Effect of vanadium content on remanent polarization in bismuth titanate thin films prepared by liquid source misted chemical deposition

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$Bi_{4-x/3}Ti_{3-x}V_xO_{12}$ (BTV) ferroelectric thin films were fabricated by liquid source misted chemical deposition. The substitution of vanadium for titanium site changed the crystalline orientation and surface morphology of the thin film, which in turn influenced the remanent polarization (P_r). $2P_r$ of BTV thin film increased with increase of vanadium content and reached a maximum value (21.5 $\mu C/cm^2$) at $x=0.03$, as this corresponded with the largest degree of *a*-axis orientation. However, at $0.05 \leqslant x \leqslant 0.09$, $2P_r$ reduced with decrease in the degree of *a*-axis orientation. These results indicate that the P_r of the films is dependent on the degree of *a*-axis orientation. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2432226]

Ferroelectric materials have been studied extensively, primarily owing to their applicability as capacitors in ferroelectric random access memory.[1,2] This memory has a nonvolatile characteristic while offering the merits of dynamic random access memory including high-speed read/write and high degree of integration.

Among various ferroelectric materials, $Pb(Zr,Ti)O_3$ (PZT) has been widely investigated because PZT offers the advantages of large remanent polarization (P_r) (20–70 $\mu C/cm^2$) and low processing temperature (500–600 °C).[3,4] However, it has a fatal problem regarding fatigue endurance beyond 10^6–10^7 read/write cycles.[5] To overcome this problem, the utilization of bismuth-layer-structured ferroelectrics including $SrBi_2Ta_2O_9$ (SBT) and $Bi_4Ti_3O_{12}$ (BTO) has been proposed. However, rather than improve fatigue properties, SBT carries the disadvantages of high processing temperature (750–850 °C) and relatively small P_r (4–16 $\mu C/cm^2$).[6–9] On the other hand, BTO can be synthesized at low processing temperature (700 °C).[10,11] Unfortunately, the ferroelectric BTO film exhibits small P_r (5–8 $\mu C/cm^2$) and poor fatigue endurance properties due to the instability of TiO_6 and the volatility of Bi.[4,12,13] To improve the P_r and fatigue endurance of BTO, many research groups have performed the substitution of lanthanide atoms for the Bi site in BTO.[14–19] It has also been reported that the substitution of higher-valent cations such as V^{5+}, W^{6+}, and Nb^{5+} for the Ti^{4+} site could improve P_r.[12,13,20–22]

In the present work, we fabricated $Bi_{4-x/3}Ti_{3-x}V_xO_{12}$ (BTV) using liquid source misted chemical deposition (LSMCD) as a function of vanadium content ($x=0$–0.09). We also investigated the influence of vanadium content on the ferroelectric properties and crystalline orientation of the fabricated films.

In LSMCD, mists of complex precursors are generated from a liquid mixture via an ultrasonic nebulizer. The size of the mist (1–5 μm) is much smaller than that of droplets (20–100 μm) generated during sol-gel coating processes. Therefore, this technique can provide better thickness uniformity and higher film density. This leads to improvement of the interface adhesion between the film and substrate compared with the conventional sol-gel deposition process. In addition, LSMCD allows control of the chemical composition at a ppm level through precise weighing of the metal precursors in fabricating the solution. These characteristics of LSMCD have been demonstrated in synthesizing various thin film materials such as the cathode films of lithium ion batteries, dielectric thin films, etc.[23–26]

For the fabrication of BTV thin films, bismuth nitrate $[Bi(NO_3)_3 \cdot 5H_2O]$, titanium isopropoxide $[Ti(O^iC_3H_7)_4]$, and vanadium oxytriisopropoxide $[(C_3H_7O)_3VO]$ were used as metal precursors. Each metal precursor was dissolved in 2-methoxyethanol. Here, we made a 14% bismuth excess metal precursor solution to compensate bismuth loss during the annealing process. Each metal precursor solution was mixed and then a small amount of 2-ethylhexanoic acid was added as a chelating agent. The resultant solution was converted to mist by an ultrasonic nebulizer (frequency: 1.65 MHz). The generated mists were transported to (111) $Pt/TiO_2/SiO_2/Si$ substrate placed on a substrate holder in a vacuum chamber by Ar carrier gas and deposited for 2 min and 30 s. The deposited BTV films were dried at 230 °C for 2 min. The deposition and drying steps were repeated as necessary to obtain the desired thickness (300 nm). After these processes, the film was baked at 400 °C for 10 min and annealed at 700 °C for 1 h under an oxygen atmosphere in a furnace.

