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Effects of Ta-substitution on the dielectric properties of $Ba_6Ti_2(Nb_{1-x}Ta_x)_8O_{30}$ thin films

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Abstract

Tunable $Ba_6Ti_2(Nb_{1-x}Ta_x)_8O_{30}$ (BTN-xTa; $x = 0, 0.25, 0.4$) thin films with a tetragonal tungsten bronze structure (TTB) were deposited on platinized Si substrates using the pulsed laser deposition (PLD) technique and their properties were investigated from the viewpoint of orientation and ferroelectric phase transition. Crystal structures and dielectric properties were characterized using an X-ray diffractometer and an impedance analyzer. Pure BTN (BTN-0Ta) thin films showed tunability as high as 60% and the tunability decreased as the amounts of Ta-substitution increased at 150 kV/cm and at 1 MHz. The dielectric constants also decreased from 436 to 88 at 1 MHz through the Ta-substitution. The low tunability and dielectric constants of Ta-substituted thin films were mainly ascribed to the lowered ferroelectric transition temperature (T_c). Ferroelectric BTN (BTN-0Ta) thin films may have been changed into a paraelectric state through the Ta-substitution since the T_c of BTN thin films were shifted to temperatures far below room temperatures (approximately −60 °C).

Keywords: Films; X-ray methods; Dielectric properties; Ferroelectric properties; PLD

1. Introduction

Recently, ceramics with tetragonal tungsten bronze (TTB) structure such as strontium barium niobate ($Sr_xBa_{1-x}Nb_2O_6$) have attracted much attention as these materials show great potential in dielectric, ferroelectric, electro-optic,[1] photorefractive,[2] large pyroelectric[3] and piezoelectric[4] properties. These materials present opportunities for potential applications in various electronic devices, such as resonators, transducers, actuators, capacitors, and ferroelectric random access memory. It has been reported that the TTB structure consists of a complex array of distorter BO_6 octahedral sharing corners in such a way that three different types of interstices (A1, A2, and C) are available for cation occupying in the general formula $(A1)_2(A2)_4(C)_4(B1)_2(B2)_8O_{30}$.[5] Generally, the smallest interstice C is empty; thus, the general formula is $A_6B_{10}O_{30}$ for the filled tungsten bronze structure and TTB structure might be a complex crystal structure. The properties of TTB ceramics are complex and promising as they greatly vary when using different elements.

According to recent research,[6–8] most TTB niobates generally indicate a ferroelectric or relaxor ferroelectric nature; furthermore, they all possess diffuse ferroelectric transition induced by a disorder of A sites. With the increase of alkaline earth and the decrease of the rare earth, the TTB structure becomes more stable. In contrast with TTB niobates, TTB tantalates are paraelectrics at room temperature.[9,10] For TTB tantalates containing rare earth elements Ln (Ln = La, Nd, and Sm), the typical compositions with stable tungsten bronze structure may be described as $A1_pLn_{6-p}Ti_{8-p}Ta_{2+p}O_{30}$ (A1 = Sr and Ba, $p = 3, 4, 5$). Since all the TTB tantalates containing rare earth elements such as La and Nd have a very low dielectric loss and good temperature stability, they are promising candidates for high frequency dielectric materials. Moreover, TTB tantalates without a rare earth element might also be possible, where the chemical formula would be $A_6Ti_2Ta_8O_{30}$ (A = Sr and Ba). The electric nature of these materials has been of interest in the development of new low-loss dielectric materials.

In this work, we studied the effect of Ta substitution for Nb ions in $Ba_6Ti_2Nb_8O_{30}$ thin films on dielectric properties. In addition, the effects of the phase transition and the processing variant in fabricating thin films on the dielectric properties were investigated.

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2. Experimental procedures

The stoichiometric sintered ceramic targets of $Ba_6Ti_2(Nb_{1-x}Ta_x)_8O_{30}$ (BTN-*x*Ta; $x = 0$, 0.25, 0.40) were prepared by conventional mixed oxide methods. The BTN-*x*Ta thin films were grown on (2 0 0) preferred $Pt/TiO_2/SiO_2/Si$ substrate (Inostek, Korea) using pulsed laser deposition (PLD) with a laser flounce of 2–4 J/cm^2. All the films were deposited at 700 °C under 400 mTorr. The deposited films were cooled down in an oxygen partial pressure of 350 Torr without any further thermal treatment.

