The influence of using different substrates on the structural and optical characteristics of Bi$_2$VO$_{5.5}$ thin films

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Abstract. The BVO thin films have been successfully grown on Si (100) and SiO$_2$/Si (100) substrates via sol-gel technique followed by rapid thermal annealing at 650 °C. The crystalline nature of the films has been studied by X-ray diffraction and indicates all the films are well-crystallized. Atomic force microscopy was used to study the surface morphology of the BVO thin films which shows the films are compact and homogeneous. The BVO film with SiO$_2$ buffer layer has a larger grain size and lower root mean square roughness than that directly grown on Si. The Raman spectra measurement in the range of 300-1500 cm$^{-1}$ reveals that the buffer SiO$_2$ layer definitely influences the structure of BVO thin films. The optical properties of the BVO thin films are investigated using spectroscopic ellipsometric in the wavelength range of 400–900 nm. In the visible range, the refractive index of the film is about 2.42 and the extinction coefficient is 0.036.

1. Introduction

Ferroelectric thin films have been studied for many years owing to their interesting electronic and optical properties, which have led to a wide range of technical applications. In recent years, there has been much significative progress in the applications of ferroelectric thin films in practical devices such as nonvolatile ferroelectric memories, infrared sensors, and electro-optic devices$^{[1-4]}$. Bi$_2$VO$_{5.5}$ (BVO), as a typical ferroelectric material with a layered perovskite structure, is promising and has attracted much attention$^{[5-7]}$. It is an interesting member with n=1 of Aurivillius family (Bi$_2$O$_3$)($A_{n-1}$Bi$_n$O$_{3n+1}$)$_2^-$ of Bi-based layered structured oxides consisting of (Bi$_2$O$_3$)$_{2+}$ layers interleaved with pervoskite blocks like sheets of (VO$_{3.5}$)$^{2-}$ octahedra$^{[8]}$.

Metal/ferroelectric/insulator/semiconductor (MFIS) structure is a key part of ferroelectric field effect transistor (FeMFET)$^{[9]}$. Therefore it is necessary to investigate the influence of insulating buffer layers on the structural characteristics of the BVO films. In our works, Sol-gel technique, which is good for grown large area of high quality thin films, is the method we have used to prepare the BVO thin films on Si (100) and SiO$_2$/Si (100) substrates, while SiO$_2$ is the insulating buffer layer. Furthermore, the rapid thermal annealing (RTA) has also been adopted to avoid the interface diffusion.

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and the formation of interfacial layer between the BVO films and the substrates \([10]\). In addition, because of the applications in electro-optic devices, optical sensors and waveguide, the optical characteristics of \(\text{Bi}_2\text{VO}_{5.5}\) thin films grown on Si substrate are obtained.

2. Experimental

The ferroelectric BVO thin films were prepared on p-Si (100) and the configuration SiO\(_2\)/Si (100) substrates by the sol-gel process with rapid thermal annealing techniques. In order to obtain the precursor solution, ammonium metavanadate and bismuth nitrate were selected as starting materials. The amount of bismuth nitrate is excessive by 5% for compensating the loss of Bi. The solvent was acetic acid. The details about the process of preparing the precursor solution are described in our previous work \([11]\). The resultant precursor solution was coated on Si and SiO\(_2\)/Si substrates by spin coating at 4000 rpm for 20s, followed by heating at 380 °C for 3 min to remove organic solvent and other volatile materials. Then, the films were annealed at 650 °C for 5 min. The deposition as well as the heating and annealing procedure was repeated for eight times.

The crystalline nature of the BVO films was characterized by X-ray diffraction (XRD; D/max 2200 VPC) using CuK\(\alpha\) radiation. Atomic force microscope (AFM; Dimension 3100) was used to investigate the surface morphology and microstructure. Raman scattering spectra in the range of 300-1500 cm\(^{-1}\) were obtained by Jobin-Yvon LabRAM HR 800UV micro-Raman spectrometer. And the optical properties of the BVO films deposited on Si were studied via Spectroscopic ellipsometry (SC630) in the wavelength range of 400-900 nm.

