Structure, optical and electrical properties of Bi$_2$VO$_{5.5}$ films deposited on ITO/glass substrates by chemical solution method

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Abstract

Bismuth vanadate (Bi$_2$VO$_{5.5}$) thin films were fabricated on indium-doped tin oxide (ITO)-coated glass substrates by chemical solution method combined with a rapid thermal annealing process. The structure of the films was characterized with X-ray diffraction and atomic force microscopy. The Bi$_2$VO$_{5.5}$ films annealed at 600 °C showed a good match with the ITO coated glass substrates and had a desired perovskite structure with high (00l) preferred orientation. The spherical grains with a homogeneous distribution of high crystallinity and packing density were observed. Optical properties of the Bi$_2$VO$_{5.5}$ thin films were studied by Raman spectra and the lattice vibration modes of the films were obtained. A low frequency dielectric dispersion was observed in the films. Dielectric constant and loss was about 75 and 0.076 at 10kHz, respectively. The ac conductivity obeyed Jonscher’s universal power law, which may be originated a possible hopping mechanism for Bi$_2$VO$_{5.5}$ thin films. The complex impedance traces revealed material dielectric dispersion nature and the presence of grain effects in the films.

BVO; chemical solution method; (00l) preferred orientation; optical properties; electrical properties

1. Introduction

Recently, the ferroelectric materials belonging to the family of the Aurivillius phases have attracted great attention for a variety of integrated device applications such as nonvolatile memories, optical memories, piezoelectric and electro-optic devices[1, 2]. Bi$_2$VO$_{5.5}$ (BVO), a member of bismuth layer family, has a relatively low crystallization temperature and low dielectric constant, and thus BVO thin films have many potential and demonstrated applications, such as integrated ferroelectric devices[3]. The BVO films have been fabricated on metallic as well as oxide electrodes and their structural and electrical properties were investigated[3-7]. Indium-doped tin oxide (ITO) is the most extensively used material as a transparent electrode to fabricate oxide thin films. However, few studies have involved the optical and electrical properties of BVO thin films deposited ITO/glass (ITO/glass) substrates by chemical solution deposition (CSD) processing. In this paper, we grew BVO thin films on ITO/glass substrates by CSD process annealing at 600 °C, and studied their structural, optical and electric properties.

2. Experimental

The BVO films were prepared on ITO/glass substrates by a CSD method. Bi(NO$_3$)$_3$·5H$_2$O and NH$_4$VO$_3$ were used as raw materials. All the chemical agents were analytical grade purity. Transparent green precursor solutions were obtained by dissolving corresponding stoichiometric reactants into the
acetic acid, respectively. Using the aged solution, BVO thin films were deposited on ITO/glass substrates. The spin-coated films were annealed at 120 °C for 180 s, 380 °C for 180 s and crystallized at 600 °C for 240 s in a rapid thermal process (RTP) furnace. These coating and annealing processes were repeated several times to achieve desired film thickness. For the electric measurements, the platinum top electrodes of $9 \times 10^{-4}$ cm$^2$ area were deposited on the surface of the BVO films through a shadow mask and thermal evaporation technique.

Phase identification of the samples were performed by X-ray diffraction (XRD; D/max2200VPC, Cu Ka, $\lambda=1.54056\,\text{Å}$). The surface features of the films were examined by means of a tapping mode atomic force microscope (AFM) (Veeco CP-II). The Raman spectra in the 1000–200 cm$^{-1}$ range were measured using a Jobin-Yvon LabRAM HR 800UV micro-Raman spectrometer. The electric properties were measured by a HP 4194A impedance analyzer in the frequency range of 100 Hz–10 MHz with an applied voltage of 0.1 V. All measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of BVO/ITO thin films annealed at 600 °C. XRD results showed that the films in our study had a high degree of crystallinity and a desired perovskite structure with preferred (00l) preferred orientation for the selective peaks at (002) and (006) are strong and sharp$^{[3, 7]}$. It indicates that the BVO films match well with the ITO/glass substrates and have a lower crystallinity sintering temperature in the CSD process$^{[8]}$.

![XRD patterns of BVO/ITO thin films annealed at 600 °C.](image)

Fig. 1. XRD patterns of the BVO/ITO/glass thin films annealed at 600 °C.

![AFM images of BVO/ITO thin films annealed at 600 °C.](image)

Fig.2 The AFM images of BVO/ITO/glass films annealed at 600 °C. (a) surface morphology and (b) three-dimensional topography
The surface morphology and three-dimensional of BVO/ITO/glass thin film were characterized through AFM (Fig. 2). The spherical grains with a homogeneous distribution of high crystallinity and packing density were observed. The homogeneous crack-free appearance and dense structure in all scanned areas of the sample indicated the BVO thin film have a good match with the ITO/glass substrates. The surface showed a mean grain size about 200 nm and the root-mean-square (RMS) value of the surface roughness is about 10-12 nm.