The structure of BTN-*x*Ta target and thin film were observed using X-ray diffraction (XRD, Model MX18HF-SRA, Macscience Instrument, Japan). The microstructure and thickness of the films were examined using a field emission scanning electron microscope (FE-SEM, Model JSM-6330F, JEOL, Japan). The chemical composition of the films was examined using electron probe microanalysis (EPMA, Model JXA-8900R, JEOL, Japan) on several different points for each sample.

Upper platinum electrodes (200 μm in diameter) were deposited using RF magnetron sputter onto the film surface using a metallic mask. The capacitance and the loss tangent ($\tan\delta$) of the Pt/BTN-*x*Ta/Pt capacitor were measured with an impedance analyzer (Model HP 4194A, Hewlett-Packard, USA) in the frequency range from 100 Hz to 10 MHz.

3. Results and discussion

3.1. Thin film fabrication

Fig. 1 shows X-ray diffraction profiles of BTN-*x*Ta ($x = 0$, 0.25, 0.4) thin films on (2 0 0) preferred $Pt/TiO_2/SiO_2/Si$ substrate using the PLD technique at 700 °C under 400 mTorr oxygen partial pressure with two laser power conditions: 0.42 W (2 J/cm^2) and 0.84 W (4 J/cm^2). All the peaks corresponded to the peak position in the JCPDS card (# 38–1329) except for the substrate and holder (marked as *). Also, the chemical composition of the BTN-*x*Ta thin films were analyzed by using EPMA and the result indicated that the composition of the each films were the same as the target composition (not shown in this study). These results demonstrate that the thin films comprise a single phase of BTN-*x*Ta without any secondary phase.

It is noticeable that the thin film's growth orientation varied according to the composition of thin film and the laser power. At first, the films with increasing Ta substitution were not grown like pure BTN-0Ta direction at 0.42 W of the laser power condition. The pure BTN-0Ta thin film had the preferred ($h\,k\,0$) orientation, but the films with increasing Ta substitution had grown in an un-preferred direction. This result may have been induced by the lattice parameter differences between BTN-*x*Ta and Pt substrate. According to JCPDS card #38–1329, pure BTN-0Ta is a tetragonal tungsten bronze structure with lattice parameters '*a*' ($a = b$) and '*c*', which are 12.5308 and 4.0094 Å, respectively. However, Ta substitution for Nb increases the '*a*' lattice parameter and decreases the '*c*' lattice parameter in bulk BTN-*x*Ta samples. The lattice parameters '*a*' and '*c*' of the BTN-0.25Ta target are 12.5625 and 3.9829, respectively. Similarly, Tsurumi and Hoshino[11] reported Ta ion substitution could induce the decrease of the '*c*' parameter and the increase of the '*a*' parameter in Ta substituted $(Ba,Sr)Nb_2O_6$ with a TTB structure. Based on these results, it is postulated that the decrease of the '*c*' lattice parameter with increasing Ta substitution can reduce the lattice mismatch with Pt (3.923 Å) substrate and lead to growth in a *c*-axis orientation.

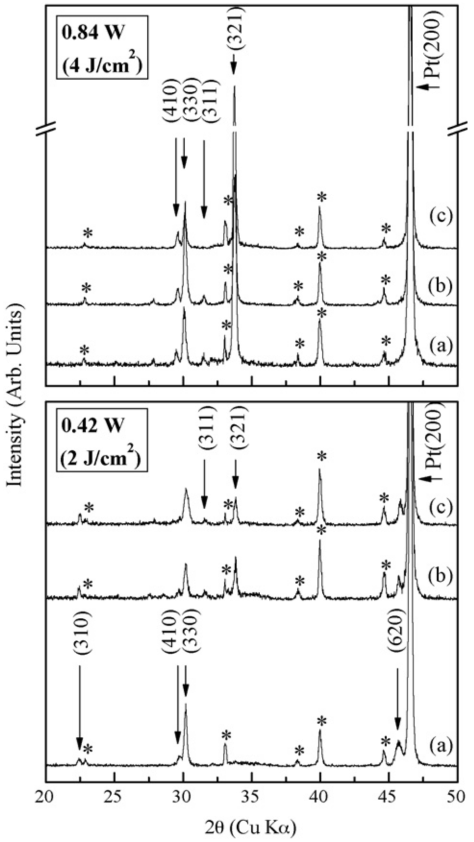

Fig. 1. XRD data of BTN-*x*Ta thin films on (2 0 0) preferred $Pt/TiO_2/SiO_2/Si$ substrate using the PLD technique at 700 °C under 400 mTorr oxygen partial pressure with 0.42 W (2 J/cm^2) and 0.84 W (4 J/cm^2); (a) $x = 0$, (b) $x = 0.25$, and (c) $x = 0.4$ (the substrate and holder are denoted by an asterisk).

