

## Research Article

# Pulsed Laser Deposition of BaTiO<sub>3</sub> Thin Films on Different Substrates

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We have studied the deposition of BaTiO<sub>3</sub> (BTO) thin films on various substrates. Three representative substrates were selected from different types of material systems: (i) SrTiO<sub>3</sub> single crystals as a typical oxide, (ii) Si wafers as a semiconductor, and (iii) Ni foils as a magnetostrictive metal. We have compared the ferroelectric properties of BTO thin films obtained by pulsed laser deposition on these diverse substrates.

## 1. Introduction

Pulsed laser deposition or PLD is a reliable method to fabricate oxide thin films [1, 2]. Deposition parameters play an important role in achieving good-quality thin films. Key PLD deposition parameters include deposition temperature, laser pulse repetition rate, laser energy, and ambient gas pressure. Further, all of these conditions depend on the lattice parameters and atomic coordinations of the substrate and thin film material. Previous experiments have shown that the substrate can be adjusted to change the quality and nanostructure of the films to satisfy different needs [3]. For example, single-crystal substrates with different lattice parameters can be used to tune the lattice mismatch of a film [4]: a suitable epitaxial strain can then enhance the ferroelectric properties [4]. Clearly, understanding the behavior of oxide films on various substrates is a meaningful approach to control the film quality and performance.

Barium titanate (BTO) is an important perovskite ferroelectric oxide due to its high-dielectric constant and large piezoelectric coefficient. BTO thin films have been studied for many applications such as piezoelectric detectors, thin film capacitors, and magnetoelectric (ME) devices [3]. In most cases, SrTiO<sub>3</sub> (STO) single-crystals are used as the substrate as it also has a perovskite structure and its lattice parameters are close to those of BTO [5]. It is easy to obtain epitaxial growth of BTO films on STO crystals. However, new

and promising applications have created a demand to deposit BTO films on different types of substrates: these include semiconducting Si and magnetic/magnetostrictive Ni.

Presently, silicon wafers are extremely utilized substrate to build electronic devices, such as complementary metal-oxide-semiconductor (CMOS) chips. If one could deposit BTO thin films on the Si substrates, it would pave the way to integrate BTO into microelectronic devices [6]. Epitaxial BiFeO<sub>3</sub> films have previously been deposited on SrRuO<sub>3</sub>-(or SRO-) buffered Si by PLD [7]. Epitaxial BTO thin layer with a TiN bottom layer has also been deposited on Si by RF sputtering technique [8]. These prior successes inspire us to find a method to grow BTO on Si by PLD technique. In addition to deposition, Si and metallic substrates offer other unique opportunities for deposition of BTO layers. In particular, growth of BTO on magnetic/magnetostrictive metals offers opportunity for multifunctionality [9]. Deposition of BTO films on metallic substrates and the study of the functional properties of each layer could be useful in the design of novel heterostructures, offering opportunities for BTO thin films in new applications such as magnetoelectricity or magnetocapacitance. For example, the magnetostriction of Ni is ~34 ppm at room temperature. If we could grow a BTO film on Ni, one could then develop heterolayered magnetoelectric (ME) laminates: where open application of an external magnetic field would induce elastic shapes in the Ni foil, which would then be transferred to the BTO layer

generating a voltage. Such heterostructured ME laminate Metglas/PZT-fiber composites show giant ME voltages [10, 11]. Deposition of BTO on Ni would offer a means to fabricate miniaturized engineered ME structures that does not require any epoxy bonding presently needed for the laminated composites.

Here, after discussing BTO film deposition on (111) STO substrates, we will demonstrate successful growth of BTO films on (i) Pt-buffered Si and (ii) directly on magnetostrictive Ni foil. We believe that our findings will help in the understanding of the role of various substrates on BTO films: ranging from insulating oxide to semiconducting Si and to magnetostrictive metals.

