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Control of Crystallization and Ferroelectric Properties of BaTiO₃ Thin Films on Alloy Substrates

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1. Introduction

Growth of complex oxides on different substrates has attracted tremendous interest [1,2] in the past decade due to the possibility that multifunctional devices could be realized by combining various properties of complex oxide phases with that of the functional substrates on which they are deposited. Among a variety of interesting properties that could be explored, the study of ferroelectric and ferromagnetic or magnetoelectric (ME) properties has achieved considerable research progress, driven by the development of thin film deposition technologies, discovery of new magnetoelectric materials and composite structures, and the development of an understanding and measurement methods for the coupling effect. The concept of magnetoelectricity was first proposed by P. Curie in 1872 and studies began with single phase ME materials that exhibited only limited magnetoelectric (ME) coupling. The low ME coupling is principally due to the fact that the magnetization and polarization are favored by different electronic configurations [3].

Accordingly, two phase composite materials became a better choice. Perovskite BTO and PZT materials have excellent piezoelectric properties [4], while iron-based alloys have been proven to have the highest magnetostrictive properties [5]. PZT-Metglas laminated (bulk) composites have shown the highest ME coupling coefficient, and have been used as magnetic sensors that are capable of detecting fields of <10 pTesla [4]. These ME composites consisting of a metallic ferromagnetic magnetostrictive alloy and a perovskite ferroelectric oxide have been the focus of considerable investigations for potential applications in memory and magnetic field sensing. Castel et al. [6,7] have reported preparation of BTO/Ni granular nanocomposite structures by high pressure compacting of BTO and Ni nanoparticles. A large increase of the real and imaginary components of the microwave frequency effective complex permittivity of BTO phase was found that was attributed to the large ME coupling effect between piezoelectric and magnetic phases. Israel et al. [8] used industrially produced multilayer capacitors which consisted of Ni-based magnetostrictive electrodes sandwiching a BTO-based dielectric to study the ME coupling effect. They found that both the magnetization and strain were hysteretic with applied electric field. Geprägs et al. [9] deposited polycrystalline Ni thin films on BTO single crystal substrates by electron

beam evaporation, and studied two different approaches to control the magnetization by electric field. The magnetization could be reversibly changed by more than 20%, due to the combined action of electroelastic strain and inverse magnetostriction. Zou et al. [10] deposited PZT films on Stainless Steel, Titanium and Ni foils using a LaNiO_3 buffer layer, by the sol-gel method and studied the dielectric properties. A high dielectric constant, low dielectric loss and symmetric C-V and P-E loops were obtained in all cases. More recently, Ma et al., [11] deposited $\text{Pb}_{0.92}\text{La}_{0.08}\text{Zr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PLZT) thin films on LaNiO_3 buffered Ni substrates by chemical solution deposition and studied the dielectric properties. High quality PLZT films with good dielectric properties were obtained. However, there are few reports about the study of magnetic, ferroelectric and the magnetoelectric coupling in ferroelectric thin films deposited on magnetostrictive alloy substrates. This is not only due to the fact that growth of the ferroelectric phase requires higher temperatures which may result in oxidization of the alloy substrate but also, because the ferroelectric films thus deposited may have large leakage currents due to a poor microstructure that may arise from deposition on a metallic substrate with low surface quality: thereby, limiting the possibility of reliable magnetoelectric measurements in such composite structures.

Here, we report the growth of BTO thin films on both amorphous Metglas [12] and $\text{Fe}_{81}\text{Ga}_{19}$ single crystals. Using this approach, we can realize the combination of ferroelectric and ferromagnetic properties in a semi-monolithic material. In addition to studying the property changes in metal-ceramic multilayers, we have also deposited BTO thin films on SrTiO_3 single crystal substrate predeposited with gold particles as seeds. Au layers can buffer BTO on Metglas, as the lattice parameters of Au and BTO closely match. Accordingly, Au can be used to control the growth orientation and grain size in BTO thin films.

