

Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Growth and characterization of Bi₂Se₃ thin films by pulsed laser deposition using alloy target

Lijian Meng^{a,b,*}, Hui Meng^c, Wenjie Gong^c, Wei Liu^c, Zhidong Zhang^c

^a Departamento de Física, Instituto Superior de Engenharia do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal

^b Centro de Física, Universidade do Minho, 4800-058 Guimarães, Portugal

^c Shenyang National Laboratory for Material Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, People's Republic of China

ARTICLE INFO

Article history:

Received 7 September 2010
Received in revised form 30 April 2011
Accepted 30 April 2011
Available online 7 May 2011

Keywords:

Pulsed laser deposition
Thin films
Bismuth selenide
X-ray diffraction
Electrical properties and measurements
Surface morphology
Scanning electron microscopy
Crystal microstructure

ABSTRACT

Bi₂Se₃ thin films were deposited on the (100) oriented Si substrates by pulsed laser deposition technique at different substrate temperatures (room temperature – 400 °C). The effects of the substrate temperature on the structural and electrical properties of the Bi₂Se₃ films were studied. The film prepared at room temperature showed a very poor polycrystalline structure with the mainly orthorhombic phase. The crystallinity of the films was improved by heating the substrate during the deposition and the crystal phase of the film changed to the rhombohedral phase as the substrate temperature was higher than 200 °C. The stoichiometry of the films and the chemical state of Bi and Se elements in the films were studied by fitting the Se 3d and the Bi 4d5/2 peaks of the X-ray photoelectron spectra. The hexagonal structure was seen clearly for the film prepared at the substrate temperature of 400 °C. The surface roughness of the film increased as the substrate temperature was increased. The electrical resistivity of the film decreased from 1×10^{-3} to 3×10^{-4} Ω cm as the substrate temperature was increased from room temperature to 400 °C.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Bismuth selenide (Bi₂Se₃) is a narrow band gap semiconductor (about 0.35 eV) and exhibits an unusual anisotropic layered structure. As one of the binary chalcogenides of V₂VI₃ compounds, it has attracted wide attention due to its potential applications in thermoelectric devices [1]. Recently, research on Bi₂Se₃ has attracted even much interest as it has been predicted to be a three-dimensional topological insulator, a material that behaves as an insulator in its interior while permitting the movement of charges on its boundary [2,3]. The research work on this topic has already been extended from Bi₂Se₃ bulk material to Bi₂Se₃ thin film [4,5]. Therefore, studies on Bi₂Se₃ thin films are of continued interest for researchers from the point of view of the preparation and characterization in order to test their suitability for a particular and desired application.

The techniques used for deposition of the Bi₂Se₃ films are dominated by chemical processes [6–12]. Physical processes are rarely used for depositing Bi₂Se₃ films, only the evaporation technique has been used until now [13,14]. Pulsed laser deposition has become a widely used physical technique for depositing films as it has many

advantages, such as a wide choice of materials, high instantaneous deposition rate, and a relatively high reproducibility. In addition, this technique has several unique features: a fine control on stoichiometry, the possibility to use thermally sensitive substrates and the capability to grow nanostructures and cluster-assembled films by ablating material in presence of a background gas. However, no work on pulsed laser deposited Bi₂Se₃ films has been conducted so far. In this work, we have reported the effects of the substrate temperature on the properties of the Bi₂Se₃ films on silicon substrate deposited by pulsed laser deposition.

2. Experimental details

A pulsed KrF excimer laser (Lambda Physik LPx 305i, 248 nm, 25 ns, frequency 2 Hz) was used to ablate the Bi₂Se₃ alloy target. The laser beam was focused on the target surface by lens at a 45° incident angle. The Bi₂Se₃ alloy with a purity of 99.999% was supplied by Sichuan xinlong tellurium Industry & Technique development Co., Ltd. The laser power density in the target surface was about 0.01 J/mm² which was estimated by measuring the incident laser power and the erosion area at the target surface. The target was fixed at a 40 mm distance apart from the substrate. The (100) oriented silicon wafers were used as the substrates and the substrate temperature was varied from room temperature (RT) to 400 °C. The silicon substrates were cleaned by the standard cleaning procedure before they were loaded

* Corresponding author at: Departamento de Física, Instituto Superior de Engenharia do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal. Tel.: + 351 962325429; fax: + 351 228321159.