Figure 1 shows x-ray diffraction (XRD, Rigaku, D/max-rc Cu $K\alpha=1.5405$ Å) patterns of BTV films as a function of vanadium content. According to the XRD results, there was an intermediate $Bi_2Ti_2O_7$ phase detected in the $Bi_4Ti_3O_{12}$ thin film and disappeared with the increase of vanadium content up to 0.07, revealing that the substitution of vanadium ion for the Ti site would be beneficial for the transformation of the $Bi_2Ti_2O_7$ phase into the $Bi_4Ti_3O_{12}$ phase. However, at $x=0.09$, the reappearance of the $Bi_2Ti_2O_7$ phase is attributed to solid solution limitation of vanadium on the basis of the fact that only a small amount (<0.08) of Ge, Sn, Hf, and Zr could substitute for the Ti site in bismuth titanate.[27] It is difficult to make sure that another impurity

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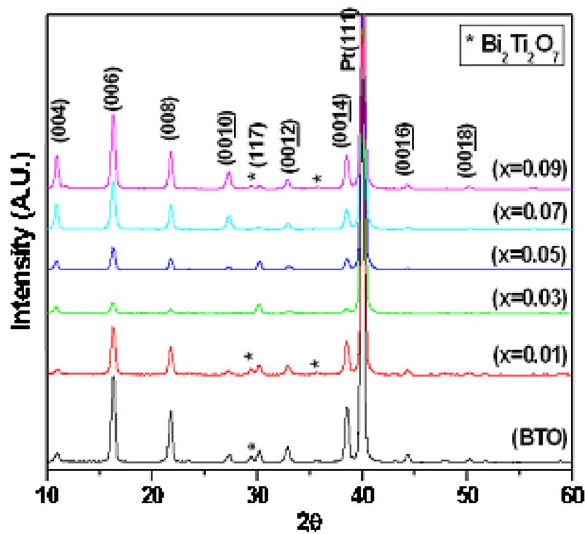

FIG. 1. (Color online) XRD patterns of $Bi_{4-x/3}Ti_{3-x}V_xO_{12}$ films as a function of vanadium content (x=0.00, 0.01, 0.03, 0.05, 0.07, and 0.09).

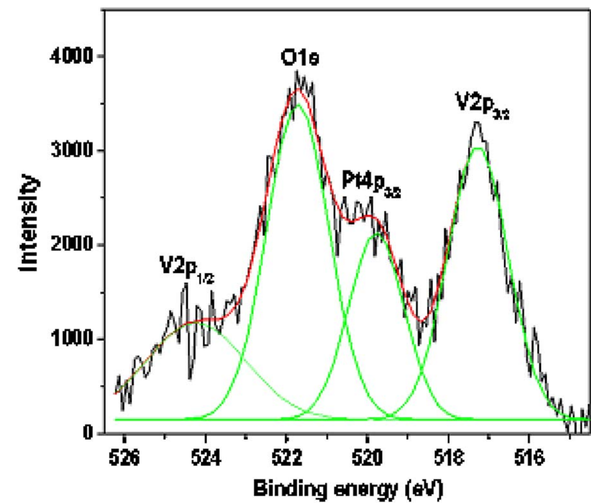

FIG. 2. (Color online) XPS spectrum of BTV of thin film (x=0.07).

phase except for the $Bi_2Ti_2O_7$ phase did not exist at x=0.09, because of the limitation of the intensity of the XRD peak detected. In fact, it was reported that BTV with x=0.08 had the impurity phase, $Bi_{2.45}Ti_{4.05}V_{0.09}O_{12}$.[28]

