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Investigation on the valence state of Te ions in the $Bi_6Ti_5TeO_{22}$ thin film using X-ray photoelectron spectroscopy

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Abstract

$Bi_6Ti_5TeO_{22}$ (BTT) thin films were grown on a Pt/Ti/SiO_2/Si(1 0 0) substrate under various conditions and the valence state of the Te ion was investigated. For the BTT films grown at 300 °C, most of the Te ions existed as Te^{4+} ions. However, for the 10 mol% Mn-added BTT films grown at 300 °C, Te^{6+} ions were found even in the film grown under low oxygen partial pressure (OPP) and their number increased with increasing OPP. This increase was attributed to the presence of Mn^{2+} ions, which assisted the transition of Te^{4+} ions to Te^{6+} ions in order to maintain the charge balance of the Ti^{4+} sites. Furthermore, in the films grown at 300 °C under a high OPP of 80.0 Pa and subsequently annealed at 600 °C under a high oxygen pressure of 101 kPa, most of the Te ions existed as Te^{6+} ions. However, for the film grown at 300 °C under low OPP, even though the film was annealed under a high oxygen pressure of 101 kPa, only a few of Te^{6+} ions were formed, whereas most of Te ions remained as the Te^{4+} ions.

Keywords: $Bi_6Ti_5TeO_{22}$; X-ray photoelectron spectroscopy; Thin film

1. Introduction

The Bi_2O_3–TiO_2–TeO_2 compounds such as $Bi_2Ti_3TeO_{12}$, Bi_2TiTeO_8 and $Bi_6Ti_5TeO_{22}$ (BTT) ceramics have been investigated for the application to low temperature co-fired ceramics because of their low sintering temperature and high dielectric constant (ε_r).[1,2] Moreover, due to the low sintering temperatures of the BTT ceramics, the BTT films with a high ε_r were easily grown at low temperatures (≤300 °C).[3–5] Therefore, their electrical properties have been studied for application to the embedded decoupling capacitors for printed circuit boards and the radio frequency (RF) metal–insulator–metal capacitors in semiconductor devices which require low processing temperatures.[3–5]

It was reported that Te^{4+} ions in the Bi_2O_3–TiO_2–TeO_2 compounds were easily oxidized and transformed to Te^{6+} ions when exposed to an oxidizing atmosphere and that this transition induced a phase change.[1,2] The changes of the crystal structure and electrical properties were also observed for the BTT films grown under various oxygen partial pressures (OPPs) and they were explained by the variation of the valence state of the Te ions.[3–5] Therefore, it is important to investigate the valence state of the Te ions in order to understand the variations of the structural and electrical properties of the BTT films. For Te-based ceramics, the oxidation of the Te^{4+} ions was indirectly identified by the mass gain resulting from the Te^{4+}–Te^{6+} oxidation.[2] However, for the BTT films, the valence state of the Te ion has not been investigated systematically despite its considerable influence on the type of phase formed in the BTT films and their electrical properties.[4,5] In this work, therefore, BTT films were grown under various process conditions using RF magnetron sputtering or pulsed laser deposition (PLD). The valence state of the Te ions in these films were investigated using X-ray photoelectron spectroscopy (XPS) and the relation between the crystal structure of the films and the valence of the Te ions was also studied.

2. Experimental procedures

The BTT or the 10 mol% Mn-doped BTT films were grown at 300 °C on a Pt/Ti/SiO_2/Si(1 0 0) substrate using RF magnetron

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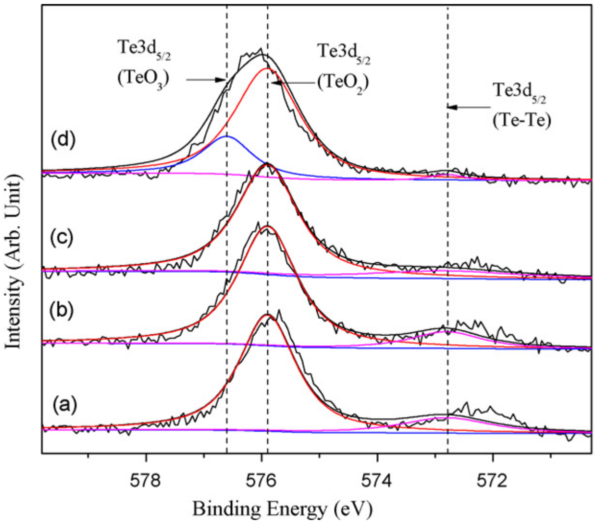