E-mail address: ljm@isep.ipp.pt (L. Meng).

into the deposition chamber. The chamber was equipped with a turbo molecular pump backed with a mechanical pump. Before the deposition started, the chamber was pumped down to less than 3×10^{-3} Pa. The deposition time was kept at 20 min for all the depositions. The thickness of all the films was about 100 nm.

The phases and the crystallographic structure of the films were determined by the X-ray diffraction (XRD) with a Rigaku RINT2000 diffractometer for the 2θ ranging from 10° to 60° with a step of 0.04° using Cu K-alpha1 radiation ($\lambda = 0.15406$ nm) operated at 56 kV and 182 mA as the incident radiation. The surface morphologies of the deposited films were studied by atomic force microscopy (AFM) (Digital Instruments) performed by tapping mode using SiN tip. X-ray photoelectron spectra (XPS) were measured by a VG ESCALAB 250 multitechnique surface analysis system. Photoelectrons were excited over a spot size of 0.5 mm with Al K α radiation (1486.6 eV) operated at 150 W (15 kV and 10 mA). The detailed spectra were acquired with a pass energy of 50.0 eV and an energy step size of 0.1 eV and the survey spectra were acquired with a pass energy of 150 eV and an energy step size of 1 eV. The atomic concentrations of the elements of Bi and Se were calculated from the measured peak areas (Se3d and Bi4d5/2) using the Avantage software of Thermo Fisher Scientific. The peak positions were calibrated by using the position of the peak of the C1s (284.8 eV) as a reference value. The structures of the deposited films were observed by field emission scanning electron microscopy (FESEM) (Oxford, INCA Energy 350) with an operating voltage of 15 kV. The carrier density and the Hall mobility were measured using Lake Shore 665 with a 6 kG magnetic field intensity at room temperature.

3. Results and discussion

The effects of the substrate temperature on the crystallinity and the crystal phase of the Bi_2Se_3 films grown on Si (100) substrates were studied by the XRD as shown in Fig. 1. The XRD pattern of the Bi_2Se_3 alloy target is also shown in this figure for comparison. It can be seen that the alloy target only has the rhombohedral phase of Bi_2Se_3 (PDF card file, No. 33–0214). The Bi_2Se_3 film deposited at room temperature (RT) shows two phases of Bi_2Se_3 , rhombohedral and orthorhombic (PDF card file, No. 77–2016) and the orthorhombic phase of Bi_2Se_3 dominates the phase of the film. When the substrate temperature is higher than 200°C , the deposited films show a pure rhombohedral phase of Bi_2Se_3 . Considering the two different phases of Bi_2Se_3 , the most reported structure in the literature is the rhombohedral structure [8,10–13]. Little data are available on the orthorhombic phase of Bi_2Se_3 [6,7,9]. From these reported results in the literature it can be concluded that the

crystal phase of Bi_2Se_3 films not only depends on the deposition techniques, but also on the process parameters. Although the Bi_2Se_3 films can exist in both rhombohedral and orthorhombic phase, we believe that the orthorhombic phase of Bi_2Se_3 is a metastable phase and the rhombohedral phase of Bi_2Se_3 is a stable phase. As it can be seen from Fig. 1, a transformation from orthorhombic to rhombohedral phase occurs as the substrate temperature is higher than 200°C . It confirms the metastability of the orthorhombic phase.