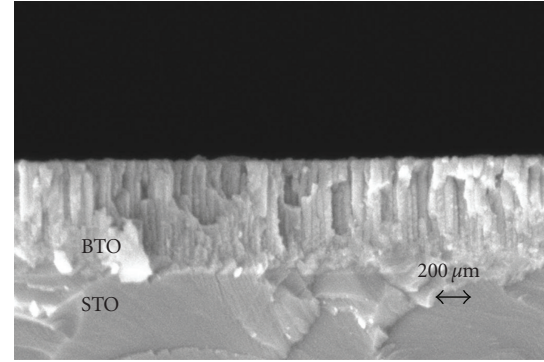
## 2. Experimental Method

We used (111)-oriented STO single-crystals, (100)-oriented Si wafers with a (111)-oriented Pt buffer layer, and magnetostrictive Ni foils as substrates for the growth of BTO layers by PLD. The substrates were ultrasonically cleaned before deposition. A KrF laser of wavelength of 248 nm (Lambda Physik 305i) was focused to a spot size of 10 mm<sup>2</sup> and was incident on the surface of a target using an energy density of 1.2 J/cm<sup>2</sup> for BTO. Deposition was done at an oxygen partial pressure of 100 mTorr using a laser pulse frequency of 10 Hz at a temperature of 750°C. For the STO substrates, a 50 nm-thick SRO buffer layer was first deposited at 700°C using an oxygen pressure of 90 mTorr which was used as a bottom electrode for polarization measurements of the BTO film. Films grown on Pt-Si and Ni do not require an additional SRO bottom electrode for these measurements.

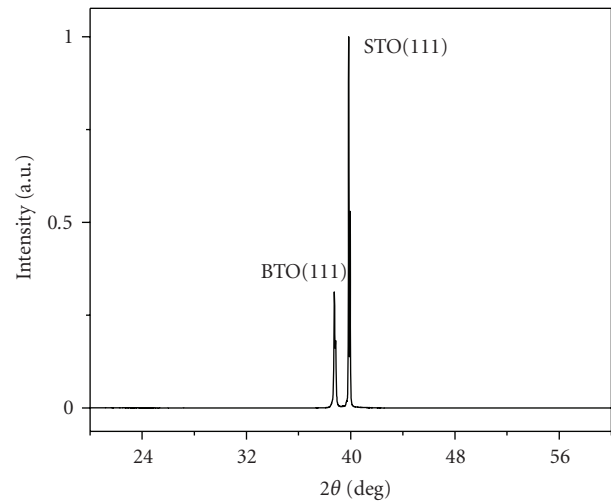
Scanning electron microscopy (SEM) images were obtained using a LEO (Zeiss) 1550 high-performance Schottky field-emission SEM. X-ray diffraction studies were performed using a Philips MPD high-resolution X-ray diffractometer equipped with a two-bounce hybrid monochromator and an open three-circle Eulerian cradle. Ferroelectric P-E hysteresis loops were measured by a modified Sawyer-Tower circuit using triangle signals of frequency 100 KHz. Magnetization H-M hysteresis loops were measured by a VSM 7304 (Lake Shore Cryotronics) magnetometer.

## 3. Results

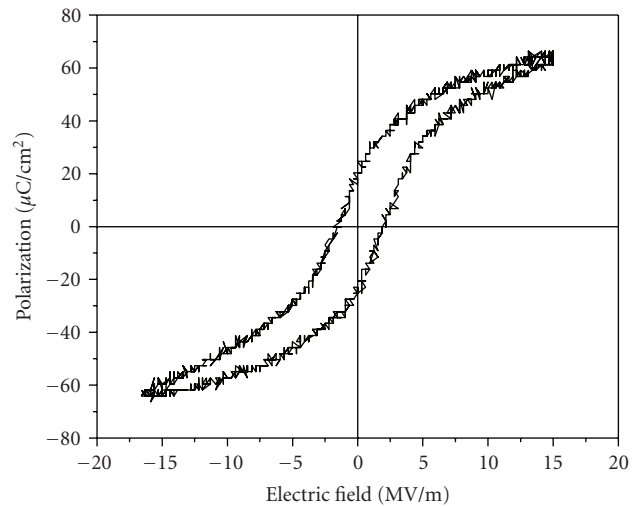
**3.1. BTO on STO Single-Crystal Substrates.** STO substrates can be used to grow epitaxial BTO piezoelectric layers where the film orientation is controlled by the substrate. First, as a control experiment to compare with layers grown on other substrates, we deposited epitaxial BTO thin films on (111) STO substrates. In Figure 1(a), a SEM cross-section image of a BTO layer is shown: a uniform nanostructure can be seen, where BTO forms a columnar structure on STO with diameters of about 80 nm. XRD revealed good epitaxy of the BTO layer on (111) STO, as identified by the line scan in Figure 1(b), where only a (111) BTO peak at 38.75° was found next to the (111) STO peak at 39.84°. Clearly, we successfully deposited epitaxial BTO thin films on top of (111) STO.



