Chalcogenide Letters Vol. 11, No. 6, June 2014, p. 281 - 285

RADIAL DISTRIBUTION ANALYSIS STUDIES OF Bi_2Se_3THIN FILMS

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X-ray diffraction patterns of Bi_2Se_3 films, deposited on glass substrates by vacuum evaporation (PVD) as well as by chemical deposition techniques (CVD) are recorded and radial distribution functions have been calculated. The inter-atomic vectors, co-ordination numbers and the coupling constants have been obtained. It has been observed that the inter-atomic distances and the co-ordination numbers are smaller than the corresponding value for the crystalline structure. It is observed that the deviations from the crystalline structure are more in case of the vacuum evaporation films as compared to that for the chemically deposited films.

(Received April 3, 2014; Accepted June 11, 2014)

*Keywords:*Bismuth Selenide, XRD, Thin films, Vapourdeposition, Chemical deposition, Coupling constant, Coordination number

1. Introduction

Bi_2Se_3 is an important member of binary chalcogenides which exhibits the unique property in the field of photo-conducting materials, thermoelectric instruments, opto-electronic devices, infra-red spectroscopy and many more [1]-[3]. It is a narrow band gap semiconductor material which has an anisotropic configuration [4]. For the desired application and suitability the synthesis and characterization of Bi_2Se_3 has gained a great interest among the researchers [5]. The liquid form of Bi_2Se_3 shows remarkable differences in its electrical properties as compared to the crystalline state[6], have made a radial distribution analysis of the neutron diffraction data and have attributed this to be due to considerable differences in the atomic arrangement in the crystalline and the liquid state. Using electron diffraction measurement they have also reported the radial distribution analysis studies on thin films of Bi_2Se_3 vacuum evaporated on to NaCl substrates kept at liquid nitrogen temperature. However, no structural investigation on amorphous thin films prepared by different methods has been reported so far. However, recently an electronic structure of Bi_2Se_3 has been studied using density functional theory with the spin orbit interaction [7]. Since in the present investigation, it was observed that thin Bi_2Se_3 films deposited on glass substrates at room temperature show non crystalline behaviour in their electric properties, an X-ray analysis of the same was undertaken for vacuum evaporated (P.V.D) films.

2. Experimental

The compound Bi_2Se_3 was prepared by the method of fusing with appropriate proportion of the constituent elements Bi(99.99%) and Se(99.99%). The vacuum evaporated (P.V.D) films were deposited by evaporating Bi_2Se_3 powder from a molybdenum boat in a vacuum of the order of 10^{-6}Torr onto properly cleaned glass substrate kept at room temperature with the help of a Hind Hivac Vacuum Coating Unit. The rate of deposition was maintained constant at the rate of 5 to 6 nm/s. The average thickness of the films was measured by the method of Stylus. The thickness of the films was 300nm.

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The chemically deposited (C.V.D) films were deposited by already established solution growth technique using bismuth complex of triethanolamine and sodium selenosulphate in ammoniacal medium as reported [8]. These chemically deposited films have film thickness of the same order as above 250 to 300 nm.

The X-ray diffraction intensities were recorded with the help of a Phillips X-ray diffractometer using monochromatised CuK_α radiation at a scanning speed $½^0$/min. The intensities were recorded up to s=-.9nm^{-1} and were suitably corrected for background scattering. It was observed that the X-ray diffraction pattern was of non crystalline type.

3. Calculation of Radial Distribution Function:

The experimental intensities were suitably corrected for background contribution from substrate and then for polarization and absorption following the procedure described by Koelble [9]. Tabulated values of the atomic scattering factor [10] and incoherent scattering factors [11] were used for obtaining the independent scattering curves. The corrected intensities were scaled to the electron units first by the high angle method and then by the integral method [12]. Contributions of the flat faced diffractometer sample in the small angle region and that due to multiple scattering were subtracted following the method described by Warren [13].

The electronic radial distribution function was calculated from the X-ray diffraction intensities scaled to electron units. It is given by

$$4\pi r^2\rho_e(r) = 4\pi r^2\rho_o(r) + \frac{2r}{\pi}\int_0^\infty s\, i(s)\, M1(s)M2(s)\, M3(s)\sin sr.\, ds$$

Where $s = 4\pi\sin\theta/\lambda$

$$i(s) = \frac{I_{obs}}{K} - \left(\sum x_i f_i^2 + \sum x_i I_{inc}\right)$$

f_i atomic scattering factors, x_i the mole fraction, k the scale factorI_{obs} the unscaled intensities, and I_{inc} the incoherent intensities.

$$\rho_{oe} = \rho_o\left(\sum x_i f_i(0)\right)^2$$

$M_1(s)$ = Sharpening function $=\left[\frac{\sum x_i f_i(0)}{\sum x_i f_i(s)}\right]^2$

$M_2(s)= \exp(-bs^2)$

Where b is an artificial temperature factor used to reduce the ripples. In the present case b=.0001nm^2 was found to be optimum.