By fitting the XRD peaks, the peak position, relative peak intensity and the crystallite size along the different orientations are obtained and given in Table 1. The peak intensities have been normalized. The crystallite sizes (D) of the films are calculated using Scherrer's formula, $D = 0.9\lambda/B\cos\theta$, where λ is the wavelength of X-ray, B is the full width at half maximum and θ is the diffraction angle. It can be seen that the grain sizes increase when the substrate temperature is increased from 200°C to 300°C and keep constant as the temperature is higher than 300°C except for the [104] direction. For that direction, the grain size always increases with the temperature. From the normalized peak intensities it can be seen that all the films have a strong diffraction peak along the [006] direction. As the substrate temperature is increased from 200°C to 300°C , the intensities of the (104) and the (0015) peaks are also increased. However, the intensities of these peaks do not change anymore as the substrate temperature is higher than 300°C . Considering both the variations of the grain sizes and the peak intensities with the substrate temperature, it can be suggested that the crystallinity of the Bi_2Se_3 films has been stabilized at 300°C temperature. The crystallinity of the films will not change clearly as the substrate temperature is higher than 300°C .

XPS survey, Bi 4d5/2 and Se 3d spectra of Bi_2Se_3 films prepared at different substrate temperatures and Bi_2Se_3 alloy target are shown in Fig. 2. The fitting results (thick black lines are the fitting results and the red symbols are experimental data in Fig. 2c) show that Se 3d spectra can be fitted perfectly using single peak for 3d3/2 (blue line) and 3d5/2 (green line), and the binding energy for Se 3d5/2 is about 53.5 eV for all the samples. It means that the Se exists in these films as the Bi_2Se_3 compound [15]. No evidence from the contribution of elemental Se atoms at binding energy about 54.1 eV was observed [15] for all the Bi_2Se_3 films. However the Bi 4d5/2 cannot be decomposed using a single peak as it can be seen from Fig. 2b. Two peaks, one located at about 439.8 eV (blue line) and another located at about 441.5 eV (green line), can give a perfect decomposition of the Bi 4d5/2 peak for the films prepared at different substrate temperatures (thick black lines are the fitting results and the red symbols are experimental data in Fig. 2b). The peaks located at 439.8 eV and 441.5 eV correspond to the states of Bi as a Bi element and the Bi_2Se_3 compound [16,17]. It means not all the Bi in the films exists as the Bi_2Se_3 compound; some of them exist as the Bi elements. Even for the Bi_2Se_3 alloy target, there are still small amount of Bi existing as the Bi elements as shown in Fig. 2b. However, XRD results do not show any diffraction peak of Bi elements. Therefore, these Bi elements exist in these films as an amorphous phase. It has been known

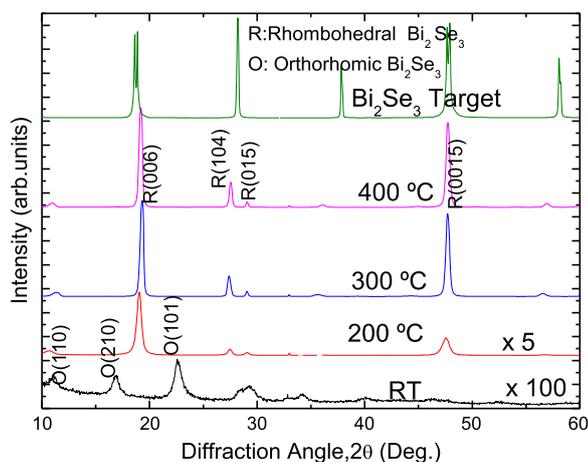


Fig. 1. XRD patterns of the Bi_2Se_3 alloy target and the Bi_2Se_3 films deposited at different substrate temperatures.

Table 1

Peak positions, relative peak intensities and grain sizes obtained by fitting the XRD diffraction peaks for Bi_2Se_3 films prepared at different substrate temperatures.

