Pulsed laser deposition of $BaTiO_3$ thin films and their optical properties

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Highly oriented *a*-axis $BaTiO_3$ thin films were grown by pulsed laser deposition on (001) MgO substrates. The full width at half-maximum of the (200) $BaTiO_3$ rocking curve was as narrow as 0.6°. A large hysteretic quadratic electro-optic effect was observed in a transverse geometry at 6328 Å. A birefringence shift up to 3×10^{-3} was measured at an applied dc electric field of 1 kV/mm. It was found that laser repetition rate plays an important role on the surface morphology of the deposited films. © *1995 American Institute of Physics.*

Due to its ferroelectricity, high dielectric constant, and large electro-optic coefficients, $BaTiO_3$ can be used in many applications. These include pyroelectric detectors, thin film capacitors, nonvolatile memory, displays, surface-acoustic wave devices, and electro-optic devices.[1] Recently, strong second harmonic generation from poled $BaTiO_3$ thin films has also been reported.[2] It has also been shown that $BaTiO_3$ works as an excellent buffer layer for $YBa_2Cu_3O_{7-\delta}$ high-T_c superconductor on various substrates, in particular Si and Al_2O_3.[3–6] Well-aligned and epitaxial thin films are advantageous, if not essential, for many applications. In particular, epitaxial thin films with smooth surfaces are necessary for optical waveguide electro-optic devices, due to the requirement of low propagation loss. There have been a number of reports on $BaTiO_3$ thin film growth with various deposition techniques, such as rf sputtering,[7] reactive evaporation,[8] metalorganic chemical vapor deposition (MOCVD),[2] molecular beam epitaxy (MBE),[9] and pulsed laser deposition (PLD).[10–13] While early studies were devoted to the structural and electrical properties of $BaTiO_3$ thin films, there have been recent reports in exploiting electro-optic effects[13] and waveguide applications.[14]

Since MgO has a lower index of refraction than $BaTiO_3$ along with a small optical loss, a $BaTiO_3$/MgO structure is favorable for use in waveguide applications. In addition, MgO has previously been deposited on both Si and GaAs.[15,16] The use of MgO as a buffer layer reduces problems related to interdiffusion and oxidation which are prevalent for these semiconductor substrates.[15] Therefore, MgO seems to be a suitable material for use in integrated optics in that it would be an integral part of a waveguide device as well as allow for the growth of high quality $BaTiO_3$ thin films on semiconductor substrates. Conducting oxides including RuO_2 and La–Sr–Co–O are also proven to be suitable buffer layer materials between ferroelectrics and semiconductors and can be used in applications such as thin film capacitors and nonvolatile ferroelectric memories.[17,18]

In this letter, we would like to report on the observation of a large quadratic electro-optic effect from high quality pulsed laser deposited $BaTiO_3$ thin films on (001) MgO substrates. The improvement in the surface morphology via lower laser repetition rates is also discussed.

Our PLD system has been described elsewhere in detail.[19] Briefly, an ArF excimer laser at a wavelength 193 nm was focused onto a sintered $BaTiO_3$ target with a fluence of 1.5 J/cm^2 at various repetition rates. The distance between the target and the substrates was fixed at 6 cm. In our study, single crystal (001) MgO was used as the substrate. The *a* axis and *c* axis of $BaTiO_3$ have lattice mismatches of 5.2%, and 4.2% with the MgO substrate, respectively. While actual depositions were performed in an ambient pressure of 140 mTorr of oxygen, the deposition chamber was pumped to $<10^{-5}$ Torr prior to the deposition. The substrate temperature was maintained at 720 °C. After the deposition, the chamber was filled with oxygen to 1 atm, while the sample was cooled down to room temperature. The deposition rate was found to be ~0.08 Å/pulse.

The crystalline structure of the *in situ* $BaTiO_3$ thin films was examined using x-ray diffraction (XRD) analysis. Figure 1 shows the result of x-ray θ-2θ scan of a typical $BaTiO_3$ thin film on a (001) MgO substrate. As it can be seen, only (*l*00) peaks of $BaTiO_3$ were revealed. It should be mentioned that while the (*l*00) and (00*l*) peaks of $BaTiO_3$ are located close to each other, the XRD peaks could be determined with a sufficient resolution to distinguish the crystal orientation of deposited $BaTiO_3$ thin films. The *d* spacing for the peak at 45.26° was calculated to be 2.002 Å, which is closer to the

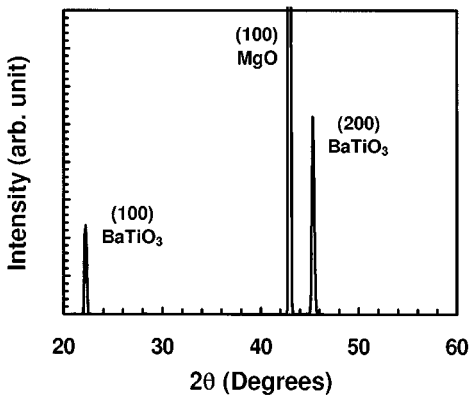

FIG. 1. X-ray diffraction θ-2θ scan of a $BaTiO_3$ thin film grown on a (001) MgO substrate. Only (*l*00) peaks of $BaTiO_3$ are revealed.

