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Preparation and Properties of Nd-Substituted $Bi_4Ti_3O_{12}$-$SrBi_4Ti_4O_{15}$ Thin Films by Chemical Solution Deposition

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Ferroelectric $Bi_4Ti_3O_{12}$-$SrBi_4Ti_4O_{15}$ (BiT-SBTi) thin films have been prepared by the chemical solution deposition method on $Pt/TiO_x/SiO_2/Si$ substrates. In this study, the effect of Nd substitution into BiT-SBTi on the crystallization, the surface morphology and the ferroelectric properties was examined. Homogeneous and stable precursor solutions were prepared by controlling the reaction of starting metal-organic compounds in solution. BiT-SBTi precursor films were found to crystallize in the intergrowth BiT-SBTi structure on the substrates. BiT-SBTi thin films with an optimum Nd substitution in amount exhibited the ferroelectric properties with a 2Pr value of 30 $\mu C/cm^2$. Furthermore, the surface morphology of synthesized thin films was also improved by controlling the amount of Nd substitution.
Keywords : $Bi_4Ti_3O_{12}$-$SrBi_4Ti_4O_{15}$, thin film, intergrowth, chemical solution deposition, Nd substitution, ferroelectric properties

1. INTRODUCTION

Recently, intergrowth $Bi_4Ti_3O_{12}$-$SrBi_4Ti_4O_{15}$ (BiT-SBTi)-based compounds have attracted considerable attention for their application in various electronic thin film devices, such as nonvolatile ferroelectric random access memories, due to their larger ferroelectricity compared with BiT and SBTi.[1-4] Also, recent research studies revealed that the microstructures and ferroelectric properties of Nd-substituted BiT-based thin films were greatly improved compared with those of non-substituted BiT.[5-8]

The chemical solution deposition (CSD) method using metal-organic compounds is considered to be useful for low-temperature fabrication and precise control of chemical composition including homogeneous doping to thin films.

Therefore, in this work, fabrication and characterization of Nd-substituted $Bi_4Ti_3O_{12}$-$SrBi_4Ti_4O_{15}$ (BN_xT-SBN_yT : $x+y = 0$, 0.75, 1.0, 1.5) thin films on $Pt/TiO_x/SiO_2/Si$ substrates have been carried out by the chemical solution deposition method. The effects of Nd substitution into BiT-SBTi on the crystallization and the surface morphology of crystallized films were investigated. The electrical properties of BiT-SBTi thin films were also evaluated.

2. EXPERIMENTAL PROCEDURE

Experimental procedure for preparing $Bi_{4-x}Nd_xTi_3O_{12}$-$SrBi_{4-y}Nd_yTi_4O_{15}$ (BN_xT-SBN_yT) precursor solutions and thin films is shown in Fig.1. $Sr(O^iPr)_2$, $Bi(O^tAm)_3$, $Ti(O^iPr)_4$ and $Nd(OAc)_3$ were selected as starting materials.

2-Methoxyethanol was dried over molecular sieve and distilled prior to use. The desired amounts of $Sr(O^iPr)_2$, $Ti(O^iPr)_4$, $Nd(OAc)_3$ and $Bi(O^tAm)_3$ with 3% Bi excess composition were dissolved in 2-methoxyethanol. The mixed solution was refluxed for 20h yielding a homogeneous solution. The entire procedure was performed in a dry N_2 atmosphere. The precursor solution was concentrated to approximately 0.1M by removal of the solvent by vacuum evaporation.

BN_xT-SBN_yT precursor films were prepared by spin-coating on $Pt/TiO_x/SiO_2/Si$ substrates using the BN_xT-SBN_yT precursor solutions. As-deposited precursor films were dried at 150℃ for 5 min and calcined at 350℃ for 10 min by rapid thermal annealing (RTA) at a rate of 100℃ /min in an O_2 flow. And then, they were crystallized at 750℃ for 30 min by RTA at a rate of 180℃/min. Film thickness was adjusted to 250 nm by repeating coating/calcining process.

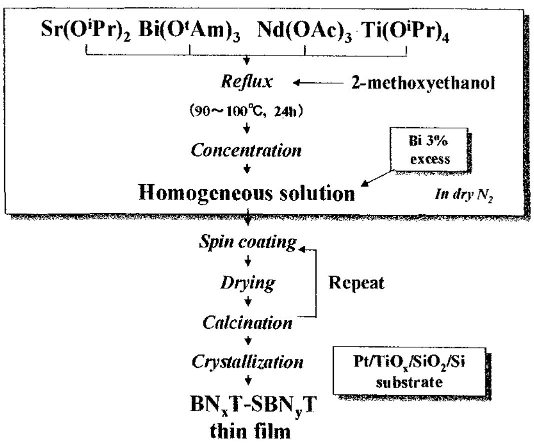

Fig.1 Experimental procedure for preparing BN_xT-SBN_yT precursor solutions and thin films.