(a)



(b)



(c)

FIGURE 1: (a) SEM, (b) XRD, and (c) P-E loop of BTO thin film grown on STO substrate.

Figure 1(c) shows a polarization hysteresis loop of BTO on STO. A remnant polarization of  $P_r \approx 23 \mu\text{C}/\text{cm}^2$  was found which is very close to the single-crystal BTO value of

$26 \mu\text{C}/\text{cm}^2$ . The saturation polarization of  $P_s \approx 60 \mu\text{C}/\text{cm}^2$  was also comparable to that of BTO single-crystal; however, the coercive field of  $E_c \approx 1.86 \text{ MV}/\text{m}$  was much larger than  $E_c \approx 0.1 \text{ MV}/\text{m}$  for BTO crystals. The larger  $E_c$  value for the film can be attributed to the epitaxial strain from the substrate and the resultant elongation of the BTO  $c$ -axis [12], requiring higher field levels for polarization reversal.

**3.2. BTO on Si Substrates.** Bare Si wafers are easy to oxidize at high temperature, so we used Pt-buffered Si and studied the buffer layer effect on BTO thin film growth. Figure 2(a) shows a cross-section SEM image of BTO on Pt-buffered Si. BTO columns of about 100 nm in diameter can be seen. The XRD line scan in Figure 2(b) shows good epitaxy of the BTO (111) peak at  $38.8^\circ$  on the Pt (111) at  $39.9^\circ$ . Other peaks were not present for BTO in the scan, indicating good epitaxial growth of single-crystal BTO layers. The Si (100) peak was at  $69.13^\circ$ . The reason for (111) BTO growing on (100) Si is that Pt forms a highly oriented (111) buffer layer, which subsequently has a small lattice mismatch with the (111) BTO lattice parameter.

A well-defined polarization hysteresis loop is shown in Figure 2(c) with  $P_r \approx 7 \mu\text{C}/\text{cm}^2$  and  $P_s \approx 27 \mu\text{C}/\text{cm}^2$ , which are much higher than the values previously reported for polycrystal BTO on platinized Si substrates [13–15], again confirming the high quality of epitaxially grown single-crystal BTO films on platinized silicon wafers.

**3.3. BTO on Ni Foil Substrate.** As an important and widely used electrode metal in the electronics industry, Ni was selected as a metal foil substrate on which BTO thin films are to be deposited by PLD. To decrease metal foil oxidation, we first deposited 6000 pulses at a vacuum of 0.01 mTorr, and then deposited the remaining numbers of pulses to achieve the desired thickness at an oxygen pressure of 100 mTorr. From the SEM image of the cross-section (please see Figure 3(a)), we can see that the BTO film was about 700 nm in thickness. Unlike the epitaxially grown BTO films on STO and Pt-buffered Si (which had grains that grew out perpendicular from the substrates), the BTO films on Ni foil were polycrystalline with a small BTO grain size. In addition, the Ni surface was not as smooth as the STO substrate after deposition at a temperature of  $750^\circ$ . Even though we had deposited 6000 pulses in a vacuum, a thin layer of NiO still formed at the interface (please see Figure 3(b)). The highest intensity peak for NiO at  $43.3^\circ$  was weaker than the highest intensity one for BTO at  $31.4^\circ$ . Please note that only Ni, BTO and NiO phases were identified by the XRD line scan (Figure 3(b)). The NiO layer may serve as an important buffer layer, preventing further Ni oxidation.

The P-E loop, given in Figure 3(c), shows a saturation polarization of  $P_s \approx 6 \mu\text{C}/\text{cm}^2$  and a remnant polarization of  $P_r \approx 5 \mu\text{C}/\text{cm}^2$ . Both of these values are notably decreased, compared to BTO films grown on STO or Pt-Si. The rounding of the P-E loop indicates that there is some loss introduced due to using Ni metal as the substrate and electrode. From the M-H loop shown in Figure 3(d), we can see that a saturation magnetization of  $M_s \approx 47 \text{ emu}/\text{g}$  was achieved for this heterostructure. Compared with a pure Ni