		200 °C	300 °C	400 °C
(006)	Position (2θ)	19.02	19.30	19.18
	Grain size (nm)	10	17	17
	Intensity	100	100	100
(104)	Position (2θ)	27.47	27.40	27.55
	Grain size (nm)	13	17	20
	Intensity	9	19	21
(015)	Position (2θ)	29.07	29.05	29.06
	Grain size (nm)	12	27	27
	Intensity	4	3	4
(0015)	Position (2θ)	47.54	47.72	47.74
	Grain size (nm)	7	16	16
	Intensity	48	97	98

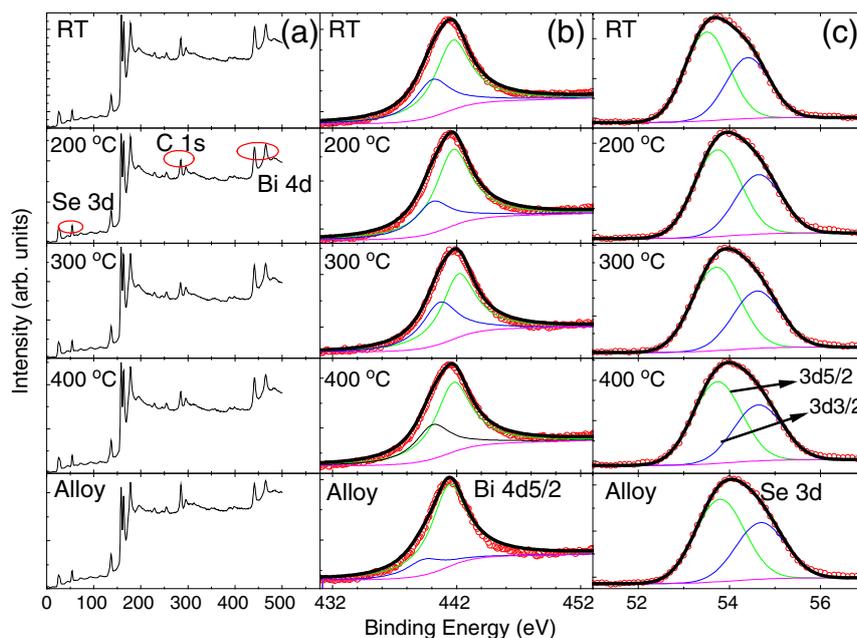


Fig. 2. XPS survey (a), Bi 4d5/2 (b) (thick black lines: fitting results; red symbols: experimental data; blue line: peak of Bi 4d5/2 as a Bi element; green line: peak of Bi 4d5/2 as the Bi_2Se_3 compound.) and Se 3d (c) (thick black lines: fitting results; red symbols: experimental data; blue line: peak of Se 3d3/2 as the Bi_2Se_3 compound; green line: peak of Se 3d5/2 as the Bi_2Se_3 compound.) spectra of Bi_2Se_3 films deposited at different substrate temperatures and Bi_2Se_3 alloy target.

that the Se atoms escape easily during the ablation process, and thus will result in a Bi-rich Bi_2Se_3 film. The stoichiometry of the deposited Bi_2Se_3 films has been calculated by fitting the Bi 4d and Se 3d spectra. It has been found that the Se/Bi ratio is about 1:2 for films prepared at room

temperature and 200 °C, and is about 1:1 for films prepared at 300 °C and 400 °C substrate temperatures. These results confirm that the deposited Bi_2Se_3 films are not stoichiometric. The extra Bi exists as Bi atoms in these films. In order to improve the stoichiometry of the Bi_2Se_3