Fig. 1. XPS spectra of the Te $3d_{5/2}$ spin-orbital taken from the BTT films grown at 300 °C under an OPP of (a) 0.21 Pa, (b) 0.32 Pa, (c) 0.48 Pa and (d) 0.59 Pa by using RF sputtering.

sputtering and PLD. Three-inch diameter BTT or 10 mol% Mn-doped BTT targets for the sputtering were synthesized using the conventional solid-state method. Deposition was carried out at 300 °C in various mixed oxygen and argon atmospheres with a total pressure of 1.07 Pa and a sputtering power of 100 W. For the PLD, a Nd-YAG laser beam (NL303HT, EKSPLA, Lithuania) with a wavelength of 266 nm (the fourth harmonic generation, FHG), a repetition rate of 10 Hz and an energy fluency of 4 J/cm^2 was focused on the sintered BTT ceramic target rotating in a vacuum chamber under OPPs of 9.3–80.0 Pa. The films were annealed at 600 °C under various oxygen pressures. The film structure was examined by X-ray diffraction (XRD: Rigaku D/max-RC). XPS (VG Scientific, ESCALAB250) measurements were conducted to obtain information on the valence state of the Te ion.

3. Results and discussion

Fig. 1(a)–(d) shows the XPS spectra of the Te $3d_{5/2}$ spin-orbital taken from the BTT films grown at 300 °C under various OPPs using RF magnetron sputtering. The peaks at 576.6, 575.9 and 572.8 eV correspond to TeO_3, TeO_2 and metallic Te, respectively. For the films grown under OPPs <0.59 Pa, only the TeO_2 peak was observed, indicating that most of the Te ions existed as Te^{4+} ions in these films. However, when OPP was increased to 0.59 Pa, the TeO_3 peak appeared, as shown in Fig. 1(d), suggesting that some of the Te^{4+} ions were transformed to Te^{6+} ions in the film grown under 0.59 OPP. According to our previous work, for the films grown at 300 °C, an amorphous phase was observed with a small amount of crystalline phase which was considered to be a cubic BTT phase, in which Te ions existed as Te^{6+} ions.[3] However, since the XPS results implied that most of the Te ions existed as Te^{4+} ions for the films grown at 300 °C, the possibility that some of this crystalline phase may have been a bismuth-layered, orthorhombic $Bi_4Ti_3O_{12}$ (pseudo-$Bi_4Ti_3O_{12}$) phase with the composition of the $Bi_4(Ti_{3-x}Te_x)O_{12}$ cannot be ignored.

The valence state of the Te ions in the 10 mol% Mn-doped BTT films grown at 300 °C under various OPPs was also investigated, as shown in Fig. 2(a)–(d). Contrary to the pure BTT films, a TeO_3 peak was observed, even for the film grown under the low OPP of 0.21 Pa, as shown in Fig. 2(a), and its intensity increased with increasing OPP. This result indicated that Te^{6+} ions already existed in the film grown under the low OPP. In general, Mn ions take one of three valence states, Mn^{2+}, Mn^{3+} and Mn^{4+}, and the Mn ions in the BTT film were known to exist as Mn^{2+} and acted as acceptors, thereby decreasing the leakage current density.[5] Therefore, when Mn^{2+} ions occupied the Ti^{4+} site, some of the Te ions in the Ti^{4+} sites were considered to exist as Te^{6+} ions instead of Te^{4+} ions so that the charge valence of the Ti^{4+} site was maintained. Therefore, the presence of the Mn^{2+} ions expedited the transition of Te^{4+} ions to Te^{6+} ions.