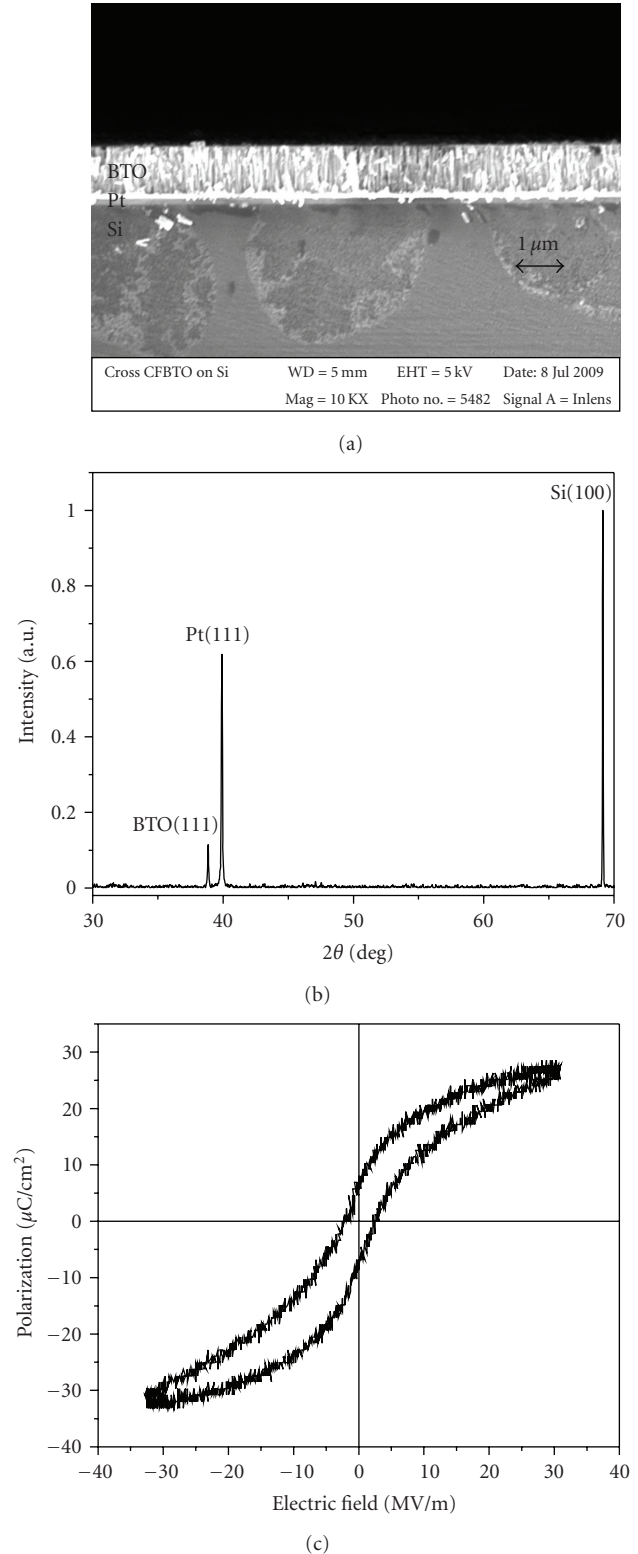


FIGURE 2: Cross-section SEM (a), XRD (b), and polarization measurement of BTO thin film grown on a Pt-buffered Si film.

foil which has  $M_s > 50 \text{ emu}/\text{g}$ , we can see that  $M_s$  decreased slightly because of the formation of a parasitic thin NiO layer, but yet still retained a good magnetization.

