Photoelectric properties of Bi$_2$Se$_3$ films grown by thermal evaporation method

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Abstract

The Bi$_2$Se$_3$ films were prepared by thermal evaporation on different substrates (FTO, ITO and Glass). The structure and morphology are characterized by XRD and SEM. The optical band gap ($E_g$) is 1.47 eV, 1.54 eV, and 1.59 eV, respectively. The I-V and C-V curves have been obtained by a photoelectrochemical (PEC) cell system, and the results indicated the Bi$_2$Se$_3$ film is $n$-type semiconductor. The transient photocurrent response of Bi$_2$Se$_3$/FTO and Bi$_2$Se$_3$/ITO were measured to evaluate the application potential of Bi$_2$Se$_3$ films in solar cell. The above results indicated that the Bi$_2$Se$_3$ films have advantages in the application of solar cells.

1. Introduction

Bi$_2$Se$_3$ is one of the important V-VI binary compounds with a layered structure has a direct band gap [1]. Bi$_2$Se$_3$ has been focused due to its potential applicability in electromechanical devices [2], optical recording system [3], thermoelectrical devices [4], that has been used in photosensitive devices [5], thermoelectric applications [6], infrared detectors [7]. The theoretical work suggests that this compound can be used as a solar cell [8, 9], but few experimental data were found to support interesting expectations. Sankapal et al reported that power conversion efficiency ($\eta$) and the fill factor (FF) of the cell are 0.032 and 0.43 respectively [10]. Formation of Mo-doped Bi$_2$Se$_3$ thin films with light conversion efficiency ($\eta$) were found less than 0.10% by Kharade et al [5]. After annealing, Jana et al obtained the optical conversion efficiency of Bi$_2$Se$_3$/FTO (fluorine-doped tin dioxide) thin films is 3.70%, which has a promising application prospect for the solar cells [11]. Bi$_2$Se$_3$ films are being prepared by various techniques: electrodeposition [9], physical vapor deposition (PVD) [12] chemical vapor deposition (CVD) [13], molecular-beam epitaxy (MBE) [14], ionic layer adsorption and reaction (SILAR) method [15]. Among these methods, vacuum thermal evaporation is an inexpensive and easy method [16–20]. It can be effectively used to prepare doped films and composites materials [21–23]. High quality V-VI compounds films prepared by vacuum evaporation have been reported [24, 25]. In this paper, we report synthesis of Bi$_2$Se$_3$ films were obtained by vacuum thermal evaporation. The structural and morphological of the samples were investigated. The optical and photoelectric properties of Bi$_2$Se$_3$ films on different substrates were discussed.

2. Experimental

Bi$_2$Se$_3$ films were prepared on different substrates by the thermal evaporation method. Before that, Bi$_2$Se$_3$ crystal powder were prepared by melt growth reaction [26]. The schematic diagram of the thermal evaporation equipment is shown in figure 1, and about 1.0 g of Bi$_2$Se$_3$ crystals powder was added into a tungsten boat. After the pressure in the vacuum chamber reaches $4 \times 10^{-4}$ Pa, adjust the speed of the sample holder to 10r/min, close the vacuum chamber gate valve, and turn on the evaporation current until the evaporation is completed. Films were deposited on transparent conductive glass FTO, ITO and ordinary glass in a thermal evaporation vacuum.
system. The deposited films were placed in an annealing furnace for post-annealing with temperature region of 300 °C. Finally, Bi₂Se₃ films were obtained.

The crystal structures of Bi₂Se₃ thin were analyzed by x-ray powder diffractometer (XRD, TD3500) with Cu-K radiation (λ = 1.5418 Å). The morphologies of Bi₂Se₃ films were detected by the field emission scanning electron microscopy (FESEM, merlin compact). The energy dispersive x-ray analysis (EDX) equipped of FESEM system has been used to identify the compositions for the films. Get the binding energy of excited electrons by x-ray photoelectron spectrometer (XPS, Thermo Fisher K-Alpha). The optical spectra were obtained using a Varian UV–vis-NIR spectrophotometer (Agilent Cary 5000). Photocurrents were recorded on an electrochemical workstation of CHI760E, and a Xenon lamp (PLS-SXE 300/300UV) was a light source with 420 nm filter.

3. Results and discussions

The x-ray patterns of Bi₂Se₃ films on different substrates are shown in figure 2. With reference to the standard data of Bi₂Se₃ (JCPDS no. 33-0214), all the diffraction peaks are centered at 9.54, 18.8, 29.72, 35.76, 40.8, 43.34, 60.66, respectively, it is to belong to the Bi₂Se₃ crystals, and no diffraction peaks from other impurities were found. The results of XRD indicated that the Bi₂Se₃ crystals films have been grown on the glass, ITO and FTO at 300 °C. The highest intensity diffraction peak at 2θ = 29.72 (0 1 5) shown in figure 2, the grain size on the surface of the films for are 193 Å, 198 Å, and 221 Å by using the Debye–Scherrer (DS) [17, 27].