The BTO film showed highly c-axis oriented crystalline growth. The (00n) diffraction peak of BTV films was suppressed with increasing vanadium content and reached the minimum peak intensity at x=0.03. In a range of x between 0.05 and 0.09, the c-axis orientation increased again. These results indicate that a small amount of vanadium substitution for the Ti site (x=0.03) minimizes the degree of c-axis orientation in the BTV films. Bismuth perovskite structured ferroelectrics show an anisotropic property in P_s. The P_s is 50 $\mu C/cm^2$ along the a axis but no less than 4 $\mu C/cm^2$ along the c axis.[2] Therefore, the degree of a-axis orientation is an important factor with respect to obtaining large P_r. In the XRD pattern, the (117) diffraction peak is the most closely related to the a-axis orientation. To quantify the degree of a-axis orientation, we introduced the parameter $R_{(117)}$. $R_{(117)}$ can be calculated by the equation $R_{(117)} = I(117)/[I(006)+I(117)]$, where $I(117)$ and $I(006)$ are the intensities of the (117) and (006) peaks, respectively. As shown in Table I, the BTV film of x=0.03 shows the maximum $R_{(117)}$ value.

The variation of a-axis orientation is due to the fact that the substitution of vanadium for the Ti site in $Bi_4Ti_3O_{12}$ induces the TiO_6 octahedron tilting. This is attributed to the smaller ionic radius and higher oxidation state of vanadium compared with Ti (Fig. 2). In addition, this is proven by the morphological change shown in the scanning electron microscopy (SEM) image (Fig. 3).

To verify that the oxidation state of vanadium in BTV thin film is higher than that in Bi^{3+}, x-ray photoelectron spectroscopy (XPS) was performed, as the substituted vanadium ions can have various oxidation states such as V^{5+}, V^{4+}, and V^{3+}. As shown in Fig. 2, the peaks of $V2p_{3/2}$ and $V2p_{1/2}$ of the BTV thin film of x=0.07 were found at 524.3 and 517.3 eV, respectively. It was reported that $V2p_{3/2}$ of V^{5+}, V^{4+}, V'^{3+}, and V^{0+} have binding energies of 517.7, 515.8, 515.3, and 512.4 eV, respectively.[29] Hence, it can be concluded that the oxidation state of the vanadium ion in the BTV film is +5. The oxygen vacancy of BTO arising from Bi loss during the annealing process can be removed by doping a small amount of V^{5+}, because the oxidation state of V^{5+} is higher than that of Bi^{3+}.

TABLE I. Calculated $R_{(117)}$ of $Bi_{-x/3}$ Ti_{3-x} V_xO_{12} films (x=0.00, 0.01, 0.03, 0.05, 0.07, and 0.09).

		BTV				
Samples	BTO	(x=0.01)	(x=0.03)	(x=0.05)	(x=0.07)	(x=0.09)
$R_{(117)}$	0.124	0.134	0.440	0.272	0.038	0.030

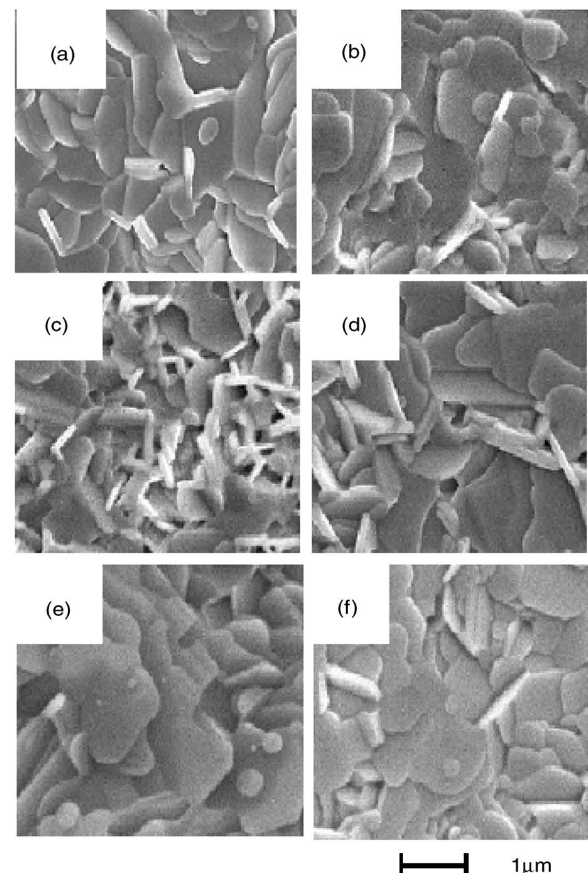

FIG. 3. SEM images of $Bi_{4-x/3}Ti_{3-x}V_xO_{12}$ films: (a) x=0.00, (b) x=0.01, (c) x=0.03, (d) x=0.05, (e) x=0.07, and (f) x=0.09.