$M_3(s)$ is a slip function with values one upto $s = s_{max}$ and zero after that.

Some of the overlapped peaks in the radial distribution curve were resolved by fitting Gaussian profiles to the curves. The coupling constants, associated with the various inter atomic distances were estimated following the procedure described by Kaplow et al [14] in order to obtain an approximate idea of the relative strength of the bonds.

4. Results and discussion

The films deposited both by vacuum evaporation as well as by chemical methods showed amorphous type diffraction patterns. The variation of the X-ray diffraction intensity with $\sin\theta/\lambda$ has been shown in Fig1.

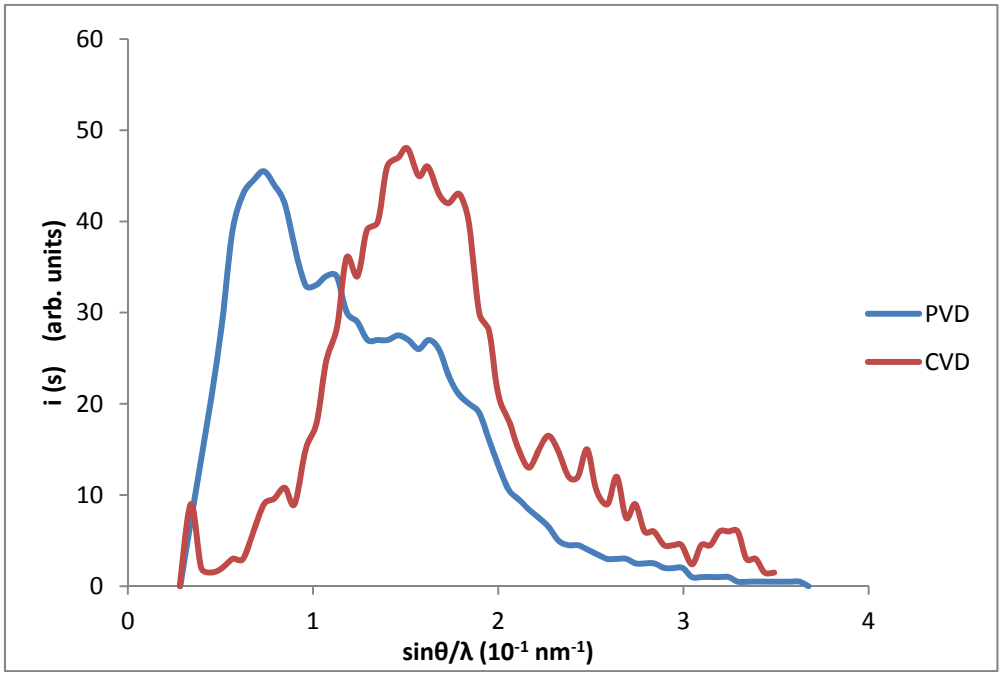

Fig.1Variation of the intensity with sinθ/λ for the Bi_2Se_3 films deposited on glass substrates

The radial distribution functions have been shown in Figure 2.