In addition, the laser power affected the orientation of BTN-*x*Ta thin films. At low laser power (0.42 W), the orientation of pure BTN-0Ta thin film indicated a ($h\,k\,0$) direction. However, at high laser power (0.84 W), the growing orientation of BTN-*x*Ta thin films differed from those at low laser power and the peak of the (3 2 1) direction had a strong intensity. In other words, the films did not have a preferred orientation. It is not clear that the high laser power let the film mainly grow in the (3 2 1) direction. We think that an applied high energy of the high laser power can result in the films having a random orientation. These results indicate that the orientation of the BTN-*x*Ta films is affected by the composition of the targets as well as the applied laser power.

Fig. 2 shows the FE-SEM images of BTN-*x*Ta thin films. All the films were densely deposited on platinized Si substrates and the thickness of all the films was approximately 350–400 nm. The microstructure of the films was similar irrespective of the composition of the targets and the applied laser power.

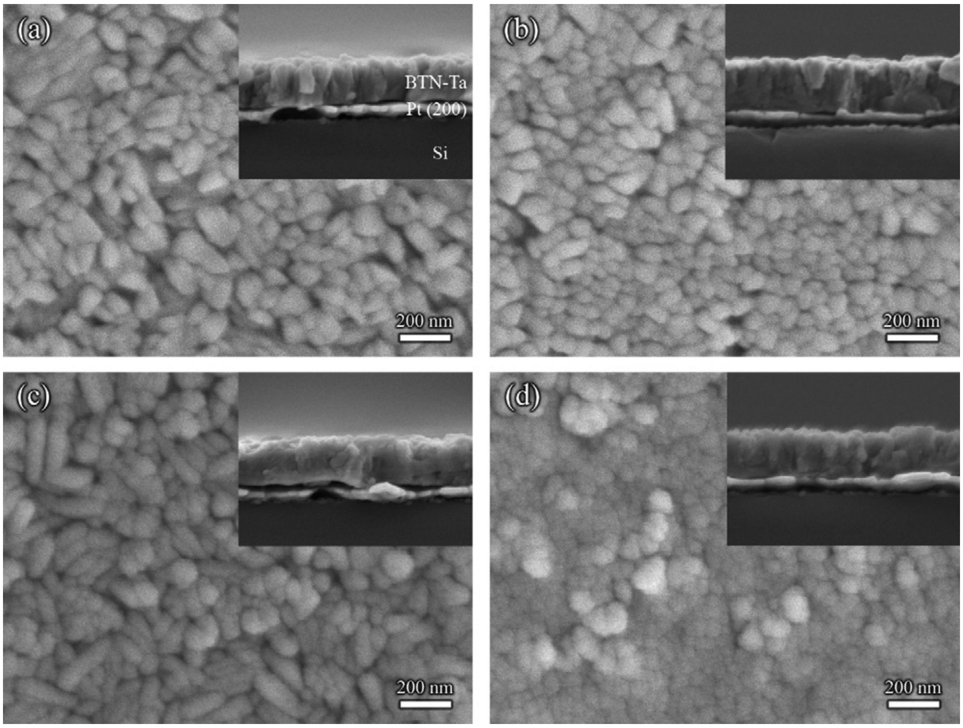

Fig. 2. SEM image of BTN-*x*Ta thin films on (2 0 0) preferred Pt/TiO$_2$/SiO$_2$/Si substrate using the PLD technique at 700 °C under 400 mTorr oxygen partial pressure and various laser power conditions; (a) $x = 0/0.84$ W, (b) $x = 0.4/0.84$ W, (c) $x = 0/0.42$ W, and (d) $x = 0.4/0.42$ W.

