Pulse laser deposition of BiFeO₃ films by polished targets

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Abstract. BiFeO₃ films had been deposited by pulse laser deposition using BiFeO₃ target. Nearly pure phase BiFeO₃ film had been grown simply by polishing target before deposition. X-ray diffraction (XRD), UV-visible-near infrared transmission spectrum and magnetization-magnetic field intensity (M-H) hysteresis loops had been measured. It was found that BiFeO₃ film deposited at 700 ºC by polishing target had (010) preferred growth orientation. The bandgap is determined to be 2.25eV. The magnetic domain distribution had been investigated by magnetic force atomic force microscopy.

1. Introduction
Multiferroics, which exhibit both electric and magnetic orders in single phase, provide new opportunity to design multifunctional magneto electronic devices. In recent years, BiFeO₃ has been intensively researched for its potential application in multifunctional devices due to the coexistence of ferroelectricity (Curie temperature 830ºC) and antiferromagnetism (Neel temperature 370 ºC) [1-3]. As a new lead free ferroelectric material, the polarization value of BiFeO₃ film can be as high as 110μc/cm², which is close to the polarization value of PbTiZrO₃[4].

BiFeO₃ film has been successfully deposited by many researchers using sputtering [5, 6], pulse laser ablation [7-9], sol-gel [4, 10], etc. Pure phase and well crystalline film is very essential for multiferroics application. Unfortunately, impurity phases, usually Bi₂Fe₄O₉ and Fe₂O₃, often emerge in the films and deteriorate the multiferroic properties. In vacuum deposition, bismuth rich targets are often used to overcome bismuth loss in order to deposit stoichiometric BiFeO₃ film [6]. Other growth parameters, such as oxygen pressure [5] and growth rate should also be carefully controlled. In our research, we find pure phase BiFeO₃ films could be deposited by polishing target before deposition. This method is much easier and time consuming for deposition of BiFeO₃ films.

2. Experimental details
Sintered Stoichiometric BiFeO₃ target were used to deposit BiFeO₃ films on quartz substrate by pulse laser deposition (excitation wavelength 193nm). Quartz substrates were carefully cleaned by distilled water and then by anhydrous ethanol. The films with thickness about 80nm were deposited at different growth temperature from ambient temperature to 700 ºC. In
order to control the phase of film, BiFeO₃ film was deposited at 700 °C with polished target. BiFeO₃ film was also deposited at 700 °C without polishing target. Crystal structure of the films was characterized by XRD from 15° to 70°. The transmission spectra of the films were measured from 320nm to 2500nm. Optical constants (n and k) were calculated by Lorentz oscillator model. Bandgap of the film were obtained by the cross point of tangential line of plot $\alpha^2 - h\gamma$ with energy axis. Magnetic domain distribution was investigated by magnetic force model of atomic force microscopy. Magnetization-magnetic field intensity (M-H) hysteresis loops were measured at low temperature at 298K, 273K 150K and 80K.

3. Results and discussions

As is depicted previously, bismuth loss is inevitable during vacuum deposition of BiFeO₃ films. Loss of bismuth always leads to the growth of Bi₂Fe₄O₉ and other impurity phase, which had also happened in our experiment. As is shown in figure.1, Bi₂Fe₄O₉ phase is predominant for the films deposited at all temperature without polishing the target. However, BiFeO₃ becomes the predominant phase if the target is polished before deposition, which is shown as curve E in figure.1. The BiFeO₃ phase shows (010) preferred growth orientation. It is thought that the loss of bismuth only occurs at the surface of target. Polishing process could make a stoichiometric fresh surface. Therefore the pulse laser ablation could make a stoichiometric BiFeO₃ phase and reduce the growth of impurity f Bi₂Fe₄O₉ phase.

![Figure 1](image-url)  
Figure 1. XRD spectrum of different samples deposited at different growth condition.

Optical transmission property in visible light range is very important for its potential application in magnetic-optic storage. In this experiment, UV-visible-near infrared transmission spectra of the samples have been measured and shown in figure.2 It is found the film deposited at different condition have good transmission from about 700nm to the near infrared. It is also found that BiFeO₃ films deposited at the center and rim of the glass substrate have different transmission properties, which indicates non-uniform of film thickness and even the different absorption. It is reasonable if the non-uniform intrinsic property of pulse laser ablation is considered. The cutoff wavelength of BiFeO₃ film at the center (BiFeO₃_700center in fig.2) and rim (BiFeO₃_700rim in fig.2) of substrate does not
change very much, which indicates they have nearly the same band gap. It is much interesting that Bi2Fe4O9 phase have larger band gap than BiFeO3, which is also shown in figure.2.

![Figure 2](image)

**Figure 2.** UV-visible-near infrared transmission spectrum of BiFeO3 films

The optical constants of BiFeO3 films are also calculated by fitting the transmission spectra (BiFeO3_700rim curve in fig.2) using Lorentz oscillator model. The refractive index (n) and extinction coefficient (k) is about 2.6 and 0.32 at 635nm, respectively, which is shown in figure.3. The absorption coefficient can be calculated by $\alpha = 4\pi k/\lambda$, where $\lambda$ is the wavelength. The optical band gap can be obtained by intersect of tangential line at energy axis in the plot $\alpha^2 - h\nu$, where $h\nu$ is optical energy in eV. The optical band gap of BiFeO3 films is about 2.25eV, which is shown in figure.4.

![Figure 3](image)

**Figure 3.** Calculated optical constants of BiFeO3 films

![Figure 4](image)

**Figure 4.** Band gap plot of BiFeO3 films

Magnetic force mode of atomic force microscopy was used to investigate magnetic domain distribution of BiFeO3 films. In first step, the top morphology image was recorded by constant-current mode, which is shown in figure.5. The surface is quite smooth and covered with homogeneous crystal particles. The crystal particle size of BiFeO3 film is about 200nm. In second step, the tip was lift 80nm higher than the surface of film. Far field force image was recorded as magnetic force image, which is shown in figure.6. The size of irregular magnetic domain is estimated to be about 400-500nm.
Figure 5  AFM top morphology picture of BiFeO₃ films deposited at 700°C with polished target.

Figure 6. MFM morphology picture of BiFeO₃ films deposited at 700°C with polished target.

Magnetization (M) vs. magnetic field intensity hysteresis loops of BiFeO₃ films at different temperature are shown in figure 7. In this experiment, the magnetization of quartz substrate could not be neglected because magnetization of BiFeO₃ is very weak for its thin film thickness. Magnetization of BiFeO₃ film overlaps with quartz substrate, which leads to the rotation of magnetic hysteresis loops. The area of hysteresis loop increases with decreasing of measurement temperature. The rotation of magnetic hysteresis loop makes the determination of saturated (remnant) magnetization much difficult. However, one can find that the saturated magnetization increase qualitatively with decrease of temperature.

Figure 7. Magnetization hysteresis loops of BiFeO₃ film on quartz substrate at different temperature.

4. Conclusions
BiFeO₃ films had been deposited on quartz substrate at different deposition temperature. It was found that nearly pure phase BiFeO₃ films could be easily deposited by polishing the targets before deposition. The films deposited at 700 °C by polishing targets have (010) growth orientation. The transmission spectrum were measured and fitted to get absorption coefficients. The bandgap of BiFeO₃ film was calculated to be 2.25eV. The magnetic domain distribution was measured by magnetic force microscopy. It was found the saturated magnetization of BiFeO₃ film was increased at low temperature.
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