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Optical properties of $BaTiO_3$ thin films: Influence of oxygen pressure utilized during pulsed laser deposition

J. Hiltunen · D. Seneviratne · R. Sun · M. Stolfi · H. L. Tuller · J. Lappalainen · V. Lantto

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Abstract The crystallographic properties of $BaTiO_3$ thin films, grown by pulsed laser deposition on MgO substrates, were found to be strongly influenced by the oxygen pressure used during growth. Low pressure grown films were c-oriented while increasing oxygen pressure produced films with preferred a-orientation. The crystal reorientation resulted in the shift of optical birefringence from +0.04 to −0.025 with low levels of birefringence in films possessing low tetragonal distortion. Mach-Zehnder electro-optic waveguide modulators were fabricated to characterize the electro-optic properties of the deposited films and to evaluate the suitability of these films for planar optical applications. An effective electro-optic coefficient of 23 pm/V was obtained for a *c*-axis oriented film near the crystal $c \rightarrow a$ reorientation point.

Keywords $BaTiO_3$ · Thin film · Electro-optic · Birefringence

J. Hiltunen · D. Seneviratne · R. Sun · M. Stolfi · H. L. Tuller
Department of Materials Science and Engineering,
Massachusetts Institute of Technology,
77 Massachusetts Avenue,
Cambridge, MA 02139, USA

J. Hiltunen (✉)
Technical Research Centre of Finland,
Kaitovayla 1,
Fin-90571 Oulu, Finland
e-mail: jussi.hiltunen@vtt.fi

J. Lappalainen · V. Lantto
Microelectronics and Materials Physics Laboratories,
University of Oulu,
P.O. Box 4500, FIN-90014 Oulu, Finland

1 Introduction

$BaTiO_3$ (BTO) is an intensively studied ferroelectric material possessing technologically interesting functional properties that can be utilized in microelectronics and photonics applications. Recently, directly etched ridge [1] and strip-loaded [2] type optical waveguide structures based on BTO thin film technology were reported with promising electro-optic response. Thin film technology promises to achieve high levels of component integration in micro-photonic applications including light source, modulators, waveguides and detectors with reduced device size [3].

Control of oxygen partial pressure during film growth has been demonstrated to be a means for tuning the lattice parameter mismatch between perovskite thin films and substrates. Variation in oxygen partial pressure during growth has resulted in changes in film orientation [4–6] and even the crystalline phase of some thin film compositions, e.g., paraelectric or ferroelectric phase, depending on working pressure [5]. Most studies on oxygen partial pressure effects during BTO and $Ba_xSr_{1-x}TiO_3$ deposition were focused on crystal and dielectric properties. Our motivation was to examine its influence on optical properties. In this paper, we report on the effects of oxygen partial pressure during PLD film deposition on the direction-dependent refractive indices. In addition, BTO-based Mach-Zehnder waveguide modulators were used to study the effect of oxygen working pressure on the film's electro-optic properties and to evaluate their suitability in guided wave devices.