3.2. Dielectric properties with various Ta compositions

Fig. 3 shows the dielectric constant and dielectric loss of BTN-*x*Ta thin films on a (2 0 0) preferred platinized Si substrate via the PLD technique. At some laser power, the dielectric constant of pure BTN-0Ta thin film is higher than Ta substituted BTN-*x*Ta ($x = 0.25$, 0.4) thin films. In particular, the dielectric constant of pure BTN-0Ta thin film is the highest at 0.42 W of the laser power. The polar axis of BTN-*x*Ta is perpendicular to the substrate, and pure BTN-0Ta is deposited with long axis orientations ($h\,k\,0$) at 0.42 W of the laser power; however, Ta substituted BTN-*x*Ta thin films as well as pure BTN-0Ta deposited at a high laser power are grown with short axis orientations ($h\,k\,1$), which is verified from the XRD data shown in Fig. 1. Therefore, the pure BTN-0Ta thin film with ($h\,k\,0$) direction deposited at a low laser power may possess a higher dielectric constant than Ta substituted BTN-*x*Ta thin films with a ($h\,k\,1$) direction. This property is similar to strontium barium niobate ($Sr_{0.75}Ba_{0.25}Nb_2O_6$; SBN), which has a tetragonal tungsten bronze structure. According to Jamieson et al.[12] the polar axis of SBN is parallel to [0 0 1], so the ratio of lattice parameter (‘*c*’/‘*a*’) may be the main element of the dielectric properties.

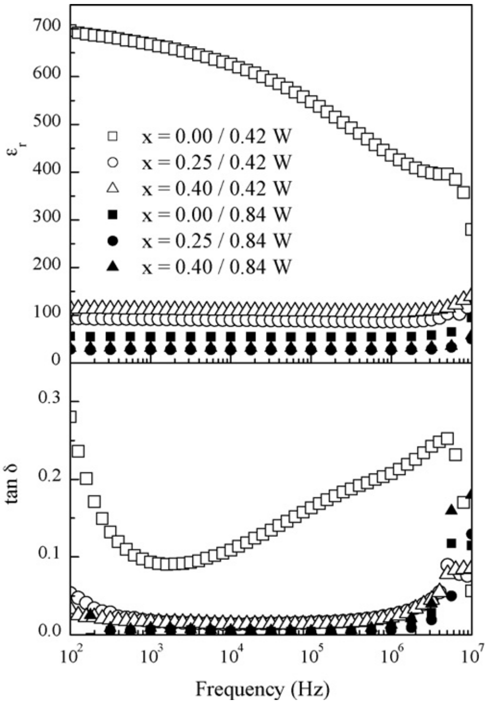

Fig. 3. Dielectric properties of BTN-*x*Ta thin films on (2 0 0) preferred Pt/TiO$_2$/SiO$_2$/Si substrate using the PLD technique at 700 °C under 400 mTorr oxygen partial pressure and various laser power conditions.

Fig. 3 shows the frequency dependence of the dielectric properties of BTN-*x*Ta thin films deposited at a low laser power (0.42 W). In the case of pure BTN-0Ta thin film, as frequency increased the dielectric constant and the dielectric loss (tan δ) is decreased and increased, respectively. However, Ta substituted BTN-*x*Ta thin films remained constant. The result may indicate that the pure BTN-0Ta thin film has an additional polarization mechanism, dipolar polarization. It is thought that pure BTN-0Ta thin film is at the ferroelectric phase, but Ta substituted BTN-*x*Ta thin films are at the paraelectric phase. In order to verify the ferro/paraelectric phase in BTN-*x*Ta thin films, the temperature coefficient of capacitance (TCC) was measured.

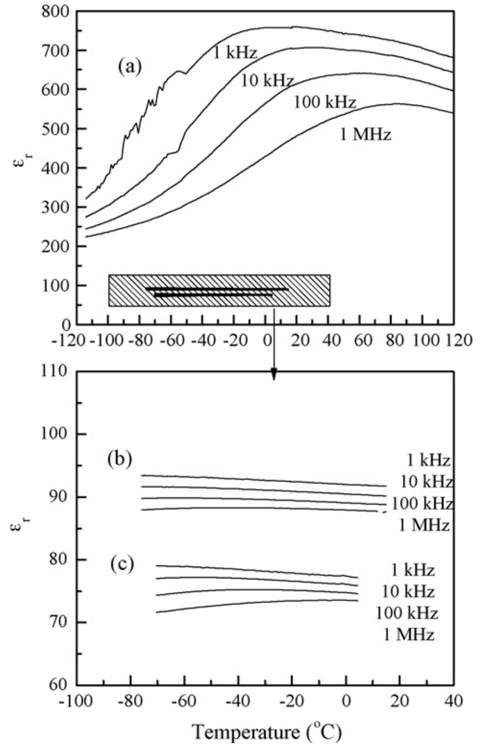

Fig. 4. TCC of BTN-*x*Ta thin films on (2 0 0) preferred Pt/TiO_2/SiO_2/Si substrate using the PLD technique at 700 °C under 400 mTorr oxygen partial pressure and 0.42 W (2 J/cm^2); (a) $x = 0$, (b) $x = 0.25$, and (c) $x = 0.4$.