The samples were analyzed by EDX to determine the composition of Bi₂Se₃ films. From the results of surface scanning, it was found that the films consisted of Bi element and Se element. The EDX results demonstrate that the atomic ratio of samples is about 2:3, which match to the stoichiometric composition of Bi₂Se₃, as shown in table 1. The atomic ratio of Se/Bi is larger than the ideal atomic ratio of 1.5. It indicates that Se atoms escape from
the Bi\textsubscript{2}Se\textsubscript{3} films and there are Se vacancies. FESEM images showing the surface morphology of the samples were shown in figure 3.

As seen in the figures 3(a)–(c), the grains were dense and evenly distributed on the different substrates, and the grain size is about 15~25 nm for different samples. This is basically the same as the results we observed with XRD. The grain size of thin films on glass substrate is smaller than that on FTO and ITO substrates, which may be due to the fact that FTO and ITO are conductive substrates. And they offer more multicore centers than non-conductive glass substrates, so they are more likely to form large particles [27]. From the cross-sectional images, it can be seen that the thickness of the Bi\textsubscript{2}Se\textsubscript{3} films on the three substrates is 389 nm (FTO), 385 nm (ITO), and 364 nm (glass), respectively. The Bi\textsubscript{2}Se\textsubscript{3} films on the conductive glass substrate is thicker than that of glass, which may be due to the better adhesion of the conductive film substrate.

XPS spectrum further explored the elemental composition of Bi\textsubscript{2}Se\textsubscript{3} deposited on different materials. The content and valence of the studied elements were obtained, and the results shown in figure 4. From figure 4(a), we found that Bi, Se, C and O elements consisted in the Bi\textsubscript{2}Se\textsubscript{3}/ITO films. The peak of O1s and C1s is weak, which is attributed to impurities from surface of the films. The Bi and Se element information indicates that the films were prepared as expected by XPS images. In the figure 4(b), the two peaks of Bi4f appear in 163.58 eV and 158.28 eV, respectively, and the Bi4f peak of FTO, ITO is smaller than the peak of glass and a significant accompanying peak appears. For the Bi\textsubscript{2}Se\textsubscript{3} films on FTO, ITO and glass, the difference of the binding energy between the peaks of Bi4f\textsubscript{5/2} and Bi4f\textsubscript{7/2} is 5.4 eV, 5.3 eV and 5.3 eV, respectively, corresponding to the Bi\textsuperscript{3+} oxidation state [28, 29]. Figure 4 (c) shows the core energy level spectrum of Se3d, which assigns peaks at 54.68 eV and 54.08 eV to Se3d\textsubscript{3/2} and Se3d\textsubscript{5/2}, respectively. The values are basically consistent with previous reports [30–32]. The value of binding energy was given in table 2. According to the XPS results, the Se and Bi ratio was calculated to be closer to 1.5, it is consistent with EDX.

Figure 5(a) shows the optical absorption spectrum of Bi\textsubscript{2}Se\textsubscript{3} films on the different substrates (FTO, ITO and glass). An obvious absorption peak of the films was observed at 250~800 nm. The result indicated the Bi\textsubscript{2}Se\textsubscript{3} films have been successfully grown on different substrates, which is consistent with the XRD. Meanwhile, with the Tauc method [20, 33], we have calculated the optical band gap by using the optical absorption spectrum and the following equation:

\[(\alpha h\nu)^2 = A(h\nu - E_g)\]  

Here \(\alpha\) is absorption coefficient, \(A\) and \(h\nu\) is the constant and incident photon energy, respectively, \(E_g\) is the optical band gap. Figure 5(b) shows the \((\alpha h\nu)^2\) versus \(h\nu\) curve, and the optical band gap of the sample is estimated by Tauc method. And the \(E_g\) value of Bi\textsubscript{2}Se\textsubscript{3}/glass, Bi\textsubscript{2}Se\textsubscript{3}/ITO, and Bi\textsubscript{2}Se\textsubscript{3}/FTO is 1.59, 1.54, and 1.47 eV, respectively. The result shows that the optical band gap is red shifted, it is similar to semiconductor nanomaterials. As previously reported, it was known that the effective band optical gap of semiconductor nanomaterials decreases with the increase of particle size, and the quantum size effect of the films is key factor [34]. The grain size, film thickness and band gap were listed and compared in table 3. It shows that the band gap

\[
\text{Table 1. EDX of Bi}_2\text{Se}_3\text{ films}
\]

|         | FTO | ITO | Glass | Expect atomic % |
|---------|-----|-----|-------|-----------------|
| Bi      | 37.3| 37.02| 36.94 | 40              |
| Se      | 62.7| 62.98| 63.06 | 60              |