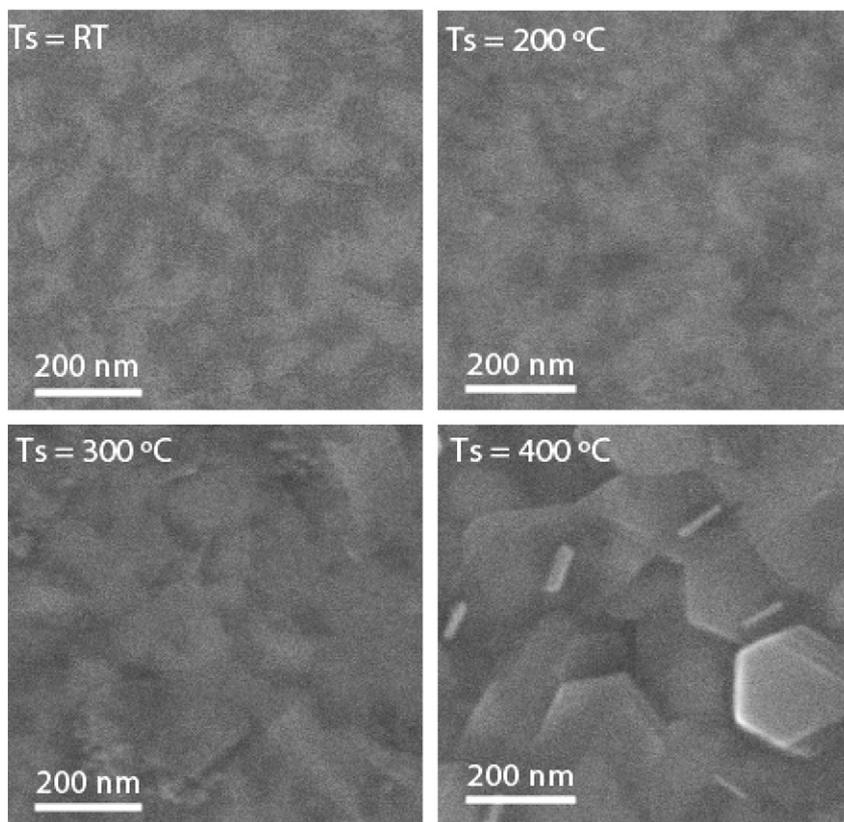


Fig. 3. SEM image of Bi_2Se_3 films prepared at different substrate temperatures.

films, the Bi_2Se_3 alloy target must be prepared with extra Se in it to compensate the loss of the Se during the ablation process.

Fig. 3 shows FESEM images of Bi_2Se_3 films prepared at different substrate temperatures. It can be seen that the film prepared at room temperature shows smooth surface with many small features. These small features form hexagonal crystal structure as the substrate temperature is increased. The image of the Bi_2Se_3 film prepared at 400 °C clearly shows the hexagonal structure. Although XRD measurements have confirmed that most Bi_2Se_3 films have the hexagonal structure, it has not been observed directly by SEM so far. It can be seen that when the substrate temperature is higher than 300 °C, large grains are formed. The formation of these large grains will result in a rough surface which has been confirmed by AFM measurements as shown in Fig. 4. The sample surface is smooth with a root mean square (RMS) roughness varied from 0.6 to 1.5 nm as the substrate temperature is increased from RT to 200 °C. However, the surface becomes rough when the substrate temperature is higher than 200 °C. The surface RMS roughness jumps to about 6.7 nm when the substrate temperature reaches to 300 °C. The film prepared at the substrate temperature of 400 °C has the most rough surface with a RMS roughness of 12.1 nm.

The electrical properties (electrical resistivity, carrier density and Hall mobility) of Bi_2Se_3 films deposited at different substrate temperatures are shown in Fig. 5. It can be seen that the film prepared at room

temperature has a high electrical resistivity. As the substrate temperature is increased from RT to 300 °C, the electrical resistivity of Bi_2Se_3 film decreases. When the substrate temperature is higher than 300 °C, the electrical resistivity of Bi_2Se_3 does not show a clear variation. It is well known that the electrical resistivity is related with both the carrier density and Hall mobility. High carrier density and high Hall mobility will result in a low electrical resistivity. From Fig. 5b it can be seen that the carrier density increases as the substrate temperature is increased from RT to 200 °C and decreases as the temperature is higher than 200 °C. It is still not clear on the variation of the carrier density with the substrate temperature. One of the possible reasons may come from the phase transition of the Bi_2Se_3 film. It has been shown in Fig. 1 that a phase transition occurs at 200 °C for the Bi_2Se_3 film. At this critical phase transition point, the structure of the energy band may be modified and this results in the variation of the carrier density. The Hall mobility of the Bi_2Se_3 films shows a very clear increase as the substrate temperature is higher than 200 °C as shown in Fig. 5c. This variation of the Hall mobility may be related to both the improvement of the crystallinity of the Bi_2Se_3 film and the formation of the large grains. From the XRD's results it has been seen that the film crystallinity is improved when the substrate temperature is increased from 200 °C to 300 °C and may result in a high carrier mobility. Although the film crystallinity does not change very clearly when the substrate temperature is higher than 300 °C as indicated by the XRD's results, large grains are formed as the substrate

