Temperature dependence of optical band gap in ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ films determined by ultraviolet transmittance measurements

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Optical properties of ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) films on quartz have been investigated using ultraviolet-infrared transmittance spectra in the temperature range of 77–500 K. The spectra can be divided into three distinctive photon regions between 1.1 and 6.5 eV. It is found that the band gap E_g decreases from 3.88 to 3.77 eV with the temperature. The parameters a_B and Θ_B of the Bose-Einstein model are 30.3 meV and 218.7 K, respectively. The band narrowing coefficient dE_g/dT is -2.65×10^{-4} eV/K at room temperature. The present results can be crucial for future application of ferroelectric BLT-based electro-optic and high temperature optoelectronic devices. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2816915]

Recently, ferroelectric film materials have received much attention in view of their wide applications, including nonvolatile memories, dynamic random access memories, electro-optic switches, pyroelectric detectors, optical modulators, and mixers.[1–6] In particular, perovskite ferroelectric films show nonlinear optical and electro-optic properties because of the interaction between spontaneous electronic polarization and incident polarized light. Among these materials, layered bismuth based films $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) are significant and considered to be very promising compounds for integrated optics applications due to their combination of large electro-optic coefficient and low processing temperature. The ferroelectric and electrical properties have been extensively studied, while there are few reports on microstructure and optical properties of BLT films in the transparent region.[7] We reported optical functions of BLT films on silicon substrates and determined optical band gap (OBG) energy only at room temperature (RT) using spectroscopic ellipsometry.[8] However, it should be emphasized that optoelectronic devices based on ferroelectric materials are still in the preliminary stage owing to the growth difficulty and scarce known physical properties.

Optical properties of films strongly depend on substrate materials, growth parameters, and deposition methods. Up to now, many physical parameters related to applications of integrated BLT-based optoelectronic devices are not thoroughly understood. BLT material belongs to a wide band gap oxide group and its OBG energy is estimated to about 4.0 eV for silicon substrate at RT.[8] This fact may help to develop potential applications, such as ultraviolet detectors, electro-optics, and high-temperature electronic devices. Transmittance spectra can directly provide optical band gap, optical constants, absorption characteristics, band tail state behavior, and optical phonon modes.[9–12] The temperature dependence plays an important role in design, optimization, and evaluation of optoelectronic devices.[13] In this letter, the optical properties of BLT films on quartz substrates are investigated by spectroscopic transmittance method. The band gap energy and band narrowing coefficient could be obtained from ultraviolet-infrared spectra at the temperature region from 77 to 500 K.

$Bi_{3.25}La_{0.75}Ti_3O_{12}$ layers on quartz substrate were prepared by chemical solution method.[8] The starting materials are bismuth nitrate, lanthanum acetate, and titanium butoxide (the molar ratio Bi:La=3.25:0.75). The deposition and annealing-treatment procedures were repeated many times to obtain the BLT films. The detailed growth process was given in Ref. 8. The crystalline structure of the films is analyzed by x-ray diffraction (XRD) using Cu $K\alpha$ radiation. Compared with the previous results on platinum and silicon substrates,[7,8] the XRD patterns from quartz substrates show the remarkably different behavior (see Fig. 1). There are more and strong diffraction peaks for the films on quartz substrates. It is further confirmed that the present BLT films have a single perovskite phase. It should be stated that the

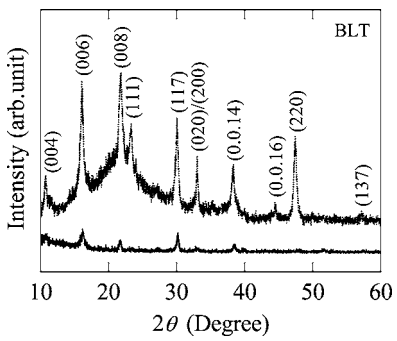

FIG. 1. Comparison between XRD patterns of the BLT films on quartz (dashed line) and silicon substrates (solid line) from Ref. 8.