2 Experimental

Pulsed laser deposition, using a KrF laser (Lambda Physik LPX200) operating at a wavelength of 248 nm, was utilized to grow BTO films on (001) oriented single crystal MgO substrates. The thin films were deposited by focusing the laser beam on a nominally stoichiometric, pressed, and sintered BTO target. All the films were grown by using the repetition rate of 5 Hz, fluence of 2.5 J/cm^2, and at a substrate temperature of 700°C. Samples were grown at oxygen working pressures of 1.5, 10, 15, 20, 25 or 30 mTorr. The thickness of the films varied between 300 and 500 nm. The directional dependence of the refractive indices was measured by a prism coupling method (Metricon 2010) and crystal structure analysis was carried out by X-ray diffraction (XRD) measurements. The out-of-plane lattice parameters were calculated from $\theta-2\theta$ patterns (Rigagu RU 300) while in-plane parameters were determined from (202)/(220) non parallel-to-surface planes (Bruker D8 equipment) together with $\theta-2\theta$ scan results. Further information on the XRD analysis and surface morphology studies are provided in ref [7]. A Si_xN_y strip-loaded waveguide design was chosen for the Mach-Zehnder modulator waveguides, allowing for the use of easily patterned materials for the guiding structure rather than having to pattern the BTO layer itself. The Si_xN_y layer (refractive index of 1.79 at 1550 nm measured from a separate single layer) was grown by plasma enhanced chemical vapor deposition (PECVD) and lithographically patterned and etched by reactive ion etching (RIE). Al electrodes adjacent to the active arm were sputter deposited and lithographically patterned and etched with standard aluminum wet etchant. A fiber coupled laser operating at 1,550 nm wavelength, together with a polarization controller, was used as the light source. The intensity was modulated with a chopper located between two free space optical fiber connectors. TE polarized light was end-fire coupled into the Mach-Zehnder waveguide modulator from the lensed input fiber. Optical field confinement at the waveguides was examined by imaging the intensity distribution at the modulator waveguide output facet with a microscope objective coupled infrared camera. During the electro-optic measurements, a voltage sweep was applied across the electrodes, and the microscope objective collected light was directed to the optical power meter instead of the camera. A phase locked amplifier, with frequency matched chopper, was used to measure the intensity detected by the optical power meter.

3 Results and discussion

Figure 1 shows the low angle region of XRD $\theta-2\theta$ measurement of the BTO films deposited at different oxygen pressures. Only the (001) peak and its multiples were observed in the thin films grown at a gas pressure <15 mTorr. The diffraction peaks of the thin film deposited

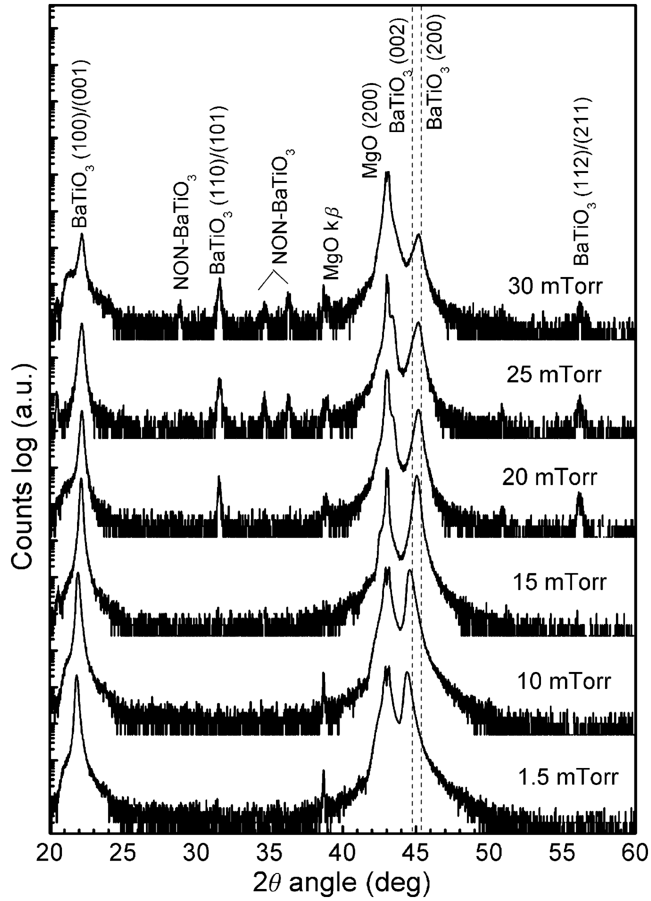

Fig. 1 Low angle region of X-ray diffraction $\theta-2\theta$ measurement of $BaTiO_3$ films deposited at different oxygen pressures. *Dashed lines* represent the positions of the characteristic bulk $BaTiO_3$ (200) and (002) reflections