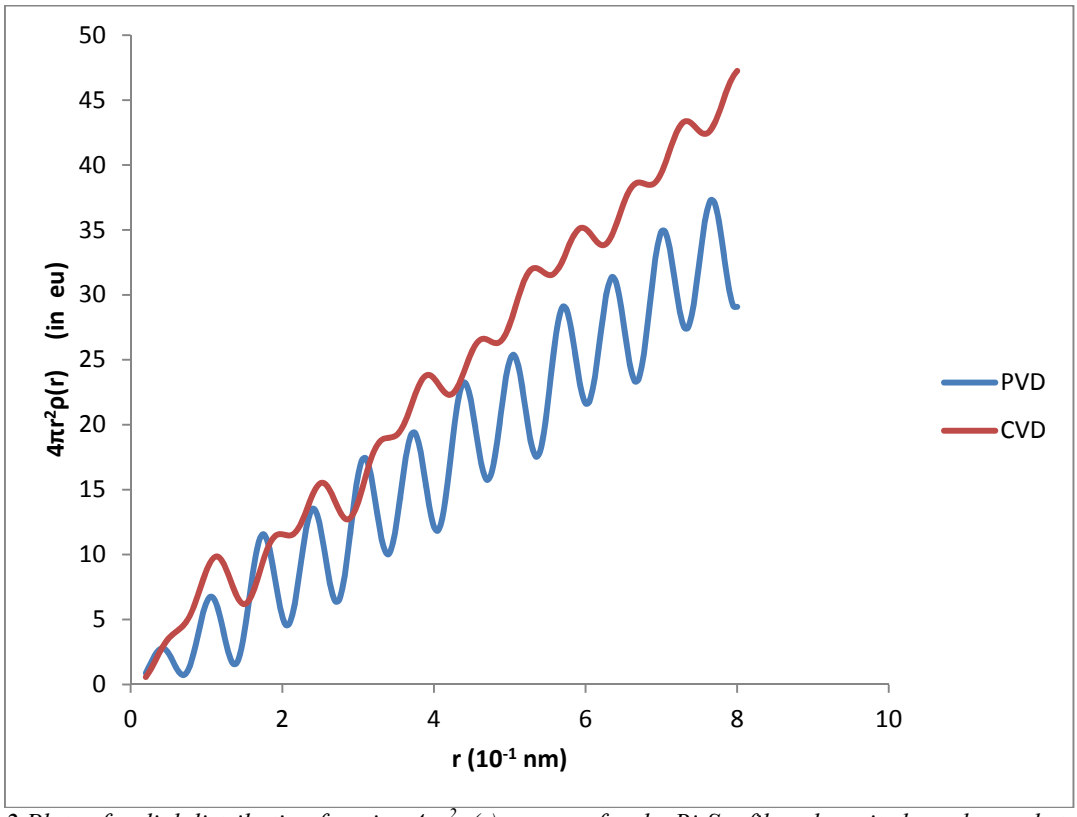

Fig.2 Plots of radial distribution function $4\pi r^2\rho(r)$ versus r for the Bi_2Se_3 films deposited on glass substrates

The differential radial distribution functions have been shown in Figure 3.

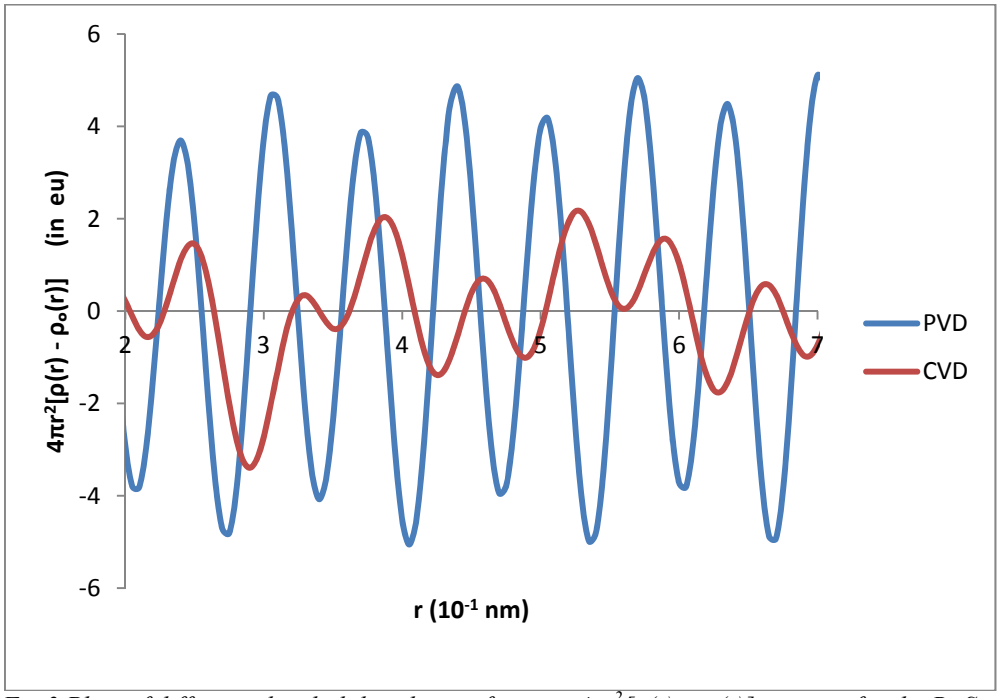

Fig.3 Plots of differential radial distribution function $4\pi r^2[\rho(r) - \rho_o(r)]$ versus r for the Bi_2Se_3 films deposited on glass substrates

The different values of the inter atomic distances for the films have been tabulated in Table-1.