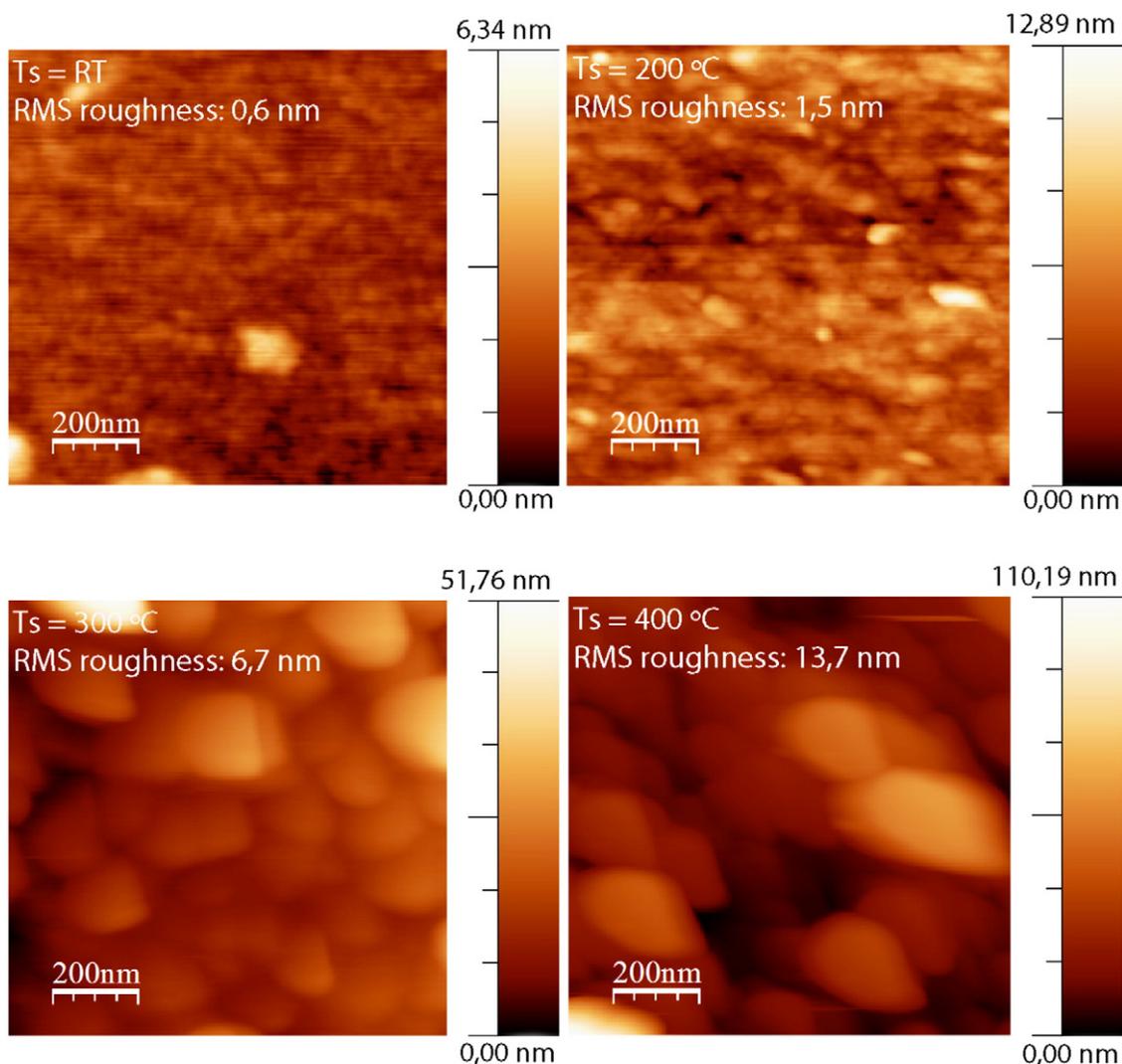


Fig. 4. AFM micrographs of Bi_2Se_3 films prepared at different substrate temperatures.