2. Experiment details

Pulsed laser deposition (PLD) utilizing a KrF excimer laser ($\lambda = 248$ nm) was used for the growth of perovskite piezoelectric thin films. To obtain the necessary high atomic mobility [13] for the crystallization and oriented growth of the BTO layer, a high energy laser density (c.a. 20 J/cm^2) was used to eject high energy particles from the target. Thus we were able to use lower deposition temperatures to prevent oxidation of the metal alloy. The size of the laser spot was 2 mm^2 and the distance between the substrate and target was 8 cm. Deposition was carried out in a 90 mTorr oxygen atmosphere with a base vacuum of 10^{-6} Torr. We used a laser frequency of 10 Hz for the first 10 minutes of deposition onto a substrate held at 300°C . This enabled a layer of BTO to be first deposited, while preventing either melting of the Au layer or the oxidation of the alloy substrate. The substrate temperature was then increased to 600°C , and deposition was carried out under the same conditions for 90 minutes. The surface and cross-sectional morphology of the BTO thin films was studied using a LEO (Zeiss) 1550 Schottky field-emission SEM. The crystal structure was measured using a Philips X'pert high resolution x-ray diffractometer. A FEI Helios 600 NanoLab FIB SEM was used to prepare and lift-out TEM samples. A FEI Titan 300 high-resolution TEM (HRTEM) was used to obtain lattice images. The magnetic properties were measured with a Lakeshore 7300 Series VSM System at room temperature.

3. BTO on Metglas substrate

Metglas has an enormous magnetic permeability, which makes it ideal for the magnetostrictive phase in ME composites. The only problem is how to make the Metglas

survive the high temperature process that is necessary for the growth of piezoelectric thin films with good properties. One option is to use a Au buffer layer to protect the Metglas from oxidization, and to use a higher laser energy so that deposition can be done at lower temperature.

Fig. 1. (a) XRD of BTO/ Au/ Metglas, and (b) surface SEM result (inset is the cross-section view SEM, scale bar is 1 μm).

Figure 1a shows the XRD line scan for a BTO thin film deposited on Au-buffered Metglas foil. The Au-buffer layer reached a thickness of about 60 nm after a deposition time of 12 minutes. In Figure 1, we can observe only a (111) diffraction peak at about $2\theta \approx 38.38^\circ$, which indicates that Au-buffer layer is highly textured. The Au (111) orientation has the lowest surface energy and thus Au thin films grown on amorphous substrates have a (111) texture. The lattice parameter of Au ($a=4.08$) has a very small crystal mismatch with that of BTO ($a=3.994$), and thus the subsequent growth of a BTO thin film will also occur along the (111). This is confirmed by the intense BTO (111) peak at $2\theta \approx 38.90^\circ$. Good in-plane alignment and crystalline ordering was confirmed by the small full width at half maximum of $\text{FWHM} \approx 0.14^\circ$ for the BTO (111) peak. There are also several other weaker peaks which are not from the (111) BTO; which may be induced by the relative rough surface of the Au layer, compared with a single crystal substrate.

Figure 1b shows a top-view SEM image for BTO on Au/Metglas. In this image one can see that BTO formed with a uniform columnar morphology with size of about 40 nm in diameter. From the cross-sectional view, we can see that Au could form a dense and uniform interface between Metglas and BTO with a thickness of about 60 nm: which was sufficiently thick to prevent significant oxidation of the Metglas alloy, while preserving the (111) orientation of BTO. The inset shows a higher resolution SEM image of this same structure. The BTO layer thickness reached 2 μm after 2 hours of deposition, while preserving the columnar morphology of diameter about 40 nm which is in accordance with the top-view image.

Figure 2a shows a polarization hysteresis measurement of the BTO ferroelectric thin film. A well-defined ferroelectric hysteresis loop can be seen with a saturation polarization of $P_s \approx 25 \mu\text{C}/\text{cm}^2$ and a remnant polarization of $P_r \approx 7.5 \mu\text{C}/\text{cm}^2$. The value of both P_r and P_s are much larger compared with BTO structures deposited on Pt-buffered Si substrates [14, 15]. The coercive field was $E_c \approx 12.5 \text{ kV}/\text{cm}$, which is also much smaller than that of BTO thin films on either STO or Si substrates [16]. After the polarization measurement, the BTO thin films were poled in the out-of-plane direction. Piezoelectric measurement revealed a well-defined butterfly-like shape with a saturation value for the out-of-plane piezoelectric coefficient $D_{33} \approx 11 \text{ pm}/\text{V}$, which is relatively small compared to epitaxial thin films on STO substrates.

Figure 3a shows a typical M-H loop for Metglas after the BTO deposition process, which was measured using a VSM. The saturation field was $\sim 400 \text{ Oe}$, and the inset shows that the coercive field was $\sim 60 \text{ Oe}$. Figure 3b shows the magnetostriction of this same Metglas foil after BTO deposition, measured by a strain gauge method. Under a DC magnetic field of 80 Oe, the magnetostriction reached a maximum value of about 14 ppm. Although this magnetostriction value is smaller than that of Metglas before deposition, Figure 3c shows that the effective linear piezomagnetic coefficient was about $0.34 \text{ ppm}/\text{Oe}$, which is comparable to that of Terfenol-D [5].