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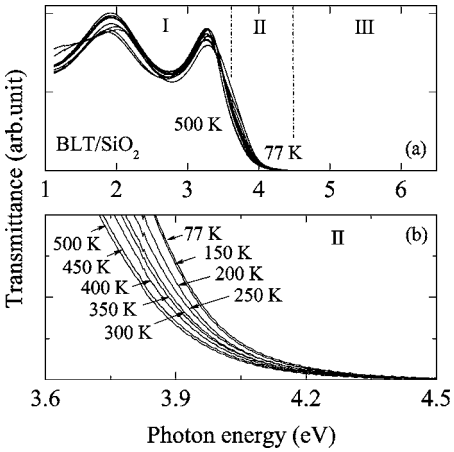

FIG. 2. Transmittance spectra of the BLT film at the temperature region from 77 to 500 K: (a) in the ultraviolet-infrared photon energy of 1.1–6.5 eV and (b) near the OBG region of 3.6–4.5 eV. The arrows indicate the corresponding temperature values.

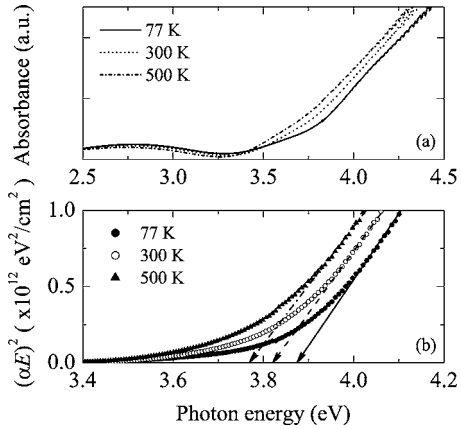

FIG. 3. (a) The absorbance spectra of the BLT film and (b) variations of $(\alpha E)^2$ with the photon energy E are used to determine the OBG energy at three typical temperatures: 77, 300, and 500 K, respectively.

pronounced preferential orientation is not observed in the present work.[14] The optical transmittance was recorded with a double beam ultraviolet-infrared spectrophotometer (PerkinElmer UV/VIS Lambda 2S) at the photon energy from 1.1 to 6.5 eV. The samples were mounted into an optical cryostat (Optistat CF-V from Oxford Instruments) and the temperature was continuously varied from 77 to 500 K. Note that no mathematical smoothing has been performed for the experimental data.

Typical transmittance spectra of the BLT films at different temperatures are shown in Fig. 2(a). The spectra can be roughly separated into three specific regions: a transparent oscillating one (labeled with "I"), a low transmittance one ("II"), and a strong absorption one ("III") at higher photon energies. The Fabry-Pérot interference behavior observed in the transparent region, which is due to the multireflectance between the film and substrate, is similar to those on silicon substrates.[8] The transmittance differences with the temperature are ascribed to the thermal expansion and variations of optical constants in lower photon energies. The changes of the refractive index are derived from increasing structural disorder and result in the oscillation pattern fluctuations at elevated temperatures.[15] Note that the absorption edge is near the end of the interference oscillations and located in the photon region II. As shown in Fig. 2(a), the absorption edge shows a blueshift trend with decreasing temperature, which agrees well with most of the semiconductor materials.[10,16,17] It indicates that the OBG energy increases with decreasing temperature and the BLT material has a negative temperature coefficient. In order to elucidate the temperature effects on the OBG energy in detail, an enlarged transmittance spectral region near the absorption edge (3.6–4.5 eV) is plotted in Fig. 2(b). As we can see, the spectral transmittance value intensively decreases with the photon energy and down to zero in the ultraviolet region beyond 4.5 eV. This is due to the strong absorption from fundamental band gap and high-energy critical point transitions, which cannot be detected by the present transmittance spectra.

It is important to note that the absorbance of the BLT films can be directly obtained from the transmittance spectra due to the complete transparency of quartz substrate in the photon region of interest.[12] Moreover, the absorption coefficient α can be calculated if the film thickness is known. From the interference oscillations in the transparent region, the BLT film thickness is estimated to be about 145 nm, which is closer to the nominal growth thickness. Figure 3(a) shows the absorbance data of the BLT film at three typical temperatures: 77, 300, and 500 K, respectively. The α value is located between 10^4 and 10^5 cm^{-1} among the photon energy region of 3.6–4.0 eV. The data agree with those from wide band gap semiconductors and further confirm that the BLT films have a wide OBG energy. Correspondingly, it clearly indicates that the absorption edge presents a blueshift trend with decreasing temperature.