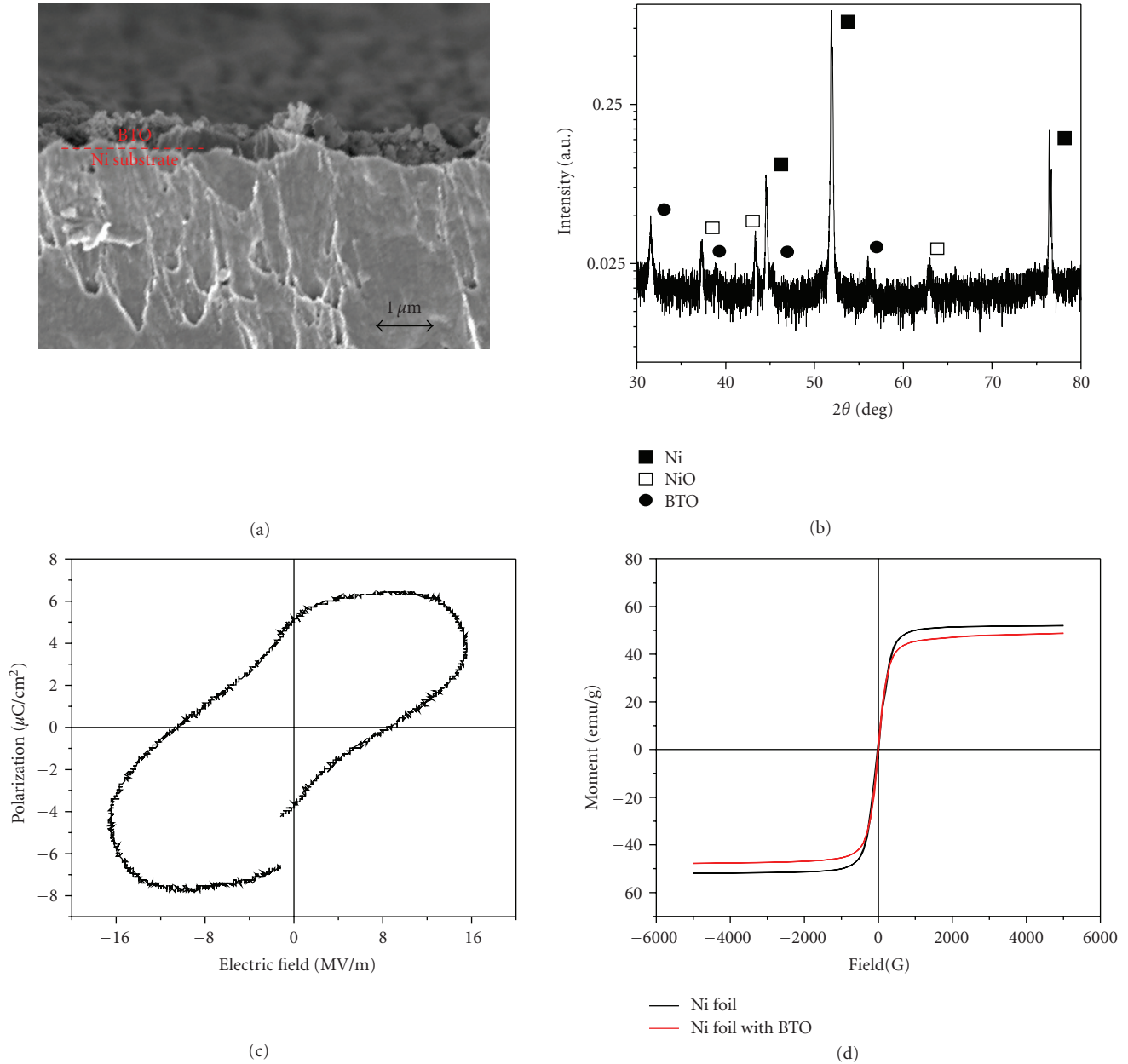


FIGURE 3: (a) Cross-section view SEM images of BaTiO<sub>3</sub> film on Ni foil, (b) is the XRD line scan, (c) is P-E loop from this film, and (d) H-M loop measured from a pure Ni foil and Ni foil after depositing BTO layer.

After comparing the ferroelectric polarization of BTO thin films on different substrates, we could see that BTO on STO single-crystal shows highest polarization value, followed by BTO on platinized silicon and BTO on Ni foil shows the lowest polarization value. BTO on STO substrate shows obvious epitaxial growth property and this structure guarantees well-crystallized uniform BTO thin films which favors long ordering of the electric dipoles of BTO. BTO grown on platinized Si is highly textured structure with only (111) XRD peak while BTO on Ni shows obvious polycrystal XRD peaks with a rough interface, thus BTO on Pt/Si shows much larger polarization property than BTO on Ni foil.

#### 4. Summary

We successfully deposited ferroelectric BTO thin films on STO, Pt-buffered Si and Ni substrates. We achieved epitaxial growth of BTO on Pt-buffered silicon substrates for the first time, which had much better ferroelectric properties of  $P_s \approx 27 \mu\text{C}/\text{cm}^2$  than previous polycrystalline BTO films on Pt-buffered Si. We also achieved deposition of BTO films on Ni foils for the first time. These Ni-BTO heterostructures were polycrystalline, had a thin parasitic NiO layer that reduced  $P_s$  and  $P_r$ , and slightly suppressed  $M_s$ . However, they offer promise with additional research of being multiferroic.

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