These results demonstrate the successful deposition of BTO thin films on Metglas foils with a highly oriented (111) texture. In addition, good ferroelectric and ferromagnetic properties were obtained from the BTO layer and Metglas foil respectively. Thus, the approach offers promise to achieve ME coupling in semi-monolithic heterostructures that have lattice coherency across their interface.

Fig. 2. Ferroelectric hysteresis loop (a) and piezoelectric D₃₃ hysteresis loop (b) of BTO on Metglas.

Fig. 3. (a) Normalized magnetization vs applied magnetic field curve of Metglas with BTO on top. (b) Magnetostrictive and (c) piezomagnetic properties of Metglas with BTO on top.

4. BTO on Au-buffered STO

We used a Au-buffer layer to control the orientation of BTO on Metglas foils. “How does Au affect BTO grains?” and “what is the influence of an Au buffer layer on the micro and/or nanostructure of BTO?” are interesting questions that need answers. To obtain a better understanding of the relationship between BTO and the Au layer, a series of experiments were performed. We used (111) oriented single crystal STO substrates that were near atomically flat. Au was deposited via sputtering for different deposition times. Subsequently, we deposited BTO thin films on the different Au buffered layers by PLD.

Figure 4 shows a notable difference between samples with Au layers of different thicknesses. Parts (a) and (b) both exhibit uniform nanostructure although the BTO grains in Figure 4a are smaller than those in Figure 4b. Furthermore, one can see that both areas have pyramidal grain morphologies that are indicative of a preferred (111) texture for BTO. However, in parts (c) and (d), one can see there are numerous upheavals or “hills” of the BTO phase. In part (d) these “hills” are even larger than those in (c). A schematic diagram is given in part (e) that illustrates the BTO growth mechanism for the different cases, which helps explain why the surface consists of numerous “hills” as shown in Figs. 4c and 4d. When the buffer layer becomes thicker than about 10 nm, the Au layer separates into discontinuous nanoparticles of size about 20 nm in diameter. These Au-buffer layers then serve as nucleation sites for the formation of BTO grains. However, on the thicker Au-buffer layers with nanoparticle morphology, BTO grain nucleates and grows out from the Au surface without preserving a unique orientation. This may be because the Au clusters are too large to serve as a single nucleation site.

Fig. 4. (a) SEM image of BTO thin film on the Au layers with different thickness. (a) to (d) Au layers were deposited for (a)0s, (b)20s, (c) 40s and (d)60s. (e) is schematic to show a possible growth mechanism.

We then used FIB to lift out a small cross-sectional piece from the same area shown in Fig. 4b, to serve as a TEM sample. HRTEM images are given in Figure 5, which provide more detailed information concerning the interaction between the BTO layers grown on Au. Both the Au and BTO areas can be easily distinguished. Figure 5b shows a boundary between Au and BTO. In this figure, lattice planes can be seen to be well matched to each other. This indicates that it is possible to maintain an epitaxial relationship between the Au nanoparticle and the BTO grain.

Fig. 5. (a) TEM image of boundary between Au and BTO grain. (b) a high magnification image to show the detail.

5. BTO on Fe₈₁Ga₁₉ substrate

The magnetostriction of Fe₈₁Ga₁₉ alloys has been proved to be highly dependent on structure and composition [17]. It has been shown that the magnetostriction of Fe₈₁Ga₁₉ alloys is highest in a metastable disordered BCC phase ($a=2.91\text{Å}$) [16]. There is a large lattice mismatch between Fe₈₁Ga₁₉ and perovskite BTO ($a=3.994\text{Å}$, $c=4.038\text{Å}$). However, the difference in atomic spacing along [110] Fe₈₁Ga₁₉ and (100) BTO directions is only about 2%. Thus, if growth of Fe₈₁Ga₁₉ is carried out at deposition temperatures greater than 575 °C using a non-equilibrium deposition process, then it may be possible to achieve (101) oriented BTO thin films on (100) oriented Fe₈₁Ga₁₉ substrates. In this case, the growth relationship would be BTO(100) || Fe₈₁Ga₁₉(110), and BTO(101) || Fe₈₁Ga₁₉(100).