The crystallographic phases of prepared thin films were identified by X-ray diffraction (XRD) analysis using CuKα radiation with a monochromator. The surface morphology of thin films was observed using an atomic force microscope (AFM). Pt top electrodes were deposited onto the surface of the films by DC sputtering, followed by annealing at 600℃ for 10 min. The ferroelectric properties of the films were evaluated using a ferroelectric test system at 100Hz and room temperature.

3. RESULTS AND DISCUSSION

3.1 Synthesis of BN_xT-SBN_yT thin films

Figure 2 illustrates XRD profiles of BN_xT-SBN_yT (x+y=0, 0.75, 1.0, 1.5) thin films prepared at 750℃ on $Pt/TiO_x/SiO_2/Si$ substrates. These films crystallized into Bi-layered perovskite single-phase and exhibited random orientation with an enhanced 118 reflection. As amount of Nd substitution increased ($x+y \geqq 1.0$), crystallinity of thin films gradually decreased. The full width at half maximum of 118 diffraction peak increased from approximately 0.02° (x+y=0) to more than 0.03° (x+y=1.5). In this study, crystallization in the intergrowth BiT-SBTi structure was also confirmed by identification of magnified 003 and 005 reflections of BiT-SBTi phase from 2θ = 5 to 15°.

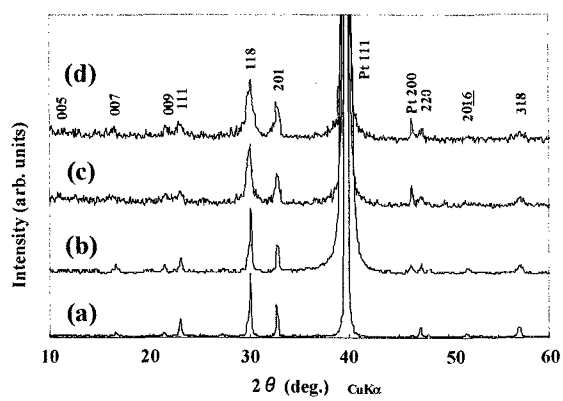

Fig.2 XRD profiles of BN_xT-SBN_yT thin films crystallized at 750℃ on $Pt/TiO_x/SiO_2/Si$ substrates, (a) x+y=0, (b) x+y=0.75, (c) x+y=1.0 and (d) x+y=1.5.

3.2 Surface morphology of BN_xT-SBN_yT thin films

Figure 3 shows AFM images of BN_xT-SBN_yT (x+y=0, 0.75, 1.0, 1.5) thin films prepared at 750℃ on $Pt/TiO_x/SiO_2/Si$ substrates. Non-substituted BiT-SBTi thin film consisted of large grains (grain size: approximately 200 nm) with rough surface (RMS (root mean square) value: 10.5 nm) and showed inhomogeneous microstructure (Fig.3(a)). On the other hand, BN_xT-SBN_yT ($x+y \leqq 1.0$) thin films exhibited different surface morphologies, although they had the similar grain size (180-200 nm). As the Nd substitution further increased in amount ($x+y \geqq 1.0$), grain size of the synthesized films gradually decreased to less than 110 nm. Also, with increasing Nd content, BN_xT-SBN_yT thin films showed not only the homogeneous microstructure but also the relatively uniform and isotropic grain shape compared with those of non-substituted BiT-SBTi. Among them, BN_xT-SBN_yT ($x+y=0.75$) thin film had the homogeneous and smooth surface (RMS value: 5.9 nm) with relatively large uniform grains. It turns out from Fig.3 that the nucleation and growth process of the BN_xT-SBN_yT thin films is found to be strongly affected by Nd content.

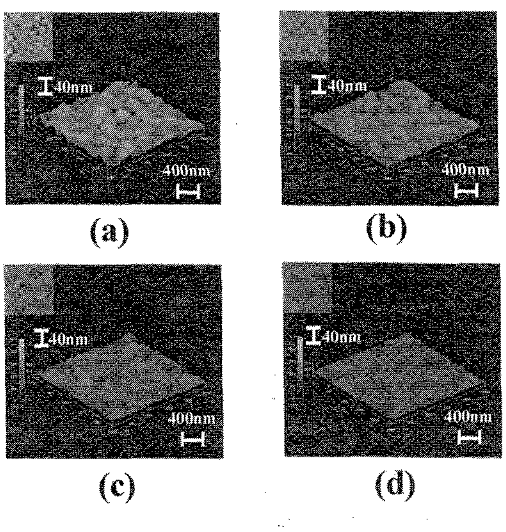

Fig.3 AFM images of BN_xT-SBN_yT thin films crystallized at 750℃ on $Pt/TiO_x/SiO_2/Si$ substrates, (a) x+y=0, (b) x+y=0.75, (c) x+y=1.0 and (d) x+y=1.5.