The relation between the phase change and the valence of the Te ions was investigated using the BTT films grown by PLD because it was relatively easy to obtain a homogeneous BTT crystalline phase for the film grown by PLD. Fig. 3(a) shows the XRD pattern of the BTT film deposited at 300 °C under 80.0 Pa OPP using PLD. No peaks for the crystalline phase were observed in this film, but a broad peak was found at around 28 degree, indicating that this film consisted of an amorphous phase with a small amount of small crystals. When this film was annealed at 600 °C under a high oxygen pressure of 101 kPa, the crystalline BTT phase was formed, as shown in Fig. 3(b). However, for the film grown under a low OPP of 53.3 Pa and subsequently annealed at 600 °C under a high oxygen pressure of 101 kPa, peaks for both BTT and pseudo-$Bi_4Ti_3O_{12}$ phases were found. According to the previous works, Te^{6+} ions in a Te-based compound are easily transformed to Te^{4+} ions under low oxygen pressure and induced phase transition.[6–8] Therefore, the variation of the crystalline phase formed in the film was considered to be related to the valence of the Te ions. XPS analysis was conducted on these films to clarify the valence state of the Te ions and thereby to understand the phase change of the film.

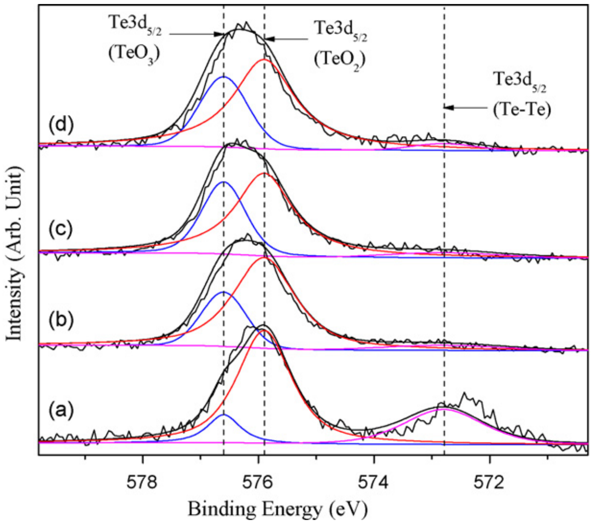

Fig. 2. XPS spectra of the Te $3d_{5/2}$ spin-orbital taken from the 10 mol% Mn-doped BTT films grown at 300 °C under an OPP of (a) 0.21 Pa, (b) 0.32 Pa, (c) 0.48 Pa and (d) 0.59 Pa by using RF sputtering.

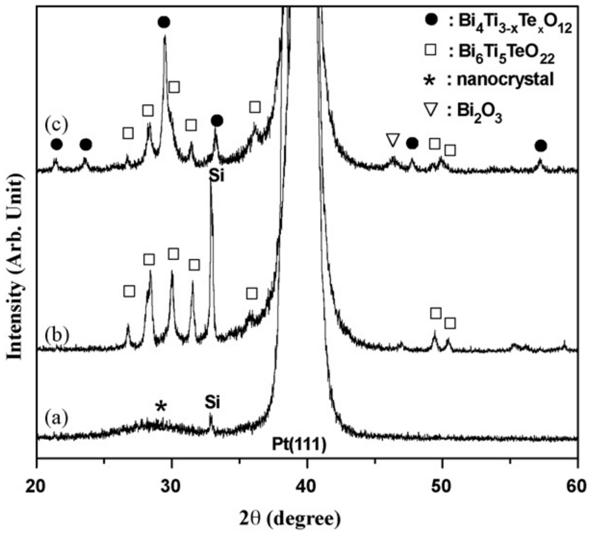

Fig. 3. (a) XRD pattern of the films deposited at 300 °C under 80.0 Pa OPP using PLD and XRD patterns of the films deposited at 300 °C under various OPPs using PLD and subsequently annealed at 600 °C under 101 kPa oxygen pressure: (b) 80.0 Pa and (c) 53.3 Pa.