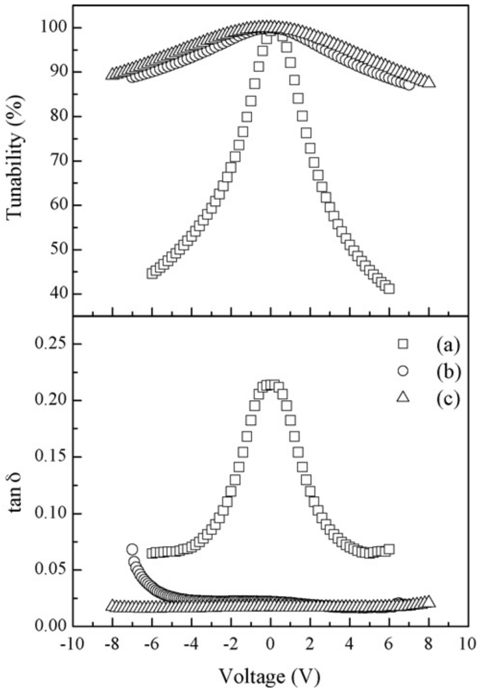

Fig. 5. Tunability and loss data of BTN-*x*Ta thin films on (2 0 0) preferred Pt/TiO_2/SiO_2/Si substrate using the PLD technique at 700 °C under 400 mTorr oxygen partial pressure and 0.42 W (2 J/cm^2); (a) $x = 0$, (b) $x = 0.25$, and (c) $x = 0.4$.

Fig. 4 shows the TCC of BTN-*x*Ta thin films deposited at a low laser power. It is clear that the critical temperature (T_c) of the pure BTN-0Ta is present at near room temperature; furthermore, the pure BTN-0Ta thin film sample shows a relaxor appearance according to frequency. However, Ta substituted BTN-*x*Ta thin films have a broad T_c located below the room temperature. Synthetically, it may be postulated that pure BTN-0Ta thin film is relaxor-ferroelectric and Ta substituted BTN-*x*Ta films are at the paraelectric phase at room temperature.

The tunability of the BTN-*x*Ta thin films deposited at low laser power is shown in Fig. 5. The tunability of pure BTN-0Ta was near 60%, and the tan δ was below 0.2; however, the tunability of Ta substituted BTN-*x*Ta thin films were below 10%. In Fig. 4, Ta substitution lowered the T_c of BTN-*x*Ta thin films. Because pure BTN-0Ta thin film has a dipole polarization mechanism at room temperature, an induced electric field may affect the dipoles and the rotation of dipoles may result in high tenability; however, the Ta substituted BTN-*x*Ta thin films lost the dipole polarization, resulting in low tunability.

4. Conclusion

BTN-*x*Ta ($x = 0$, 0.25, 0.4) thin films were deposited on (2 0 0) preferred Pt/TiO_2/SiO_2/Si substrate using the PLD technique at 700 °C under 400 mTorr oxygen partial pressure with 0.42 W (2 J/cm^2) and 0.84 W (4 J/cm^2). The pure BTN thin film deposited at 0.42 W of the laser power had the preferred orientation (*h k* 0). As a content of Ta substitution increased, the preferred growing direction was changed; i.e., from (3 3 0) to (3 2 1), which can be induced by the lattice mismatch between thin film and Pt substrate. When deposited at the laser power of 0.84 W, the BTN-*x*Ta thin films mainly showed a (3 2 1) diffraction peak, regardless of the Ta substitution. The orientation of BTN-*x*Ta thin films was affected by the composition of the targets as well as the applied laser power.

In order to investigate the composition dependence on the Ta substitution, dielectric properties were measured. The pure BTN-0Ta thin film deposited at the low laser power shows a higher dielectric constant and tunability than Ta substituted BTN-*x*Ta. From the TCC measurement, the reason may be explained: pure BTN-0Ta showed a ferroelectric phase with T_c at room temperature, but Ta substituted BTN-*x*Ta showed a paraelectric phase with T_c below room temperature. The dipole polarization, induced electric field may affect the dipoles and the rotation of dipoles may result in high tenability; however, the Ta substituted BTN-*x*Ta thin films lost dipole mobility, resulting in low tunability.

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