![Fig 3](image-url)  

*Figure 3. FESEM images of Bi\textsubscript{2}Se\textsubscript{3} films in different substrates (a) FTO, (b) ITO, (c) Glass. The cross-sectional morphology of Bi\textsubscript{2}Se\textsubscript{3} films (d) FTO, (e) ITO, (f) Glass.*

![Fig 4](image-url)  

*Figure 4. Which shows the optical absorption spectrum of Bi\textsubscript{2}Se\textsubscript{3} films on the different substrates.*

![Fig 5](image-url)  

*Figure 5. (a) Shows the optical absorption spectrum of Bi\textsubscript{2}Se\textsubscript{3} films on the different substrates (FTO, ITO and glass). (b) Shows the \((\alpha h\nu)^2\) versus \(h\nu\) curve, and the optical band gap of the sample is estimated by Tauc method.*

![Table 2](image-url)  

*Table 2: The grain size, film thickness and band gap of Bi\textsubscript{2}Se\textsubscript{3} films on different substrates.*
Figure 4. XPS analysis of Bi$_2$Se$_3$: (a) survey spectrum of Bi$_2$Se$_3$ deposited on ITO, (b) core level spectrum of Bi$4f$, and (c) core level spectrum of Se$3d$.

Table 2. The binding energy of the core energy levels of Bi$_2$Se$_3$ films

|                  | FTO(eV) | Glass(eV) | ITO(eV) |
|------------------|---------|-----------|---------|
| Se$3d_{5/2}$     | 54.18   | 54.08     | 53.88   |
| Se$3d_{3/2}$     | 54.78   | 54.68     | 54.58   |
| Bi$4f_{7/2}$     | 163.68  | 163.58    | 163.38  |
| Bi$4f_{5/2}$     | 158.28  | 158.28    | 158.08  |

Table 3. For Grain Size, thickness and band gap of Bi$_2$Se$_3$ films

|            | Grain size(Å) | Thickness(nm) | Band gap(eV) |
|------------|---------------|---------------|--------------|
| FTO        | 221           | 389.4         | 1.59         |
| ITO        | 198           | 384.7         | 1.54         |
| Glass      | 193           | 364.5         | 1.47         |
the dielectric constant in vacuum and in SC compound respectively, \( \varepsilon_{SC} \) Here adjusting the grain size and thickness of the material decreases with the decrease of grain size and thickness. It is suggested that a suitable band gap can be obtained by adjusting the grain size and thickness of the material [35]. The effective band optical gap of Bi2Se3/glass, Bi2Se3/ITO, and Bi2Se3/FTO is increases with the increase of grain size and thickness. The result is closed to Yu et al [36] and Desai et al [27]. These band gap values of the Bi2Se3 films can be achieved to solar energy and optoelectronics application prospects [37].

In order to verify the potential applications of Bi2Se3 films in solar cells, the photo-electrochemical properties need to be studied in detail. The I-V curves and C-V curves of Bi2Se3 films on the ITO and FTO was measured in a photoelectrochemical (PEC) cell, shown in figures 6(a) and (b). The experiments were performed in 0.1 mol Na2SO4 electrolyte solution. CHI760E was used to collect the data of photocurrent from 1.2 to −0.75 V (versus Ag/AgCl) with a counter electrode of Pt. The light intensity is 50 W cm\(^{-2}\), the I-V curves of different light intensity have been demonstrated in the figure 6(a). The current is larger with light within the range of the applied voltage from −0.6 and 0.4 V. The I-V curves of Bi2Se3 films shows the characteristics of a typical semiconductor.

In addition, figure 6(b) shown the C-V curves of Bi2Se3/FTO, Bi2Se3/ITO have been measured at frequency of 100 Hz. The flat band potentials \( V_{fb} \) of Bi2Se3 films were fitted by the equation (2). The equation is as follows [11]:

\[
C_{SC}^{-2} = (V - V_{fb} - K_B T e^{-1})2(\varepsilon_0 \varepsilon_r N_0 e)^{-1}
\]  

(2)

Here \( C_{SC} \) is the space charge capacitance, \( V \) respectively the electrode potential and \( V_{fb} \) is the flat band potential, \( K_B \) is the Boltzmann’s constant, \( T \) is the experiment ambient temperature tested, \( e \) is electronic charge, \( \varepsilon_0 \) and \( \varepsilon_r \) is the dielectric constant in vacuum and in SC compound respectively, \( N_0 \) is the carrier concentration.

