International Journal of Thales Natural Sciences (IJTNS)
ISSN (print): 2149-5297

The Structure Characterization of n- InSe Single Crystal

Bekir Gürbulak
Department of Physics, Faculty of Sciences, Atatürk University

Afsoun Ashkhasi
Department of Physics, Faculty of Sciences, Atatürk University

Salih Zeki Erzeneoğlu
Department of Physics, Faculty of Sciences, Atatürk University

Mehmet şata
Department of Physics, Faculty of Sciences, Atatürk University

Songül Duman
Department of Basic Sciences, Faculty of Sciences Erzurum Technical University

Ahmet Mavi
Department of chemistry, faculty of science Atatürk University

ABSTRACT

Undoped InSe single crystal has been grown by using the Bridgman/Stockbarger method. There is no cracks or voids on the surface of ingots. Samples have been cleaved along the cleavage planes (001). The freshly cleaved crystals have mirror-like surfaces even without using mechanical treatment. The structure and lattice parameters of the undoped InSe semiconductor have been analyzed using a x-ray diffractometer (XRD), Scanning electron microscopy (SEM) and energy dispersive X-rays (EDX) techniques. It is found that the InSe crystals has hexagonal structure and calculated lattice constants have been found to be a=4.002 Å and c=17.160 Å. The crystallite size has been calculated to be 42-155 nm for InSe from the SEM result. The crystallite size (355.3 Å), residual strain ($10.19x10^{-4}$ lin^{-2} m^{-4}) and dislocation density (7.92x1014 lin m^{-2}) values have been calculated using powder XRD results (004). It has been observed from EDX result that InSe contains In=57.04 %, Se =38.46% and O= 4.50%. These results are in a good agreement with the ones obtained from EDX analysis.

Keywords: InSe, Growth, Single crystals

1 INTRODUCTION

Binary semiconductor compounds have attracted the technological interest owing to their promises for practical application in the areas of visible and infrared light emitting diodes, infrared detectors, optical parametric oscillators, nonlinear optics, solar cells, optical frequency conversion, second harmonic

generation devices and many other electro-optical devices. The characteristics of these crystals which are important fort the Nano and optoelectronic technology will be explored in detail by analysing the all obtained results. InSe binary semiconductor compound was grown in our crystal growth laboratory by the Bridgman-Stockbarger method. The process of the oxide film formation on the cleared InSe surface during the thermal oxidation has been studied. The methods of cathodoluminescence (CL) analysis and of X-ray diffraction (XRD) have been used for studying chemical phase compositions of films [1]. Structural studies showed the presence of In_4Se_3 with InSe [3]. X-ray diffraction spectrum reveals that the synthesized products were single-crystalline of the β -phase hexagonal structure of InSe with lattice constants a= 4.006 Å and c=16.642 Å. The strong peak due to the reflection from the (004) crystal plane reveals that most nanowires grow with a strong preferred orientation. [3].

2 BASIC EQUATION

From the XRD profiles, the inter-planar spacing d_{hkl} was calculated for the (004) plane using the Bragg's relation [4].

$$d_{hkl} = \frac{n\lambda}{2\,Sin\ \theta} \quad (1)$$

Where λ=1.54056 Å is the wavelength of the X-ray radiation, d is the lattice spacing, n (n=1, 2, 3, ..) is the order number and θ is the Braggs angle. The factor d is related to (h k l) indices of the planes and the dimension of the unit cells. The peak width at half maximum used to determine the crystallite size (D) by using Debye–Scherrer formula is,

$$D = \frac{K\lambda}{(\beta Cos\ \theta)} \quad (2)$$

Where K=0.94 is the Scherrer constant, β is the full width at half maximum in radians and θ is the Bragg diffraction angle. The strain (ε) value may be evaluated using the relation:

$$\varepsilon = \frac{(\beta Cos\ \theta)}{4} \quad (3)$$

The dislocation density (δ) may be calculated by using the formula [5].

$$\delta = \frac{15\,\varepsilon}{(axD)} \quad (4)$$

3 RESULTS AND DISCUSSION

Undoped InSe single crystal was grown by using the Bridgman/Stockbarger method. We present the results of the systematic studies on the structural analysis of the InSe. The structural characterizations of the single crystal deposited films were analysed by means of XRD and EDX measurements. The structural and lattice parameters of the undoped InSe semiconductor was analyzed using a X-ray diffractometer (XRD) using Cu-Kα radiation with a wavelength of λ=1.54050 Å (Bruker). The values of 2θ were altered between 10 deg and 90 deg with the step of 0.1 deg/sec.

Figure 1 shows the XRD pattern of the undoped InSe semiconductor. It is found that the InSe crystal has hexagonal structure, quite close 2θ peak values and dominant diffraction peak around 2θ= 21,89° degrees for the was the (004) plane. This result is in a good agreement with that obtained by refs. [3, 4-10]. In addition to this (004) peak, some other peaks corresponding to (002), (103), (006) [6-8;9;10-13], (008) [6;10;11], (0018) [6], (0110), (205), (0012) [12] and (0014), orientations was also observed. The results given in Figure 1 are in good agreement with those in the literature.