We deposited BTO thin films on single crystal Fe₈₁Ga₁₉ substrates by the PLD technique at 650 °C. During the first 10 minutes of deposition, a vacuum condition was used and after that an oxygen pressure of 75 mTorr was used for 1 hour. After deposition, the mirror-like surface of the alloy substrate was well-preserved, indicating that oxidation of the substrate has been prevented by the initial deposition in high vacuum conditions. XRD and SEM was used to check the crystallization and the nanostructure of the BTO phase.

Figure 6a shows a XRD line scan for the sample before and after BTO deposition. The black curve indicates the (110) peak of the Fe₈₁Ga₁₉ single crystal substrate: please note the lack of other Fe₈₁Ga₁₉ peaks in both case. After BTO deposition, the BTO thin film had an intense (111) peak, but much weaker (110) and (100) peaks. This indicates that the BTO thin films develop a (111) texture, but are not highly oriented. Also, a strong Fe₈₁Ga₁₉(110) peak, is seen, which indicates that oxidization and phase change could be prevented during the high temperature deposition process. Figure 6b shows the SEM top view of BTO thin films. We could clearly see uniform, nano-sized, triangle and polygonal BTO grains aligned densely with each other. The presence of an ordered nanostructure indicates well crystallized BTO nanocrystals which promises good ferroelectric and piezoelectric properties.

Fig. 6. (a) XRD of $\text{Fe}_{81}\text{Ga}_{19}$ (FG) substrate and $\text{BTO}/\text{Fe}_{81}\text{Ga}_{19}$, and (b) top-view SEM result.

Fig. 7. Ferroelectric hysteresis loop (a) and piezoelectric D₃₃ hysteresis loop (b) of BTO on Fe₈₁Ga₁₉.

Figure7a is the ferroelectric property measurement of the BTO ferroelectric thin film on Fe₈₁Ga₁₉. Well-defined ferroelectric hysteresis loop shows a P_s of ~40μC/cm² and a P_r of about 18 μC/cm². Both P_r and P_s are much larger compared with BTO thin film on Metglas. The coercive field is about 220kV/cm, which was much larger than that for BTO thin films on Metglas. This indicates that the BTO thin films experience much larger strain effects on

Fe₈₁Ga₁₉ single crystal substrates than that on amorphous Metglas substrates. Piezoelectric property measurements in Figure7b show well-defined butterfly shape with a saturation out-of-plane piezoelectric coefficient value (D_{33}) of ~ 15 pm/V, which is a little larger than BTO on Metglas. In summary, we have obtained BTO thin films on Fe₈₁Ga₁₉ substrate with good ferroelectric and piezoelectric properties.

Also, VSM and strain gauge methods were used to measure the ferromagnetic and magnetostrictive properties of the Fe₈₁Ga₁₉ substrate respectively. Figure8a shows a typical M-H loop of Fe₈₁Ga₁₉ in the in-plane direction after high temperature deposition process. The saturation magnetic field is about 2000 Oe. Also, since Fe₈₁Ga₁₉ is a soft magnetic material, the coercive field is very small. Figure8b shows the magnetostriction measured by a strain gauge method. At a dc magnetic field of about 500 Oe, the magnetostriction reaches a value of about 70 ppm. This is almost the value measured before the PLD process. Also, the calculated piezomagnetic value of 0.32 ppm/Oe is comparable with Metglas as shown in Figure8.c.

Fig. 8. (a) Normalized magnetization vs applied magnetic field curve of Fe₈₁Ga₁₉ with BTO on top. (b) Magnetostrictive and (c) piezomagnetic properties of BTO/Fe₈₁Ga₁₉.

6. Conclusion

In summary, we have successfully deposited well-crystallized ferroelectric BTO thin films on both Metglas and Fe₈₁Ga₁₉ substrates. The measured values of D_{33} were 11 pm/V and 15 pm/V, respectively. Also, good ferromagnetic and magnetostrictive properties were found after the high temperature BTO deposition process. The relationship between the Au-buffer layer and the BTO thin film was also studied. Ferroelectric thin films on ferromagnetic substrate may enable the coupling of the two different ferroic order parameters, which might in turn be useful for multifunctional devices. The approach is compatible for the growth of various functional oxide thin films on functional amorphous or crystalline alloy materials, and accordingly may allow for different coupling effects.

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Ferroelectrics - Material Aspects

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Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on ways to obtain high-quality materials exhibiting large ferroelectric activity. The book covers the aspect of material synthesis and growth, doping and composites, lead-free devices, and thin film synthesis. The aim of this book is to provide an up-to-date review of recent scientific findings and recent advances in the field of ferroelectric materials, allowing a deep understanding of the material aspects of ferroelectricity.

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