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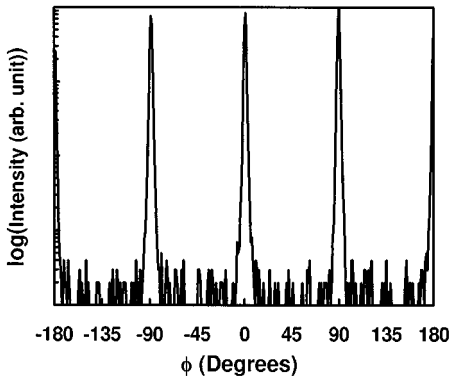

FIG. 2. Off-axis ϕ scan of a $BaTiO_3$ (301) peak to examine the in-plane texturing of a $BaTiO_3$ thin film on (001) MgO substrate.

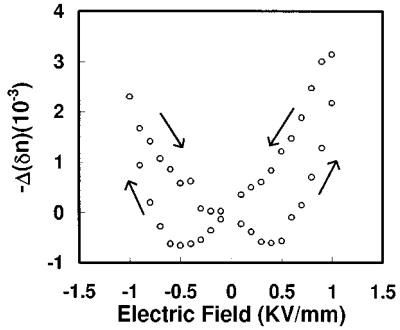

FIG. 3. Birefringent shift as a function of applied dc electric fields for a $BaTiO_3$ thin film on (001) MgO substrate at 6328 Å.

(200) spacing of bulk $BaTiO_3$. The *d* spacings for (002) and (200) of bulk $BaTiO_3$ found from the XRD database[20] are 2.019 and 1.997 Å, respectively. The full width at half-maximum (FWHM) of the x-ray rocking curve for the (200) peak was measured to be as narrow as 0.6°. This indicates that our $BaTiO_3$ thin films are highly oriented with *a* axis perpendicular to the surface of the film. The smaller lattice mismatch between the *c* axis of $BaTiO_3$ and the MgO substrate may be the reason for the *a*-axis orientation of the $BaTiO_3$ thin film. Previously, *c*-axis $BaTiO_3$ thin films were obtained on (001) MgO substrate by PLD.[10,11] It is not known at this point what caused the difference in resulting films' orientations. To investigate the in-plane texturing, the Schulz reflection method[21] with a three-axis diffractometer was used. For our sample, an off-axis scan of the $BaTiO_3$ (301) plane was performed to determine the in-plane alignment. As a reference, an off-axis scan of the MgO (022) plane was completed prior to the scan for the thin film. The off-axis scan of the $BaTiO_3$ (301) peak is shown in Fig. 2. Although only two peaks are expected for an epitaxial *a*-axis oriented tetragonal structure, peaks were observed at multiples of 90° and coincided with the ⟨100⟩ directions of the MgO substrate. It turns out that the (310) peak is very close to the (301) peak and it is difficult to distinguish between them. Therefore, x-ray diffraction data can only show that the *c* axis of the $BaTiO_3$ thin films must be aligned along either the [100] or the [010] direction of MgO substrates. While $BaTiO_3$ is a negative uniaxial material with $n_0 - n_e = 0.051$ at 6328 Å,[22] the measured birefringence of ~ 0.014 for the $BaTiO_3$ thin films on a MgO substrate is small and indicates a random orientation of the *c* axis. In other studies, the lack of ferroelectric hysteresis and low second-harmonic generation from the as-deposited $BaTiO_3$ on (001) MgO substrate deposited by MOCVD[23] suggested a random orientation of the *c* axis along one of the four possible orientations.