The \( V_{fb} \) of Bi2Se3/FTO and Bi2Se3/ITO is −0.22 and −0.24, listed in table 4. The n-type semiconductor Bi2Se3 film is confirmed by the positive slope of the C-V curve. This is consistent with the earlier report [38].

Calculated the light conversion efficiency (\( \eta \)) of light to chemical energy by using the following expression [39]:

\[
\eta = \frac{J_{sc} (E_{app} - |E_{rev}|)}{I_0} \times 100
\]

(3)

Here \( J_{sc} \) is the photocurrent density, \( E_{rev} = 1.23 \) V, the value is the potential corresponding to the change of the single photon Gibbs free energy during water splitting. \( E_{app} = E_{mean} - E_{sc} \), and \( E_{mean} \) is the electrode potential (vs. Ag/AgCl) of the working electrode, \( E_{sc} \) is the electrode potential (vs. Ag/AgCl) of the working electrode at open-circuit conditions, and \( I_0 \) is the incident light intensity, respectively. The values of \( J_{sc} \) (the short circuit), \( V_{oc} \) (the open circuit voltage), \( FF \), \( \eta \) and \( V_{fb} \) (the flat band potential) are obtained and listed in table 4.

The transient photocurrent response of Bi2Se3/FTO and Bi2Se3/ITO were shown in figure 7. The test bias has been set to 0.6 V, and the interval of Xenon lamp (\( \lambda > 420 \) nm) irradiation is 20 seconds. In the figure 7, we found that the photocurrent of Bi2Se3/FTO and Bi2Se3/ITO films can be responded quickly and stabilized with the light and without light. A series of quick response of the photocurrent can be used to indicate that the relaxation time of photogenerated carriers is very short in the Bi2Se3 films. The separation/recombination time

Table 4. Solar cell parameters for Bi2Se3 films

| Sample       | \( J_{sc} \) (mA cm\(^{-2}\)) | \( V_{oc} \) (mV) | \( E_{app} \) | FF | \( \eta \) (%) | \( V_{fb} \) (versus (SCE)) |
|--------------|-------------------------------|------------------|---------------|----|---------------|----------------------------|
| Bi2Se3/FTO   | 0.363                         | 607              | 0.31          | 0.152 | 0.067        | −0.22                      |
| Bi2Se3/ITO   | 0.180                         | 631              | 0.242         | 0.159 | 0.036        | −0.24                      |

\[\text{Figure 6. (a) I-V curves of Bi2Se3 films deposited on FTO, ITO, (b) C-V curves (Mott-schottky plot) for Bi2Se3/FTO, Bi2Se3/ITO at frequency of 100 Hz}\]
of photogenerated carriers plays a crucial role in the solar cell application. The results of transient photocurrent response in Bi$_2$Se$_3$ films shown the separation efficiency of photogenerated carriers is high and stable, it is an advantage in the application of solar cells.

4. Conclusion

In summary, Bi$_2$Se$_3$ films have been grown on FTO, ITO and glass by thermal evaporation method. The structure, morphology, composition and optoelectronic properties of Bi$_2$Se$_3$ films were studied in detail. The results of XRD and SEM indicated that the Bi$_2$Se$_3$ crystals films have been grown smooth and uniform on different substrates. The results of EDX and XPS demonstrated that the Bi/Se atomic ratio was about 1.5, which match to the stoichiometric composition of Bi$_2$Se$_3$ films. The thickness of the Bi$_2$Se$_3$ films on the FTO and ITO are thicker than that of on glass. The optical band gap of Bi$_2$Se$_3$/FTO, Bi$_2$Se$_3$/ITO, and Bi$_2$Se$_3$/glass has been calculated to be, 1.47 1.54, and 1.59 eV, respectively. The band gap decreases as the grain size and thickness decrease, which implies that the band gap can be controlled by adjusting the grain size and material thickness. The results of I-V and C-V curves indicated that the Bi$_2$Se$_3$ films have been exhibited $n$-type semiconductor behavior. The transient photocurrent response of Bi$_2$Se$_3$ films shown the separation efficiency of photogenerated carriers is high and stable. These results evaluate the potential application of Bi$_2$Se$_3$ thin films in solar cells.

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Figure 7. Transient photocurrent responses of Bi$_2$Se$_3$/ITO and Bi$_2$Se$_3$/FTO electrodes at 0.6 V.
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