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Surface, bulk, and interface electronic states of epitaxial BiFeO₃ films

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The authors report on the depth-resolved cathodoluminescence spectroscopy studies of the surface, bulk, and interface-localized electronic states in the band gap of epitaxial BiFeO₃ thin films. The BiFeO₃ films show a near band edge emission at 2.7 eV and defect emissions at energies varying from 2.0 to 2.5 eV. The overall results clearly suggest that the electronic structure, especially the defect states and their spatial distributions, of BiFeO₃ films are strongly dependent on the growth conditions and method, stoichiometry, and strain, so that understanding and controlling them are crucial to optimize BiFeO₃ film properties. © 2009 American Vacuum Society.

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BiFeO₃ thin films have recently received considerable interest due to the simultaneous ferroelectric and magnetic properties and potential applications in magnetoelectric devices.^{1,2} Investigations of the electronic structure, in particular, the band gap and defect states of BiFeO₃ films, are of particular importance due to their effects on internal electric fields, free carrier density and recombination, and high frequency dielectric loss. Therefore, a complete understanding of the state and distributions of defects in BiFeO₃ films is crucial to improving and optimizing their electric and ferroelectric properties. For example, the electrical leakage problem sometimes found in BiFeO₃ films could be due to defects.

In this article, using depth-resolved cathodoluminescence spectroscopy (DRCLS),³ we have compared the surface, bulk, and interface-localized electronic states in the band gap of epitaxial BiFeO₃ thin films grown by pulsed-laser deposition (PLD), metal organic chemical vapor deposition (CVD), and molecular-beam epitaxy (MBE). We found that different growth techniques, as well as processing conditions, have a strong effect on the electronic states of the BiFeO₃ thin films. Moreover, the states and distributions of defects also depend on the stoichiometry and strain in the film.

The BiFeO₃ samples studied are single-phase high-quality epitaxial films grown on SrTiO₃ or DyScO₃ substrates with SrRuO₃ or La_{0.7}Sr_{0.3}MnO₃ buffer layers.⁴⁻⁷ The DRCLS measurements were performed in an ultrahigh vacuum chamber with samples indirectly cooled with a helium cryotip to ~42 K. Incident electron beam current was held constant at 2 mA and the beam voltage (E_B) was varied from 0.5 to 5 kV

so that beam power increased with increasing E_B . For $E_B = 1, 2, 3, 4,$ and 5 keV, Monte Carlo simulations of the electron cascade yield penetration depths of ~18, 45, 75, 110, and 150 nm, respectively, below the bare BiFeO₃ surface.

The cathodoluminescence (CL) spectra measured at a beam voltage of 1 kV are shown in Fig. 1 for BiFeO₃ films grown by different methods. The BiFeO₃ films grown by PLD show strong emissions at 2.5 and 2.7 eV, and weak features around 2.2 eV, similar to the CL features observed in the BiFeO₃ films grown by magnetron sputtering.⁴ The 2.7 eV feature is the near band edge emission, and the 2.5 eV feature is oxygen vacancy related defect emission.^{8,9} However, for the films grown by MBE and CVD, the strong CL features shift to lower energies, 2.2 and 2.4 eV for the MBE-grown film, and 2.0 and 2.2 eV for the CVD-grown film, respectively. The shift in the CL features indicates the dependence of the electronic states of BiFeO₃ films on the growth process. For example, it is well known that proper oxygen stoichiometry control during MBE growth is a serious issue, and as a result, the MBE-grown film might have higher concentration of oxygen vacancies. In addition, it is notable that the BiFeO₃ films were grown on different buffer layers, 20 nm (La, Sr) MnO₃ for the MBE-grown film and 50 nm SrRuO₃ for the PLD- and CVD-grown films. Such differences might also affect the growth and the quality of the BiFeO₃ films. Further investigation is underway to explore the detailed effect of growth conditions, such as growth temperature and oxygen pressure, on the electronic states of BiFeO₃ films.