Table 1Inter atomic distances (r in nm) for amorphous Bi_2Se_3 films prepared by vacuum deposited (P.V.D.) and chemically deposited (C.V.D) methods are shown as:-

Neighbour/Film	**1**	**2**	**3**	**4**	**5**	**6**
P.V.D	0.240	0.308	0.372	0.440	0.508	0.570
C.V.D	0.248	0.328	0.388	0.460	0.524	0.588

The nearest neighbour distance and the next nearest distance, their co-ordination number and coupling constants have been tabulated in Table –2.

Table 2. Values of the nearest and next nearest neighbour distances, co-ordination numbers and coupling constants for the deposited Bi_2Se_3 thin films together with crystalline Bi_2Se_3

Sample	**Nearest Neighbour**			**Next nearest Neighbour**		
	Distance (nm)	**C.N**	**CC**	**Distance (nm)**	**C.N**	**CC**
P.V.D	0.240	3.5	0.36	0.308	4.4	0.4
C.V.D	0.248	4.2	0.38	0.328	4.8	0.41
Cryst	0.297	4.8	-	0.415	-	-

A comparison of the inter atomic distances of the films deposited by the two methods shows that the interatomic distances for the near neighbour in case of the vaccum evaporated films are smaller than the chemically prepared films. The nearest neighbour distance in the vacuum deposited films is 0.240 nm as compared to 0.248 nm in the chemically deposited film; these values are much smaller than the crystalline value of 0.297 nm quoted by Satow et al. The values of the nearest neighbour co-ordination number as estimated from the areas under the peaks in the radial distribution curves are 3.5 and 4.2 for the vacuum deposited and chemically deposited films respectively as compared to 4.8 for the crystalline case. The coupling constants estimated from the relative broadening of the Gaussian profiles fitted to the radial distribution curves following the procedure described by Kaplow et al gives an approximate idea of the relative strength of the inter atomic bonds. The coupling constants for the nearest and the next nearest neighbours were estimated to be 0.36 and 0.40 in case of the vacuum evaporated films and 0.38 and 0.41 in case of the chemically prepared films. Since the coupling constant has a value equal to unity in case of the perfectly uncoupled case, the coupling constant has an inverse relationship with the strength of the bonds. Hence the values of the coupling constants indicate that the bonds are stronger in case of vacuum evaporated films as compared to the chemically deposited ones. This is expected because of the smaller inter atomic distances in case of evaporated films.

5. Conclusion

In the present investigation, it is observed that the near neighbours are closer and co-ordination numbers are smaller in case of the amorphous films as compared to the crystalline value. Departure from the crystalline value is greater in case of the vacuum deposited films as compared to the chemically deposited ones. This nature is also indicated by the relative strengths of the bonds.

Reference

[1] L E Brus, Appl. Phys. A **53**, 465 (1991)
[2] J F Smyth, science, **258**, 414(1992)
[3] D Arivouli, F D Gnanam, P Ramasamy, J Mater. Sci. Lett., **7**, 711(1988)
[4] D R Lovett, semi-metals and narrow band gap semiconductors, pion ltd, London, **181**(1977)
[5] T E Manjulavalli, T Balasubramanian, D Nataraj, Chalco. Lett.**5**(11),297(2008)
[6] T. Satow, O Uemura and Y Sagara, PhysStalSol(a) **71**, 555 (1982).
[7] S K Mishra, S Satpathy and O Jepsen, J Phys. Condens. Matteer**9,**461 (1997).
[8] P. Pramanik, R. N Bhattacharya and A. Mondal, Journal of the Electrochemical Society, **127** (1980) 2857.
[9] E. F Koelble, Hand Book of X-rays, chap22, McGraw Hill Publ, Co., New York, (1967)
[10] D. T Cromer, J. T Weber, ActaCryst. **18,**104 (1965).
[11] F Hajdu, Acta Crystal, **A27,**73 (1971)
[12] J. Krough-Moe, ActaCryst**9,**951 (1956).
[13] B. E Warren, X-ray diffraction, Addion Wesley Publ;, Co. Massachusetts, (1969).
[14] R. Kaplow, T. A Powe, B. L. Averbach, Phy.Rev.**168,**1068 (1968).