In order to explain the behavior and temperature dependences, the OBG energy has to be determined experimentally. The OBG energy for the BLT films was calculated by considering a direct transition between the valance and conduction bands when the photon energy falls on the materials. The power law behavior of Tauc $(\alpha E)^2 \propto (E-E_g)$ for allowed direct transition, here, E_g is the direct OBG energy. So the straight line between $(\alpha E)^2$ and E will provide the E_g value, which is extrapolated by the linear portion of the plot to $(\alpha E)^2=0$, as seen in Fig. 3(b). The E_g is varied from 3.77 to 3.88 eV corresponding to decreasing temperature. In particular, the value is 3.82 eV at RT, which is less than that (4.64 eV) on silicon substrate. As the XRD patterns show (Fig. 1), the crystalline quality of the present BLT film is significantly different from those on silicon substrates. Generally, the diffraction peaks for quartz substrate are much stronger than those from silicon substrate, which indicates that the quartz substrate can induce the well-defined crystalline formation. Moreover, there are some diffraction peaks (111), (0.0.16), (220), and (137) for the present BLT films. Due to different XRD peaks appearing, the BLT films obviously are of polycrystalline structure for the quartz and silicon substrates.

It was reported that the structural distortions can affect the electronic band structures of the BLT material.[4] Based on the XRD peaks (020)/(200) and (006), the lattice constants $a(b)$ and c can be calculated. For parameters $a(b)$, the values are 5.42 and 5.46 Å for the quartz and silicon substrates, respectively. However, the c parameter is estimated to be 33.07 and 32.89 Å for two different substrates. Therefore, the BLT films on quartz and silicon show different crystalline distortions on the c or $a(b)$ axis, as compared with the theoretical results.[4] Owing to different full widths at half maxi-

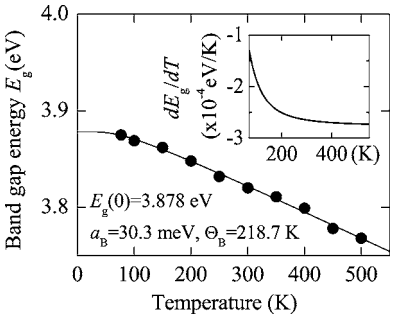

FIG. 4. Temperature dependence of the OBG energy for the BLT film. The fitting results using Eq. (1) are plotted with solid line. The inset shows the band gap narrowing coefficient.

mum, the average crystalline size was calculated to be about 28 and 37 nm for the quartz and silicon substrates, respectively. For film material, there is strain due to lattice mismatch between film and substrate, which is slightly different for two substrates from the known lattice constants. There may be larger strain in the present BLT film owing to larger distortion [0.74% along $a(b)$ axis] and less thickness compared with silicon substrate (0.54% along c axis and about 340 nm).[8] It can be believed that the OBG discrepancy is mainly ascribed to the different crystalline qualities and strains due to the diverse substrate materials.

Temperature dependence of the OBG energy can provide some information, e.g., interband transitions and electron-phonon interactions.[17] Generally, the temperature dependence can be described using the Bose-Einstein model,[16–18] in which the carrier-phonon coupling is taken into account, and can be written as

$$E_g(T) = E_g(0) - 2a_B/[\exp(\Theta_B/T) - 1]. \quad (1)$$

Here, $E_g(0)$ is the OBG energy toward 0 K, a_B is the coupling interaction strength, Θ_B is the average phonon temperature, and T is the experimental temperature. In principle, the agreement between the experimental and theoretical data is good with the model, as shown in Fig. 4. The $E_g(0)$ value is estimated to be about 3.878 eV. The parameters a_B and Θ_B in Eq. (1) are 30.3 meV and 218.7 K, respectively. These values are much less than the data from the wide band gap materials GaN (158 meV and 564 K) and AlN (670 meV and 1000 K). It indicates that the longitudinal optical phonon replicas of the carrier transition could be much weaker in BLT material than in III-nitride compounds.[17] In BLT dielectric material, the carrier transition is expected to be more difficult or forbidden. This can be due to more optical phonons in complicated perovskite crystal structure, which occupy some lower photon frequencies, as compared to most of semiconductors.[19,20] The band gap narrowing coefficient (dE_g/dT) of the BLT film is shown in the inset of Fig. 4. At RT, the coefficient is calculated to be -2.65×10^{-4} eV/K, which agrees with the data for most semiconductors reported.

In conclusion, the OBG energy of ferroelectric BLT films has been investigated using ultraviolet-infrared transmittance spectra in the temperature range of 77–500 K. It is found that the E_g decreases with the temperature and BLT material has a negative band narrowing coefficient, which is about -2.65×10^{-4} eV/K at RT.

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