at low oxygen pressure shifted towards lower diffraction angle compared to characteristic bulk BTO positions as shown in Fig. 1. This implies a strained out-of-plane lattice parameter of 4.09 and 4.07 Å in films deposited at 1.5 and 10 mTorr, respectively, compared to bulk *c*-axis value of 4.038 Å [8]. As the oxygen pressure was increased over 10 mTorr, the main peaks shifted between the characteristic bulk single crystal BTO (00m) and (m00) positions. This indicates a potential change in preferred orientation from (001) to (100) orientation and it is supported by the determination of the ratio between in-plane and out-of-plane lattice parameters together with the shift in optical birefringence discussed below. When the oxygen pressure exceeded 15 mTorr, reflections from (110)/(101) and (112)/(211) oriented planes were also observed in the $\theta-2\theta$ pattern together with (m00) main peaks indicating a change from hetero epitaxial film to a polycrystalline structure. As the oxygen pressure reached 25 mTorr, minor non-characteristic tetragonal BTO phases were also observable in the $\theta-2\theta$ pattern.

Figure 2(a) shows the in-plane and out-of-plane refractive indices at 633 nm measured by the prism coupling method. In samples deposited at 1.5, 10 and 15 mTorr oxygen pressures, the in-plane refractive index was ~2.34 while the out-of-plane value increased slightly from 2.30 to 2.33. As the pressure exceeded 20 mTorr, the refractive indices decreased significantly to approximately 2.11–2.15. This may be attributed to the decrease in crystal quality suggested by XRD measurements. Low pressure (1.5–15 mTorr) films were epitaxial, while relatively higher oxygen pressure produced films, which were highly oriented, but not epitaxial due to observed minor reflections other than (m00) planes. Similar trends have also been observed in lead-zirconate-titanate thin films with decreasing refractive index with decreasing crystallite size due to change in volume ratio of grain boundary and bulk [9]. Figure 2(b) shows the birefringence (defined as the difference in refractive indices between the in-plane and out-of-plane values) and lattice distortion from the cubic phase (defined as 1−[in-plane lattice parameter]/[out-of-plane lattice parameter]) as a function of oxygen pressure during film growth. The films deposited at 1.5 and 10 mTorr were strongly *c*-axis oriented with a high degree of birefringence. Increasing oxygen pressure decreased the tetragonal crystal distortion correlating well with reduction in birefringence. It is interesting to note the region between 15 and 20 mTorr where both the crystal distortion and birefringence change their sign as a consequence of the $c \rightarrow a$ axis crystal reorientation. In XRD measurements of the a-oriented films, i.e. the elongated unit cell axis parallel to the surface, reflections from (202) and (220) planes were undistinguishable potentially indicating other than tetragonal crystal structure. A similar lack of tetragonal peak splitting was attributed to the slightly different orthorhombic phase in the film from the orthorhombic phase in the bulk [10]. In the epitaxial film, the phase has a square in-plane lattice due to substrate constraints, while in the bulk, the unit cell is elongated along the face diagonal direction. However, in this work we believe, the substrate influence was partly relaxed due to the polycrystalline structure as indicated by the observed minor (110)/(101) and (112)/(211) peaks in $\theta-2\theta$ XRD scans. This suggests that the lack of any observable tetragonal peak splitting could be also a result of peak broadening due to strain relaxation. Consequently crystal distortion from the cubic phase could be larger than the values shown in Fig. 2(b) in the a-oriented films deposited at oxygen pressure above 15 mTorr. The crystal phase could not be determined conclusively, and this can potentially explain the deviation between birefringence and crystal distortion values in films deposited at 25 and 30 mTorr oxygen pressures. The shift from epitaxial film to polycrystalline structure was also suggested by atomic force microscope (AFM) studies as reported in [7]. The surfaces of the samples deposited at low oxygen pressures (1.5 and 10 mTorr) had RMS roughness of less than 1 nm. Near the reorientation point, the surfaces were observed to be relatively rougher: 20 mTorr sample had a surface roughness of 8 nm, while 25 and 30 mTorr oxygen pressure samples had roughnesses of approximately 20 nm.