Fig. 3 showed Raman spectra of BVO/ITO/glass thin films annealed at 600 °C. In $n=1$ perovskite materials, the Raman and IR modes can be described as following[9],

$$2A_{1g}(R) + B_{1g}(R) + 3E_g(R) + 5A_{2u}(IR) + B_{2g}(IR) + 6E_u(IR)$$

where $A_{1g}$, $B_{1g}$ and $E_g$ are Raman active modes. From the spectra, Raman band around 853 cm$^{-1}$ was the strongest of all the Raman peaks which represented the symmetric stretching of VO$_3$.5□0.5 octahedra for $A_{1g}$ vibrational stretching mode. The band 200-500 cm$^{-1}$ can be assigned the reversion and vibration of VO$_{3.5}$.□0.5 oxygen octahedra corresponding vibrational modes. These $B_{2g}$ and $B_{3g}$ mode peaks were very close and the degenerate vibrational modes make the peaks merge.

![Fig.3 Raman spectra of BVO/ITO/glass thin films annealed at 600 °C.](image)

![Fig.4 Relative dielectric constant ($\varepsilon'$) and dielectric loss (tanδ) as a function of frequency of BVO/ITO/glass films annealed at 600 °C.](image)

The electrical properties such as dielectric constant ($\varepsilon'$), dielectric loss (tanδ) and ac conductivity as a function of frequency of the annealed BVO/ITO/glass were also investigated. The frequency variation (100 Hz–10 MHz) of both the dielectric constant and dielectric loss of BVO thin films were
shown in Fig. 4. The $\varepsilon'$ was 75 with the tan$\delta$ of 0.076 at 10 kHz. A low frequency dielectric dispersion was observed for $\varepsilon'$ found to decrease gradually with the increase of frequency. It originated the ferroelectric nature of BVO material and was closely related to the grain boundaries, free charges and oxide ion vacancies[4]. The dielectric constant of as deposited BVO film in our experiments was higher than that of the BVO films on ITO/glass substrates ($\varepsilon'$~52 at 10 kHz) owing to the increased crystallinity and packing density, as reflected in AFM[10].

The $ac$ conductivity measurements by impedance spectroscopy are a useful technique for investigating the charge carriers’ nature and the $ac$ conductivity response. The frequency dependence of $ac$ conductivity for BVO films was shown in Fig. 4. It was clear that the $ac$ conductivity can be classified two different process of ionic movement: low frequency independent region ($dc$ conductivity) was arising from inter-well hopping domination and plateau at higher frequencies dependent region ($ac$ conductivity) contributing from intra-well hopping domination of this system[11]. This behavior suggested that electrical conduction in the films was a hopping mechanism and can be defined as conventional Jonscher’s power law[11],

$$\sigma_{ac} = \sigma_{dc} [1 + (f/f_p)^s]$$

(2)

where $\sigma_{ac}$ is the $dc$ conductivity, $f_p$ is a crossover frequency and $s$ is a fractional exponent related to the degree of correlation among ions. The term $(f/f_p)^s$ comprises the $ac$ dependence and characterizes all dispersion phenomena. The change in the values of $s$ is related to the charge carriers. A well-fitted solid line using Eq. (2) for sample film was also shown in the Fig. 4.

![Fig. 5. The experimental and theoretical fit for $ac$ conductivity as a function of frequency of BVO/ITO/glass thin films at different frequencies. The inset is the complex impedance spectra.](image)

The inset of Fig. 4 showed the complex impedance spectra (Nyquist plots) for the BVO thin films. Only a arc was present, exhibiting material dielectric dispersion nature[12]. Single semicircle nature predicted the grain interior charge transfer mechanism for BVO films, with higher resistance. In fact, the complex plots can be modeled with an equivalent circuit containing a parallel resistance ($R_g$) and capacitance ($C_g$) elements. When frequency $\omega$ equals to the relaxation frequency $\omega_r = 1/R_g C_g$, the imaginary part ($Z''$) achieves maximum.

4. Conclusion

High-quality BVO thin films with (001)-preferred orientation have been successfully prepared on ITO/glass substrates by CSD method. A homogeneous distribution of gains were observed in the films.
from the AFM microscopy. The lattice vibration modes of BVO thin films were obtained by Raman spectra, which mainly originated from the reversion and vibration of VO$_{3.5}$O$_{0.5}$ oxygen octahedra. Dielectric constant and loss was about 75 and 0.076 at 10kHz, respectively. The ac conductivity obeyed Jonscher’s universal power law, which may be assigned a possible hopping mechanism for BVO thin films. The complex impedance traces revealed material dielectric dispersion nature and the presence of grain effects in the films.

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