Fig. 4(a) shows the XPS spectrum of the film deposited at 300 °C under 80.0 Pa OPP using PLD. The observed TeO_2 peak indicated that the Te ions existed as Te^{4+} ions. However, when this film was annealed at 600 °C under a high oxygen pressure of 101 kPa, most of the Te ions existed as Te^{6+} ions and only a few as Te^{4+} ions, as shown in Fig. 4(b). According to the XRD result, the cubic BTT crystalline phase was observed in this film, indicating that the Te^{4+} ions in the film grown at 300 °C were transformed to Te^{6+}, resulting in the formation of the BTT crystalline phase. On the other hand, for the film grown under a low OPP of 53.3 Pa and annealed at 600 °C under a high oxygen pressure of 101 kPa, most of the Te ions existed as Te^{4+} but a few Te^{6+} ions were also found, as shown in Fig. 4(c). According to the XRD result, both BTT and pseudo-$Bi_4Ti_3O_{12}$ phases were observed in this film and their formations were attributed to the Te^{6+} and Te^{4+} ions, respectively. These results confirmed the presence of Te^{4+} ions even though the film was grown under a high OPP of 80.0 Pa. However, they were transformed to Te^{6+} ions, thereby forming the BTT crystalline phase, after annealing under high oxygen pressure of 101 kPa. However, for the film grown under a low OPP of 53.3 Pa, even though this film was annealed under a high oxygen pressure of 101 kPa, most of the Te^{4+} ions maintained their valence, thereby forming the pseudo-$Bi_4Ti_3O_{12}$ phase, although a few of the Te^{4+} ions were transformed to Te^{6+} ions and developed the BTT crystalline phase. Therefore, the OPP during the growth stage considerably influenced the valence state of the Te ions and hence the crystal structure of the films.

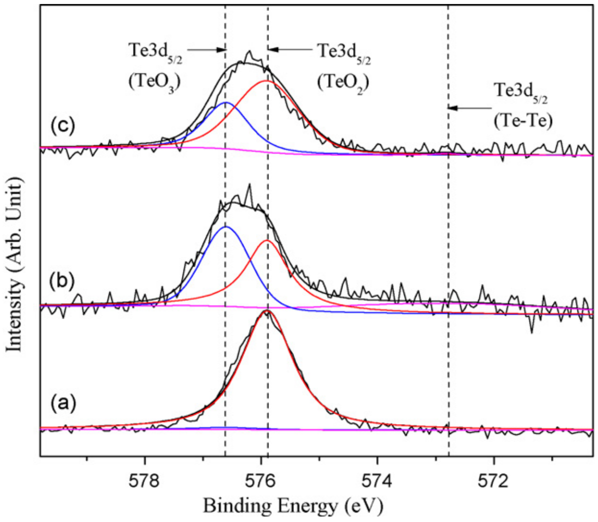

Fig. 4. XPS spectra of the Te $3d_{5/2}$ spin-orbital taken from (a) the film deposited at 300 °C under 80.0 Pa OPP using PLD and the films deposited at 300 °C under various OPPs using PLD and subsequently annealed at 600 °C under 101 kPa oxygen pressure: (b) 80.0 Pa and (c) 53.3 Pa.

4. Conclusions

Te ions existed as Te^{4+} ions in films grown at 300 °C under low OPPs ($\leq$0.59 Pa) using RF magnetron sputtering but a few of the Te^{4+} ions were transformed to Te^{6+} ions for the film grown under a high OPP of 0.59 Pa. However, for the 10 mol% Mn-doped BTT films, Mn^{2+} ions in the Ti^{4+} sites assisted the transition of Te^{4+} ions to Te^{6+} ions in order to maintain the charge balance of Ti^{4+} sites, so that Te^{6+} ions were formed in the film grown under a low OPP of 0.21 Pa and their number increased with increasing OPP. The Te ions also existed as Te^{4+} ions for the films grown at 300 °C under an OPP of 80.0 Pa using PLD. When this film was subsequently annealed under a high oxygen pressure of 101 kPa, most of the Te^{4+} ions were transformed to Te^{6+} ions during the annealing, resulting in the formation of the BTT phase with cubic structure. However, for the film grown at a low OPP of 53.3 Pa, even though the film was annealed under a high oxygen pressure of 101 kPa, only a few of the Te^{4+} ions were transformed to Te^{6+} ions, thereby forming the cubic BTT crystal, but the remnant Te^{4+} ions formed the pseudo-$Bi_4Ti_3O_{12}$ crystalline phase. Therefore, the level of OPP during the growth stage considerably influenced the valence of Te ions and thereby the crystal structure of the film.

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