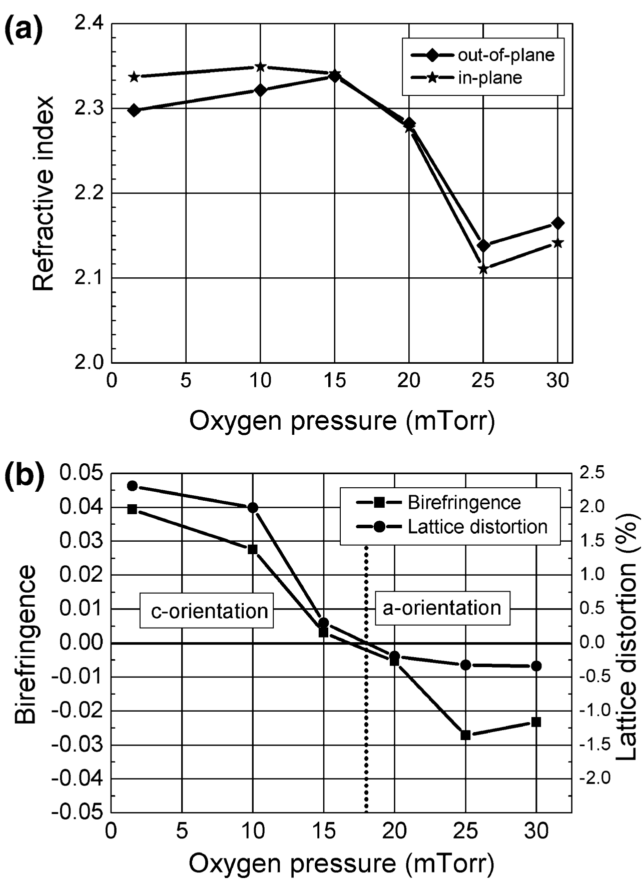

Fig. 2 (**a**) In-plane and out-of-plane refractive indices at 633 nm wavelength in $BaTiO_3$ films deposited at different oxygen pressures. (**b**) Optical birefringence and X-ray diffraction measured lattice distortion from cubic structure in $BaTiO_3$ films as a function of oxygen pressure during deposition

Due to observed crystal reorientation between 10 and 20 mTorr oxygen pressure, Mach-Zehnder waveguide modulators were fabricated with samples deposited at 10, 15 and 20 mTorr oxygen partial pressures yielding BTO films with both *c*- and *a*-axis orientations respectively. Figure 3 shows a cross-sectional SEM image of the waveguide and electrode structure fabricated in this study. The waveguiding Si_xN_y strip lies on the BTO slab and Al electrodes are patterned adjacent to one of the waveguide arms of the Mach-Zehnder structure. The electrode length was 3 mm and separation varied between 9 and 15 µm. Under an applied electric field, the refractive index of the BTO films is altered, thus modifying the phase of the guided wave. A localized intensity peak was observed at the output facet of devices fabricated with samples deposited at 10 and 15 mTorr oxygen pressures. The output

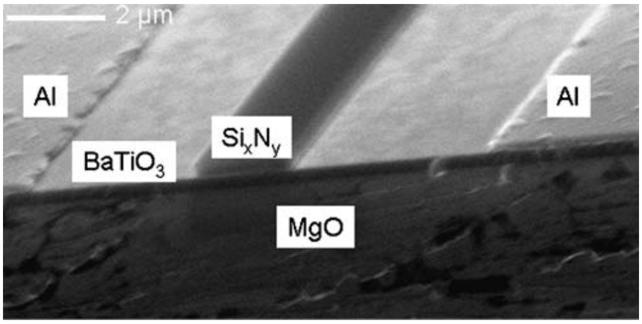

Fig. 3 Cross section image of the Si_xN_y strip-loaded waveguide structure on the $BaTiO_3$ thin film