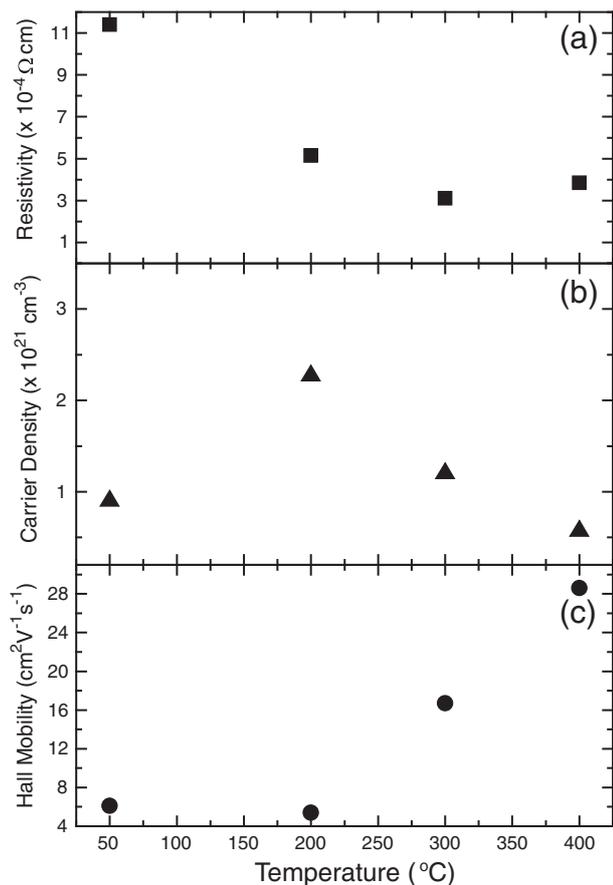


Fig. 5. Electrical resistivity (a), carrier density (b) and Hall mobility (c) of Bi_2Se_3 films deposited at different substrate temperatures.

temperature is increased from 300 °C to 400 °C as shown in the SEM picture. The formation of these large grains may reduce the possibility of carrier scattering by grain boundaries and result in a high carrier mobility too.

The carrier density in the Bi_2Se_3 thin films of this work is in the order of 10^{21} cm^{-3} , which is higher than the values reported in the literatures. The carrier density is in the order of 10^{19} cm^{-3} in Bi_2Se_3 films prepared by electrodeposition, by MOCVD and by rational design of the precursor solution [11,18–20]. The Hall mobility in Bi_2Se_3 films of this work has the same order of magnitude with the values reported in the literatures except for Bi_2Se_3 films prepared by MOCVD, in which the mobility is about an order of magnitude higher than the others. The high carrier density results in a low electrical resistivity. It means that the Bi_2Se_3 films prepared by laser ablation show a better electrical property than that prepared by other deposition techniques. Although the Bi_2Se_3 films prepared by laser ablation show a good electrical

property, they still have a polycrystalline structure, which is not adequate for the current topological insulator studies. For growing high quality single crystal-like Bi_2Se_3 thin films, more experimental work using different deposition parameters and different single crystal substrates are still needed.

4. Conclusions

Bi_2Se_3 films have been deposited on Si substrates by pulsed laser deposition technique using a Bi_2Se_3 alloy target. The Bi_2Se_3 film deposited on unheated substrate shows mainly the orthorhombic phase which is not a stable phase. As the substrate temperature is higher than 200 °C, a phase transition from the orthorhombic to the rhombohedral takes place. All the deposited Bi_2Se_3 films are non-stoichiometric and are Bi-rich. The extra Bi elements in these films do not show any crystallinity. The surface RMS roughness has a rapid increase as the temperature is increased from 200 °C to 300 °C and the hexagonal structure can be clearly observed from SEM images of the Bi_2Se_3 films prepared at the substrate temperature of 400 °C. The electrical resistivity of the Bi_2Se_3 films decreases as the substrate temperature is increased.