Electro-optic properties of our samples were measured with a transverse geometry at the wavelength of 6328 Å using a He–Ne laser. Silver pads were thermally evaporated on the thin film with an electrode spacing of 250 μm. The experimental setup for measuring the optical phase retardation was adapted from Adachi *et al.*[24] The thickness of the sample used for this experiment was 2000 Å deposited with a laser repetition rate of 10 Hz. The electric fields were applied along the [110] direction of MgO. The light entering the sample through the gap between the electrodes had a linear polarization of 45° with respect to the applied electric fields. Figure 3 shows the change of birefringence $\Delta(\delta n)$ of our sample under the influence of dc electric fields up to 1 kV/mm. A large hysteretic quadratic electro-optic effect was observed. $\Delta(\delta n)$ was calculated from the ratio of the signal I to the intensity of the incoming light I_0 as $\Delta(\delta n) = \lambda/(2\pi t)\, I/I_0$, where λ is the wavelength of the light and t is the thickness of the sample. The observed quadratic electro-optic effect is comparable to that of $Bi_4Ti_3O_{12}$ on (110) MgO.[25] It is interesting to notice that the shape of the hysteresis resembles the hysteresis of $D^2 \approx P^2$ for ferroelectric materials. In fact, PZT thin films have been shown to have $\Delta(n_e - n_0) \propto P^2$.[26] The electric field at the minimum birefringence of 5×10^5 V/m is much smaller than the coercive field of $4-7\times10^6$ V/m obtained from $D-E$ curves.[12,23] No significant electro-optic effect was observed with any other geometry, i.e., other electric field direction or polarization direction. Given the possibility that the *c* axis of $BaTiO_3$ may be randomly oriented along any ⟨100⟩ direction of the MgO substrate, only a 45° rotation is needed for approximately half of the domains to be aligned along the applied electric field when the electric field is applied in the [110] direction of the MgO substrate. This may explain why the electro-optic effect was observed only in a certain geometry. The observed negative values in $\Delta(\delta n)$ also suggest a *c*-axis alignment along the applied electric fields, since $BaTiO_3$ is a negative uniaxial material with an optic axis parallel to the *c* axis.

In waveguide applications, it is very important to have a smooth surface since large losses may result from surface scattering. The surface morphologies of $BaTiO_3$ thin films were examined using a scanning electron microscope (SEM). Figures 4(a)–(c) show the images of $BaTiO_3$ thin films deposited at laser repetition rates of 20, 10, and 2 Hz, respectively. The laser energy or laser fluence per pulse was maintained at the same level. The film deposited with repetition rate 20 Hz had a rough surface filled with outgrowth of small grains as small as 0.1 μm. The morphology of the film surface improved significantly when the repetition rate was reduced to 10 Hz as seen on Fig. 4(b). The grain size also increased. Figure 4(c) shows even better surface morphology without any significant features on the surface when the rep-

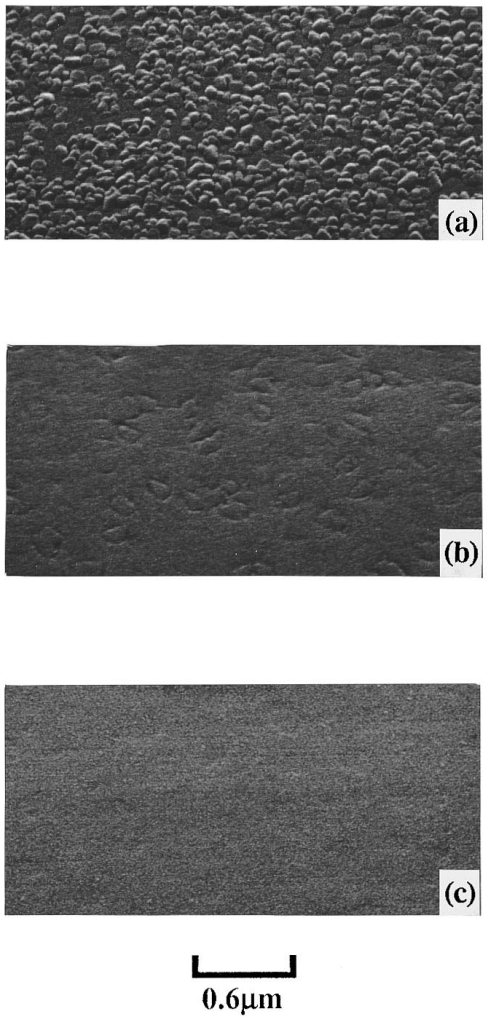

FIG. 4. SEM images of $BaTiO_3$ thin films deposited at repetition rates of (a) 20 Hz, (b) 10 Hz, and (c) 2 Hz with the same laser fluence.

etition rate was further decreased to 2 Hz. All of the deposited thin films were relatively free of any large particulates. Waveguide experiments using a coupling rutile prism showed that the films grown at lower repetition rates had lower propagation losses. However the loss was still disappointingly high even for the films deposited at laser repetition rates of 2 Hz. Light streaks in the $BaTiO_3$/MgO waveguides were visible for only 3–4 mm. Although morphologies of deposited films were improved by the use of lower laser repetition rates, it is not known at this point whether the surfaces are smooth enough for waveguide applications. The random orientation of the *c* axis is also another possible cause of the large loss observed. Further optimization of the deposition processes and an investigation into the loss mechanisms are under way.

In conclusion, highly oriented *a*-axis $BaTiO_3$ thin films were deposited on (001) MgO substrates by pulsed laser deposition. We observed a very large quadratic electro-optic effect at 6328 Å with a hysteresis resembling $D-E$ hysteresis. Improvements in surface morphology were observed with lower laser repetition rates.

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