3.3 Ferroelectric properties of synthesized films

P-E hysteresis measurement was performed to characterize the ferroelectric properties of the synthesized BN_xT-SBN_yT thin films. Figure 4 shows P-E hysteresis loops of the BN_xT-SBN_yT (x+y=0, 0.75, 1.0, 1.5) thin films prepared at 750℃ on $Pt/TiO_x/SiO_2/Si$ substrates. These films are approximately 250 nm in thickness. In this case, the measurement was performed at an applied voltage of 10V and a frequency of 100Hz, and at room temperature. The remanent polarization (Pr) and coercive field (Ec) of non-doped BiT-SBTi thin film prepared at 750℃ were 10 $\mu C/cm^2$ and 150 kV/cm, respectively. The ferroelectricity of the film was improved by forming the BiT-SBTi structure, because both BiT and SBTi thin films prepared by the same process exhibited the Pr values around 5.0 $\mu C/cm^2$ at 10V. On the other hand, BN_xT-SBN_yT (x+y=0.75, 1.0, 1.5) thin films showed the Pr values of 15, 11, 5.0 $\mu C/cm^2$, respectively. Higher Pr value than that of non-doped BiT-SBTi thin film was achieved by the Nd doping. Among several Nd-doped BiT-SBTi thin films, the BN_xT-SBN_yT (x+y=0.75) thin film revealed superior Pr and Ec values to the others. This can be explained by both the change in tilting of TiO_6 octahedron in the BiT-SBTi structure by Nd substitution and the microstructure of the crystallized films as shown in Fig.3. Since BN_xT-SBN_yT (x+y=0.75) thin film had a high crystallinity and a homogeneous and smooth surface with relatively uniform large grains, the ferroelectricity was higher than that of non-doped BiT-SBTi thin film because of the optimal Nd substitution into BiT-SBTi. The lower Pr value of BN_xT-SBN_yT ($x+y \geqq 1.0$) thin film was due to the microstructure composed of small grains compared with that of BN_xT-SBN_yT (x+y=0.75) thin film. However, the squareness of P-E hysteresis loops and the E_c values were insufficient. Further investigations, such as improvement of ferroelectric properties, low temperature fabrication of BiT-SBTi-based thin films and evaluation of fatigue properties are now in progress.

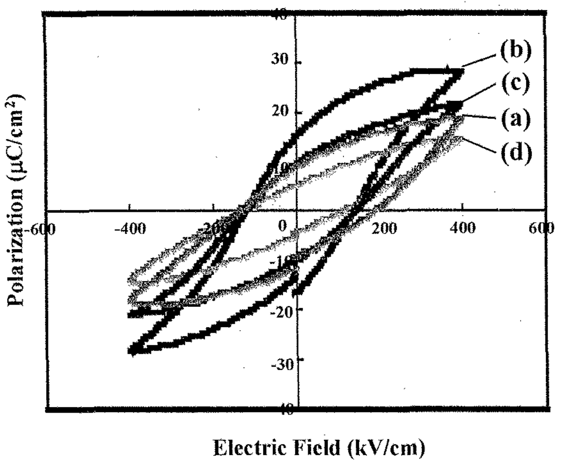

Fig.4 P-E hysteresis loops of BN_xT-SBN_yT thin films crystallized at 750℃ on $Pt/TiO_x/SiO_2/Si$ substrates, (a) x+y=0, (b) x+y=0.75, (c) x+y=1.0 and (d) x+y=1.5.

4. CONCLUSIONS

Ferroelectric Nd-substituted BiT-SBTi thin films were successfully synthesized from metal-organic precursor solutions. Synthesized thin films crystallized into the intergrowth BiT-SBTi single-phase on $Pt/TiO_x/SiO_2/Si$ substrates at 750℃. BiT-SBTi thin films with an optimum Nd substitution (in this case, $Bi_{4-x}Nd_xTi_3O_{12}$-$SrBi_{4-y}Nd_yTi_4O_{15}$: x+y=0.75) were found to exhibit the homogeneous surface morphology and superior ferroelectric properties (2Pr: 30 μC/cm²). Nd-substituted BiT-SBTi thin films developed in this study have a potential for applications in several ferroelectric thin film devices.

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