Acknowledgment

This work was done during Lijian Meng's visit to Shenyang National Laboratory for Material Science (SYNL), Institute of Metal Research, Chinese Academy of Sciences and was supported by SYNL.

References

- [1] F. Xiao, C. Hangarter, B. Yoo, Y. Rheem, K.H. Lee, N.V. Myung, *Electrochim. Acta.* 53 (2008) 8103.
- [2] H.J. Zhang, C.X. Liu, X.L. Qi, X. Dai, Z. Fang, S.C. Zhang, *Nat. Phys.* 5 (2009) 438.
- [3] D.S. Kong, J.C. Randel, H.L. Peng, J.J. Cha, S. Meister, K.J. Lai, Y.L. Chen, Z.X. Shen, H.C. Manoharan, Y. Cui, *Nano Lett.* 10 (2010) 329.
- [4] T. Hirahara, Y. Sakamoto, Y. Takeichi, H. Miyazaki, S. Kimura, I. Matsuda, A. Kakizaki, S. Hasegawa, *Phys. Rev. B* 82 (2010) 155309.
- [5] C.L. Song, Y.L. Wang, Y.P. Jiang, Y. Zhang, C.Z. Chang, L. Wang, K. He, X. Chen, J.F. Jia, Y. Wang, Z. Fang, X. Dai, X.C. Xie, X.L. Qi, S.C. Zhang, Q.K. Xue, X. Ma, *Appl. Phys. Lett.* 97 (2010) 143118.
- [6] N.S. Patil, A.M. Sargar, S.R. Mane, P.N. Bhosale, *Appl. Surf. Sci.* 254 (2008) 5261.
- [7] C.J. Xiao, J.Y. Yang, W. Zhu, J.Y. Peng, J.S. Zhang, *Electrochim. Acta.* 54 (2009) 6821.
- [8] X.F. Qiu, L.N. Austin, P.A. Muscarella, J.S. Dyck, C. Burda, *Angew. Chem. Int. Edit.* 45 (2006) 5656.
- [9] N.S. Patil, A.M. Sargar, S.R. Mane, P.N. Bhosale, *Mater. Chem. Phys.* 115 (2009) 47.
- [10] S. Subramanian, D.P. Padiyan, *Mater. Chem. Phys.* 107 (2008) 392.
- [11] X.L. Li, K.F. Cai, H. Li, L. Wang, C.W. Zhou, *Int. J. Min. Met. Mater.* 17 (2010) 104.
- [12] S. Augustine, S. Ampili, J.K. Kang, E. Mathai, *Mater. Res. Bull.* 40 (2005) 1314.
- [13] T.E. Manjulavalli, T. Balasubramanian, D. Nataraj, *Chalcogenide Lett.* 5 (2008) 297.
- [14] N.M. Abdullayev, S.I. Mekhtiyeva, N.R. Memmedov, M.A. Ramazanov, A.M. Kerimova, *Semiconductors* 44 (2010) 824.
- [15] T. Takahashi, T. Sagawa, H. Hamanaka, *J. NonCryst. Solids* 65 (1984) 261.
- [16] R.B. Shalvoy, G.B. Fisher, P.J. Stiles, *Phys. Rev. B* 15 (1977) 1680.
- [17] F.M. Ismail, Z.M. Hanafi, *Z. Phys. Chem.* 267 (1986) 667.
- [18] Z.L. Sun, S.C. Liufu, L.D. Chen, *Dalton Trans.* 39 (2010) 10883.
- [19] A. Al Bayaz, A. Giani, M.C. Artaud, A. Foucaran, F. Pascal-Delannoy, A. Boyer, *J. Cryst. Growth* 241 (2002) 463.
- [20] A. Al Bayaz, A. Giani, A. Foucaran, E. Pascal-Delannoy, A. Boyer, *Thin Solid Films* 441 (2003) 1.