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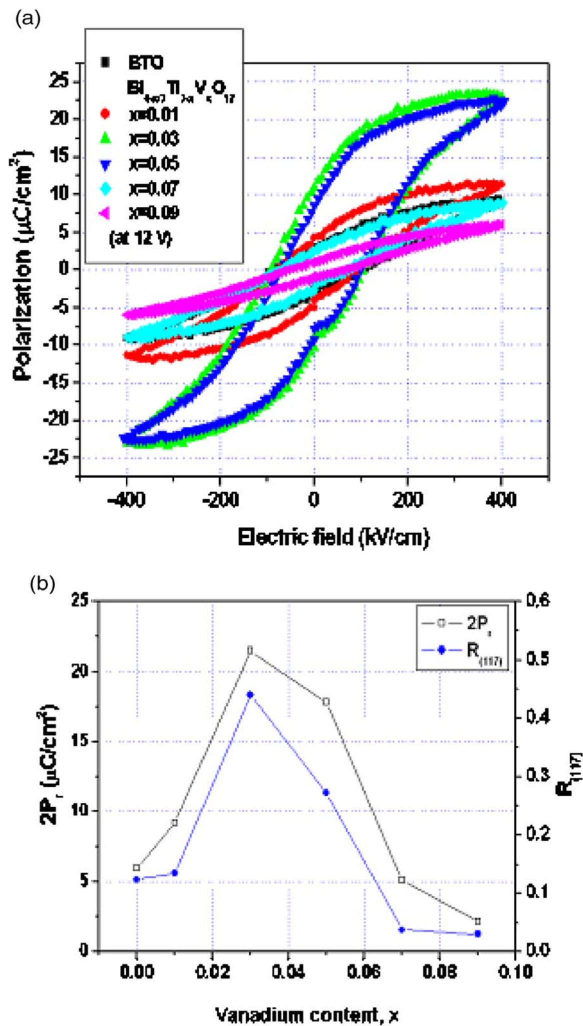

FIG. 4. (Color online) (a) *P-E* hysteresis loops of BTV films and (b) $2P_r$ as a function of vanadium content x at 12 V.

Figure 3 shows the surface morphologies of BTV films visualized by SEM (Philips 533M). According to the SEM images, the $Bi_4Ti_3O_{12}$ film mainly consists of platelike grains showing preferential growth in the *c*-axis orientation.[13] However, the surface morphology transformed at $x=0.03$. At $x=0.03$, platelike grains and rodlike grains coexist; however, the number of platelike grains increased gradually with increasing vanadium content in a range of V content between 0.05 and 0.09. This morphological transformation is in accordance with the XRD patterns, given that the platelike morphology indicates *c*-axis oriented crystalline growth.

A ferroelectric tester (RT66A, Radiant Technology) was used to obtain *P-E* hysteresis loops. Figure 4(a) shows *P-E* hysteresis loops and $2P_r$ of the BTV films as a function of vanadium content at an applied voltage=12 V. The BTV films (x=0.03 and 0.05) show large P_r. In particular, $Bi_{3.99}Ti_{2.97}V_{0.03}O_{12}$ film shows the largest $2P_r$, 21.5 $\mu C/cm^2$. For x larger than 0.03, $2P_r$ showed a gradual decrease. This trend of P_r is similar to that of the $R_{(117)}$ parameter of the XRD pattern, as shown in Fig. 4(b). Therefore, the P_r of BTV was determined to be dependent on the degree of *a*-axis orientation.

This result is different from the BTV powder data reported by Noguchi and Miyayama, where $2P_r$ increased gradually from 30 to 40 $\mu C/cm^2$ as the vanadium content of x increased from 0.012 to 0.06, and P_r saturated when x was greater than 0.06. This is due to the fact that powder samples do not have a preferred orientation of crystal growth, in contrast with thin film.

In summary, we fabricated BTV films as a function of vanadium content using LSMCD. The degree of *a*-axis orientation of BTV can be controlled by the vanadium content in the thin film, in contrast with powder samples, and the largest P_r was obtained at x=0.03. The substitution of V^{5+} for the Ti^{4+} site of BTO increased the degree of *a*-axis orientation of the film and decreased the amount of defect site, resulting in larger $2P_r$.

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