The defect states of BiFeO₃ films are sensitive to the post-growth cooling condition as well. Shown in Figs. 2(a) and 2(b) are the CL spectra of the PLD-grown BiFeO₃ films

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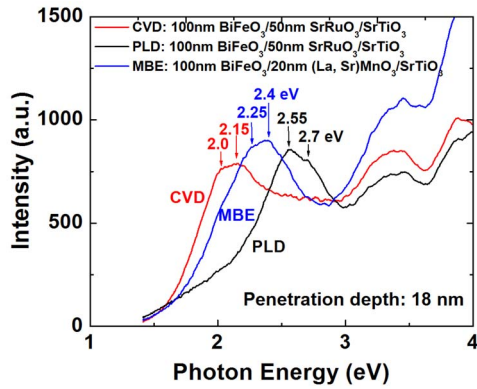


FIG. 1. (Color online) CL spectra measured at a beam voltage of 1 kV (corresponding to a penetration depth of 18 nm) for BiFeO₃ films grown by PLD, MBE, and CVD.

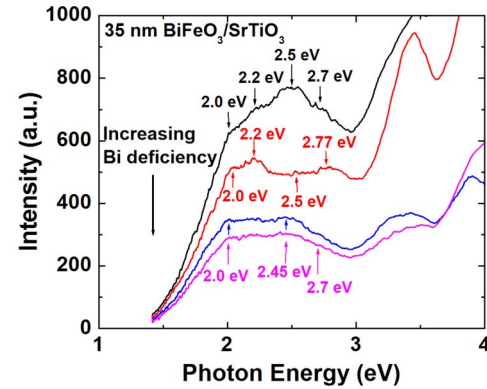


FIG. 3. (Color online) CL spectra measured at a beam voltage of 1 kV (corresponding to a penetration depth of 18 nm) for Bi-deficient BiFeO₃ films grown by MBE.

cooled in 100 mTorr O₂ and 760 Torr O₂, respectively. The film cooled at lower O₂ pressure shows a prominent 2.0 eV peak for all penetration depths, but the film cooled at higher O₂ pressure only shows weak 2.0 eV feature at the penetration depths deeper than 50 nm. The result suggests that the 2.0 eV defect is possibly oxygen vacancy related, and post-growth cooling in O₂ with higher pressure could reduce the density of oxygen vacancies in BiFeO₃ films, especially at the top surface. It is interesting that a strong emission at 2.5 eV is observed for both films and does not seem to be as sensitive to the cooling O₂ pressure as the 2.0 eV emission.

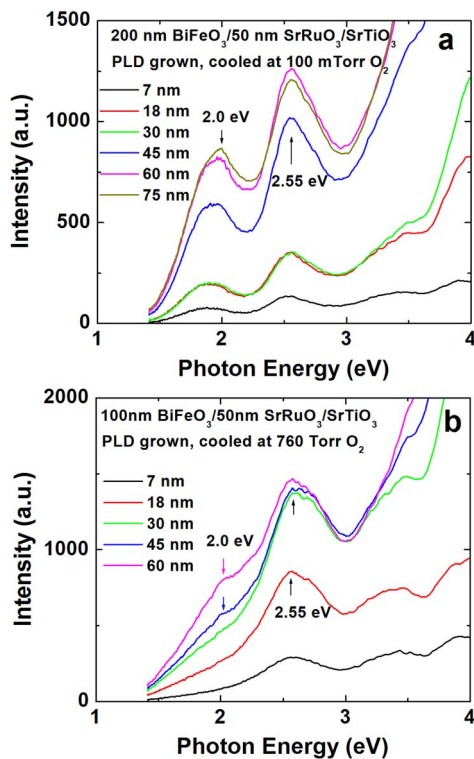


FIG. 2. (Color online) Depth resolved CL spectra of the PLD-grown BiFeO₃ films cooled at different O₂ pressures: (a) 100 mTorr and (b) 760 Torr.

The effect of stoichiometry on the defect states of BiFeO₃ films has also been studied. A series of Bi-deficient BiFeO₃ films was grown by MBE by controlling the growth temperature.⁷ It has been shown that BiFeO₃ films become more Bi deficient as the growth temperature increases.⁷ Figure 3 shows the CL spectra of these films measured at beam voltages of 1 kV, corresponding to a penetration depth of 18 nm. Although the films show very similar CL spectra, the relative intensities of the defect emissions vary with the Bi deficiency. As the Bi deficiency increases, although the overall intensity of CL spectra decreases, the intensities of the 2.0 and 2.2 eV features increase relatively to the 2.5 eV defect emission and the 2.7 eV near band edge emission. It is notable that the Bi deficiency has different effects on the different defect states. More work needs to be done to understand the relationship between Bi deficiency and the defect states and to examine the possibility that the 2.0 and/or 2.2 eV emissions may relate to Bi vacancies.

