.

Results and Discussion

Fig. 1 shows the X-ray diffraction patterns θ -2 θ of Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics and thick films on alumina substrates, which sintered at 1200 °C and 1150 °C, respectively. The X-ray diffraction patterns showed that both Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramic and thick film have a perovskite structure. The pyrochlore phase is detected near the 46 and 52 degree. The out-of-plane and in-plane lattice parameter *c* and *a* were calculated by employing the *Nelson-Rilley* extrapolation function [14] with a least mean square method:

$$\frac{C_{\cos\theta} - C_0}{C_0} = A \cdot \cos^2\theta \left(\frac{1}{\sin\theta} + \frac{1}{\theta}\right) \tag{1}$$

where $C_{cos\theta}$ is an interplane distance calculated from the apparent Bragg 2 θ peak position and A is a fitting coefficient. The calculated lattice parameters of *c* and *a* were 3.927 Å and 3.907 Å for bulk ceramic and 3.923 Å and 3.905 Å for thick film, respectively. If we



Fig. 1. X-ray diffraction pattern of the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics sintered at 1200 °C and the $Ag(Ta_{0.5}Nb_{0.5})O_3$ thick films sintered at 1150 °C.



Fig. 2. Frequency-dependent dielectric constants and loss tangents for the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics sintered at 1200 °C and the $Ag(Ta_{0.5}Nb_{0.5})O_3$ thick films sintered at 1150 °C.

close look at the (002) peak, we can observe very weak asymmetric. It is believed that this weak asymmetric come from the CuK α_1 and CuK α_2 , since Cu radiation source was used. It was found that the Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramic has a the pseudo-cubic structure.

Fig. 2 illustrates the frequency dependent-dielectric permittivities of the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics and the thick films. The capacitance and the dissipation factors of the fabricated specimens were measured through this system. The dielectric permittivity of a bulk ceramics can be calculated by using the following equation:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} (farad)$$
$$\varepsilon_r = \frac{C \cdot d}{\varepsilon_0 \cdot A}$$
(2)

The dielectric permittivity of thick films interdigital capacitors can be calculated by employing conformal mapping technologies. The concept of conformal mapping is based on the assumption of a uniform dielectric permittivity and perfect electric conductor. The conformal



Fig. 3. Temperature-dependent dielectric permittivity and dielectric loss for the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics sintered at 1200 °C and the $Ag(Ta_{0.5}Nb_{0.5})O_3$ thick films sintered at 1150 °C.

mapping can transform the Cartesian coordinates to polar coordinates and vice versa [15]. The relative dielectric permittivities of the Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics and thick films decreased with increasing frequency. From the frequency-dependent permittivity and loss tangent, the permittivities of the Ag($Ta_0 SNb_0 S$)O₃ bulk ceramics and thick films decreased from 360 to 357 and from 171 to 162 as the frequency was increased from 1 kHz to 100 kHz, respectively. The calculated dielectric dispersions of the Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics and thick films were 0.64% and 5.26%, respectively. Also, the loss tangent of the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics decreased from 0.72% to 0.17% from 1 kHz to 100 kHz, but the loss tangent of the Ag(Ta_{0.5}Nb_{0.5})O₃ thick films slightly increased from 0.103% to 0.417%. The frequency-dependent dielectric permittivities were fitted by using a power law. The simulated power law for the bulk ceramic is $\varepsilon(f) = 362.44 \times f^{-0.00128}$ Hz while that for the thick films is $\varepsilon(f) = 188.11 \times f^{-0.01334}$ Hz.

Fig. 3 shows the temperature-dependent dielectric permittivities of the Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics and thick films. With increasing temperature, the relative dielectric permittivities of the Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics and thick films increased. As we have discussed in the introduction, Ag(Ta_{0.5}Nb_{0.5})O₃ materials have very stable temperature-dependent dielectric properties. The calculated temperature-dependent dielectric properties, de/dT, of the bulk ceramics and the thick films were 0.1089 K⁻¹ and 0.07933 K⁻¹, respectively. Since the Curie temperature (T-C phase transition) of Ag(Ta_{0.5}Nb_{0.5})O₃ is around 800 K [16], near measured temperature ranges, the relative permittivity can be increased. Fig. 3 indicates that a positive temperature coefficient of the dielectric permittivity for increasing temperature. Also, with increasing temperature, the loss tangent increased in the Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics and thick films. As shown in the figure, the de/dT of the thick films was smaller than that of the bulk ceramics, which means the Ag(Ta_{0.5}Nb_{0.5})O₃ thick films is more stable to temperature variations than the



Fig. 4. (a) Current vs. voltage characteristics of the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics sintered at 1200 °C. The insert indicates the temperature-dependent resistivity of the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics on an Arrehnius plot and (b) current vs. voltage characteristics of the $Ag(Ta_{0.5}Nb_{0.5})O_3$ thick films sintered at 1150 °C. The insert indicates the temperature-dependent resistivity of $Ag(Ta_{0.5}Nb_{0.5})O_3$ thick films on an Arrehnius plot.

Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics. This can be explained by considering the role of alumina substrates. To measure the dielectric permititivy of ATN thick film, ATN interdigital capacitors on the alumina substrates were employed. As a result, the measured dielectric permittivity of ATN interdigital capacitor was the sum of both ATN thick film and alumina substrate. Since alumina substrates shows much weaker temperature dependence than that of ATN thick film, ATN thick films shows much weaker temperature dependent dielectric permittivity than that of ATN bulk ceramics.

Fig. 4 (a) and (b) display the current-voltage characteristics of the Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics and thick films in the temperature range from 303 to 393 K, respectively. Up to $\pm 100 V$ DC bias voltage was applied to the bulk ceramics and the IDC thick films. As shown in Fig. 4, we measured the leakage current densities of the Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics and thick films to determine the carrier transport mechanism.

Also, Fig. 4 (a) and (b) show good isolating characteristics for values of nA/cm^2 within $\pm 900 \text{ kV}/cm$ and $\pm 15 \text{ kV/cm}$, respectively. And then the leakage current density increased with increasing the temperature. The Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics and thick films have NTCR (negative temperature coefficient resistivity)

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Fig. 5. SEM image of (a) the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramic sintered at 1200 °C and (b) the $Ag(Ta_{0.5}Nb_{0.5})O_3$ thick films sintered at 1150 °C.

properties. It is believed that the dc resistivity was decreased with increasing temperature for the following reasons. The addition of thermal energy, electrons could be set free from O^{2-} ions. When an electron is introduced in the sample it might be associated with cations, which results in an unstable valence state. This type of resistive behaviour has also been found in many semiconductors. Due to additional carriers, the leakage current of the Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics and thick films were increased [17]. These electrons excited from trapped oxygen vacancy may be attributed to the NTCR properties the Ag(Ta_{0.5}Nb_{0.5})O₃ bulk ceramics and thick films.

The inserts of Fig. 4 (a) and (b) illustrate the temperature-dependent resistance of the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics and thick films, respectively. The resistivity of the IDC was calculated from the resistivity by considering its geometry. During the calculation, the total electrode area of the interdigital capacitor and the length of current path between the electrodes were considered. From the variation in the current-voltage properties with a temperature, an Arrhenius equation was suggested to describe the temperature-dependent resistance behaviour:

$$\rho(T) = \rho_0 \exp\left(\frac{E_a}{kT}\right) \tag{3}$$

where *T* is the temperature in Kelvin, E_a is the activation energy of carriers, *k* is the Boltzmann constant (8.62 × 10⁻⁵ eV/K) and ρ_0 is the resistance at infinite temperature. The temperature coefficient of resistance α can be written as

$$\alpha = \frac{1d\rho}{\rho dT} - \frac{E_a}{kT^2} \tag{4}$$

From the Eq. (6) the calculated temperature coefficients of ATN bulk ceramics and thick films are -3.04×10^{-11} and -1.3×10^{-10} K⁻¹, respectively.

The simulated values of ρ_0 for the ATN bulk ceramics and thick films were 2280 and 487 G Ω cm, respectively. The calculated activation energies were around 0.469 eV, 0.566 eV, respectively. These calculated activation energies were similar to their reported by

Akdogan et al [18].

Fig. 5 show the SEM image of the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramic sintered at 1200 °C and the $Ag(Ta_{0.5}Nb_{0.5})O_3$ thick films sintered at 1150 °C. By observing the grain shape and size of $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics and thick films, it was found that $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramic has more large shape of grain than $Ag(Ta_{0.5}Nb_{0.5})O_3$ thick films. The porosity of $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics and $Ag(Ta_{0.5}Nb_{0.5})O_3$ thick films was the Ag ion was volatile in the sintering process. It may be argued that this large grain size of $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramic has related with frequency dependent dielectric permittivity in Fig. 3. It can be also argued that by increasing the grain size, dielectric and crystalline properties were improved.

Conclusions

The structural and the electrical characteristics of $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics and thick films were investigated. The X-ray diffraction analysis exhibits that the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics have a pseudo-cubic structure. From the frequency-dependent permittivity and loss tangent, the permittivities of the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics and thick films were decreased from 360 to 357 and from 171 to 162, respectively, as the frequency increased from 1 kHz to 100 kHz. From the current-voltage characteristics, it was found that the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics and thick films had NTCR properties. The temperature-dependent resistivity of the $Ag(Ta_{0.5}Nb_{0.5})O_3$ bulk ceramics and thick films were simulated and were discussed through the Arrhenius equations.

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