3. Results and discussion

Figure 1 represents the X-ray diffraction (XRD) patterns of the BVO films deposited on Si and SiO\(_2\)/Si substrates, respectively. Both of the films are annealed at 650°C. As it can be seen, the film deposited on Si exhibits a highly c-preferred orientation structure and all of the diffraction peaks match well with those of typical BVO layered perovskite polycrystalline structure as well as on SiO\(_2\)/Si. There are no impure and secondary phases. And strong and sharp peaks mean the good crystallinity of films. The BVO films grown on SiO\(_2\)/Si show stronger and sharper diffraction peaks than those directly deposited on Si substrate. The reason must be that SiO\(_2\) buffer layer decreases the mismatch of lattice constant between BVO and Si. So, the existence of the SiO\(_2\) layer results in better crystallized BVO films.

![Figure 1. XRD patterns of the BVO films deposited on Si and SiO\(_2\)/Si substrates.](image)

The surface morphology and microstructure of the BVO films for a 10×10\(\mu\)m\(^2\) area have been studied by AFM. Figure 2a and 2c show the two-dimensional AFM images of the BVO thin films grown on Si and SiO\(_2\)/Si substrates, respectively. It had been proved that both of them exist no cracks and flaws, which suggests that the films compact and homogeneous. But the grain size of films
including SiO$_2$ buffer layer is larger than that directly grown on Si. Figure 2b and 2d show the three-dimensional micrographs of BVO on Si and SiO$_2$/Si substrates, respectively. The root mean square (rms) roughness of the BVO film on SiO$_2$/Si is 8.242 nm, which is better than 9.361 nm derived from the BVO films deposited on Si.

**Figure 2.** The two-dimensional (a) and three-dimensional (b) AFM images of the BVO thin film grown on Si substrate, the two-dimensional (c) and three-dimensional (d) AFM images of the BVO thin film grown on SiO$_2$/Si substrate.

Raman spectra of BVO thin films are depicted in Figure 3. We can find the Raman peaks around 324, 372, 512, 752 and 858 cm$^{-1}$ for the BVO/Si film. Because of existence of SiO$_2$ layer, the strongest peak at 858 cm$^{-1}$ becomes weaker. The symmetric stretching of VO$_{3.5}$ octahedra, which the band at 858 cm$^{-1}$ represents, shows large change $^{12-13}$. Hence, the buffer SiO$_2$ layer definitely influences the
structure of BVO thin films. However, the evident changes of other Raman peaks have not been noticed.

The optical constants of the BVO films deposited on Si substrate are detected by spectroscopic ellipsometry at room temperature. Figure 4 gives the refractive index and the extinction coefficient of the BVO film at 400-900 nm wavelength range, respectively. Initially, the refractive index decreases sharply with wavelength increasing up to 550 nm and then keeps almost constant. On the other hand, the extinction coefficient drops rapidly in the range of 400-650 nm, and reduces to 0.017 when the wavelength is larger than 650 nm. In the visible range (600 nm), the refractive index is about 2.42 and the extinction coefficient is 0.036, which is almost the same as the optical constants of the BVO films obtained by pulsed laser ablation technique [14].

Figure 4. The refractive index n (a) and the extinction coefficient k (b) of BVO film deposited on Si substrate.

Figure 5 shows the absorption coefficients $\alpha$ of BVO films in the range of 400-900 nm. It is observed that the absorption coefficients is quite high at 400 nm and then decreases dramatically with wavelength increasing up to 650 nm. After that, the change goes gently.

Figure 5. The absorption coefficients $\alpha$ of BVO film deposited on Si substrate.
4. Conclusion
The high quality BVO thin films were successfully grown on Si and SiO$_2$/Si substrates via sol-gel method. All films are c-axis orientation. The existence of SiO$_2$ buffer layer brings in better crystallized BVO films and better surface morphology and microstructure with larger grain size. Besides, the buffer SiO$_2$ layer definitely influences the internal structure of BVO thin films. The refractive index of BVO film is about 2.42 and the extinction coefficient is 0.036 in the visible range.

Acknowledgements
This work was supported by the National Natural Science Foundation of China (No. 60990312), the State Key Basic Research Program of China (2007CB924902), Shanghai Leading Academic Discipline Project (B411) and Science and Technology Commission of Shanghai Municipality (10JC1404600).

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