Finally we investigated the effect of strain on the electronic states of BiFeO₃ films. Figures 4(a) and 4(b) show the CL spectra of two BiFeO₃ thin film samples grown on SrTiO₃ and DyScO₃ substrates, respectively, with 50 nm thick SrRuO₃ buffer layers. The two samples were grown at exactly the same conditions and have the same layer structure and thickness except for the different substrates. Due to the different lattice mismatches, the BiFeO₃ film grown on SrTiO₃ substrate should be under a compressive strain of ~1.4%, while the film grown on DyScO₃ substrate should be under a compressive strain of only ~0.2%. Both films show defect emissions at 2.5 and 2.0 eV, but the film under very little strain shows an additional strong emission at 2.2 eV, which is absent for the highly strained film. Moreover, lattice distortion in substrate could also have effects on the structure and electronic states of the buffer layers and BiFeO₃ films. Compared to SrTiO₃, DyScO₃ has a highly distorted lattice and may induce more defects.

The overall DRCLS results clearly indicate that the electronic structure, especially the defect states and their spatial distributions, of BiFeO₃ films are strongly dependent on the film growth technique, process condition, stoichiometry, and

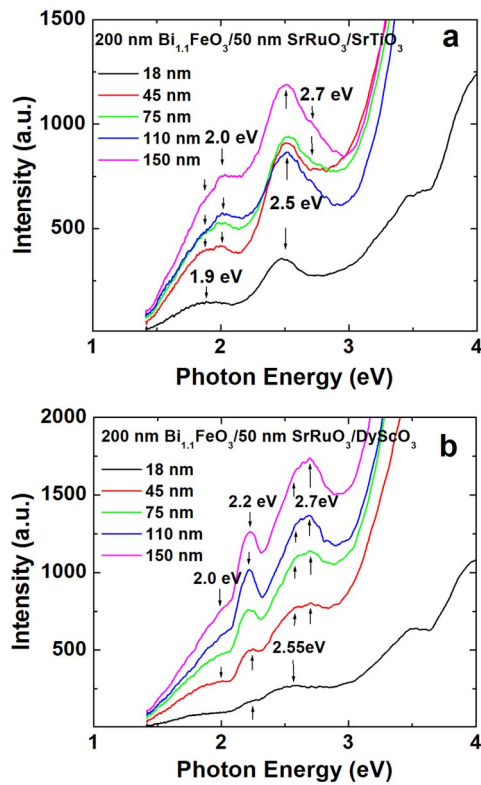


FIG. 4. (Color online) Depth resolved CL spectra of the PLD-grown BiFeO₃ films grown on different substrates: (a) SrTiO₃ and (b) DyScO₃.

strain. BiFeO₃ films show the 2.7 eV band edge emission and defect emissions at 2.0, 2.2, and 2.5 eV. The 2.7 eV band edge emission is in good agreement with the predicted band gap of 2.8 eV for BiFeO₃ using a screened exchange method⁸ and the measured band gap.^{4,10} Moreover, initial theoretical calculation suggests that defect states due to oxygen vacancies lead to transitions at ~ 0.3 eV below the band gap,⁹ which is consistent with our oxygen vacancy related defect emission observed at 2.5 eV. The effect of cooling O₂ pressure on defect states suggests that the 2.0 eV

defect state is more sensitive to cooling conditions than the 2.5 eV state. In addition, the defect states at 2.0, 2.2, and 2.5 eV show different responses to film stoichiometry and strain. The 2.0 and 2.2 eV emissions become relatively stronger than the 2.5 eV emission as Bi deficiency increases, and the 2.2 eV emission is stronger in the weakly strained films.

In summary, the DRCLS of the BiFeO₃ films show near band edge emission at 2.7 eV and defect emissions around 2.0, 2.2, and 2.5 eV. The defect states and their distributions are strongly dependent on the film growth technique, process condition, stoichiometry, and strain. In general, the films processed under high oxygen pressure and with high Bi content tend to have less oxygen vacancies. The results suggest that controlling growth conditions, stoichiometry, and strain are crucial to optimize BiFeO₃ film properties and related magnetoelectric devices.

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