intensity of the 20 mTorr sample was unlocalized presumably due to scattering from the relatively rougher surface or from the grain boundaries in polycrystalline media. The intensity at the Mach-Zehnder interferometer output on 10 and 15 mTorr BTO films as a function of applied electric field are plotted in Fig. 4. The intensity curves were nonperiodic, as a function of electric field, which is characteristic for BTO films due to the influence of the Pockels coefficient r_{51} [1] together with the domain poling effect [1, 2]. This can result in the dependence of the effective electro-optic coefficients on electric field strength. By using the expression [2]

$$r_{\rm eff} = \frac{\lambda \times g}{n^3 \times L \times V_\pi \times \Gamma}, \tag{1}$$

the effective electro-optic coefficient value $r_{\rm eff}$ can be extracted. In this expression L is the electrode length and g their separation. The overlap factor [2] Γ between the optical and the applied electric field can be obtained by a simulation method [11] while V_π is the voltage required to cause a 180 degree phase shift. The electric field (V_π/g) needed to induce peak to valley intensity modulation at high electric fields was 3.3 V/µm and 2.7 V/µm for 10 mTorr and 15 mTorr BTO film devices, respectively (see Fig. 4.). In the tested structures, the overlap factor was about 0.69 for the 10 mTorr BTO samples and 0.74 for 15 mTorr samples. Samples were tested at a wavelength λ= 1,550 nm. The refractive index n of the samples was approximately 2.24 at this wavelength. By substituting the appropriate terms into Eq. 1, an effective electro-optic coefficient of 20 and 23 pm/V was obtained for the 10 and 15 mTorr BTO films, respectively. In this calculation, the film was treated as an optically uniform material.

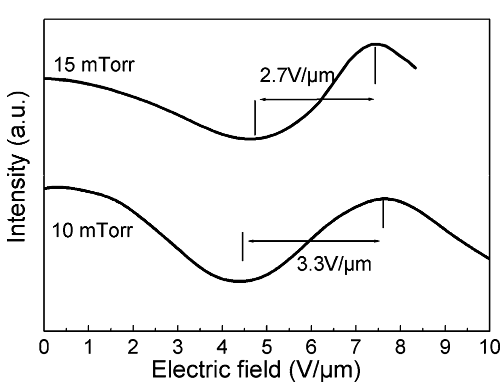

Fig. 4 Measured optical intensity at Mach-Zehnder waveguide modulator output facet as a function of applied electric field

The influence of domain structure in BTO films has been shown to be a highly significant factor in performance of microelectronics and—photonics devices. c-orientation is preferred in memory elements while a-oriented domains are desired in electro-optic devices [12] enabling reduced driving voltage for the intensity modulation [1]. In this work, the measured electro-optic response was relatively low presumably due to non-optimal domain structure in the *c*-oriented films, otherwise suitable (properly waveguiding) for Mach-Zehnder devices. As an example, in epitaxial unalloyed metal-organic-chemical-vapor deposited BTO films, the effective electro-optic coefficient has been reported to increase from 38 pm/V (Ref [2]) up to 360 pm/V [13] near the 1,550 nm wavelength by optimizing the domain structure and electrode configuration for the specific domain distribution [13]. Another demonstrated means to enhance the electro-optic response of BTO films is the formation of periodic superlattice structure with very thin $SrTiO_3$ layers [14].

4 Conclusion

In conclusion, highly oriented BTO thin-films were grown on MgO substrates by pulsed laser deposition at different oxygen working pressures. Low working pressures yielded c-oriented epitaxial films, while pressures above 15 mTorr favored a-orientation films. This reorientation was also observed by changes of sign of the optical birefringence correlating well with XRD measurements. The surface roughness of the c-oriented films was sufficiently low to enable reliable measurements of electro-optic values using guided wave Mach-Zehnder modulators. Effective electro-optic responses of 20 and 23 pm/V were determined for BTO films deposited at 10 and 15 mTorr oxygen pressures, respectively.

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