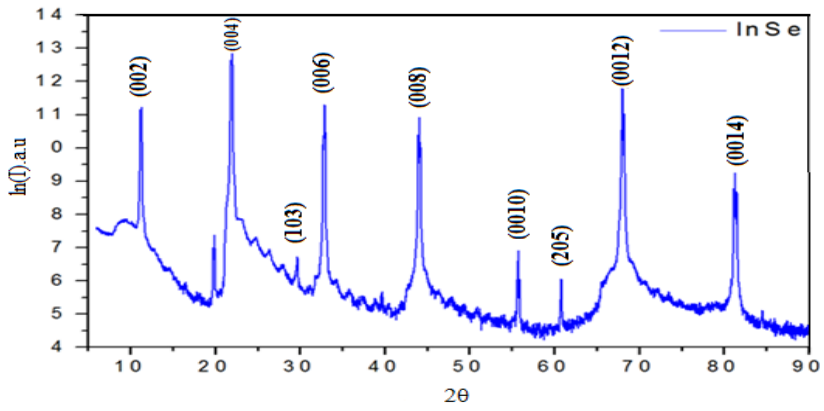

Figure 1: X-ray diffraction (XRD) spectra of InSe after annealing (T=300 °C). The Miller indices are indicated on each diffraction peak.

The values of standard interplanar distance (d) and observed interplanar distance (d_{exp}) along with the respective plane for InSe semiconductors has been given in Table 1. As clearly seen from Figure 1 and from intensity ratio data given in Table 1, the XRD peak similar behavior has also been observed in the optical properties of InSe crystal doped with Er [14]. The experimental (d_{exp}) interplanar distance value has been calculated by using Bragg diffraction law [15] have reported that InSe crystals grown by Bridgman method had generally γ-polytype hexagonal structure.

Table 1 the standard and calculated XRD results for the undoped InSe.

Peak (hkl)	**2θ**	**Intensity (a.u.)**	**d_o (Å)**	**$d_{exp.}$ (Å)**	**Structure**
(002)	11.19	72009	7.910	7.900	Hexagonal
(004)	21.89	310787	4.068	4.060	Hexagonal
(103)	29.71	827	3.010	3.004	Hexagonal
(006)	32.90	77577	2.720	2.710	Hexagonal
(008)	44.09	53923	2.055	2.052	Hexagonal
(0010)	55.75	1008	1.650	1.640	Hexagonal
(205)	60.84	427	1.523	1.521	Hexagonal
(0012)	68.05	132001	1.379	1.376	Hexagonal
(0014)	81.32	10236	1.184	1.182	Hexagonal

The crystallite size, dislocation density and residual strain for the InSe have been calculated using the Eq (2), Eq (3) and Eq (4), respectively. The analysis result obtained from EDX and XRD measurements have been presented in Table 2. The lattice parameters a and c of the hexagonal structure of InSe can be calculated using the following relation:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \qquad (5)$$

Where and (hkl) are the miller indices (004). The calculated lattice constants were found to be a=b=4.005 ± 0.004 Å and c=16.660 ± 0.004 Å for InSe. This value is almost agreed with the ones given in JPCDS card No.: 34-1431 (a=4.005 Å and c=16.640 Å). The number of crystallites per unit area (N) of the films was determined using the relation [16]:

$$N = \frac{t}{D^3} \quad (6)$$

Where t is the thickness of the semiconductor crystal.

Table 2 the crystallite size (D), dislocation density (ε) and residual strain (δ) for the InSe.

Peak (hkl)	2θ	FWHM	$d_{teo.}$ (Å)	$d_{exp.}$ (Å)	ε, ($lin^{-2}m^{-4}$) $x10^{-4}$	δ, (lin/m^{-2}) $x10^{14}$	N (m^{-2}) $x10^{18}$
(002)	11.19	0.156	568.0	534.8	6.7	2.86	5.88
(004)	21.89	0.238	377.6	355.3	10.19	7.92	22.3
(103)	29.71	0.074	1234.0	1126.3	3.2	1.26	0.629
(006)	32.90	0.097	948.4	885.5	4.09	1.27	1.43
(008)	44.09	0.153	622.1	585.9	6.18	2.91	4.47
(0010)	55.75	0.072	1378.4	1304.2	2.77	0.587	0.405
(205)	60.84	0.098	1042.8	983.2	3.68	1.03	0.946
(0012)	68.05	0.060	1779.9	1670.9	2.16	0.356	0.193
(0014)	81.321	0.121	964.6	905.0	4.0	1.22	1.21

These results are in a good agreement with the ones obtained from EDX analyses. Figure 2 show the EDX spectra of InSe.

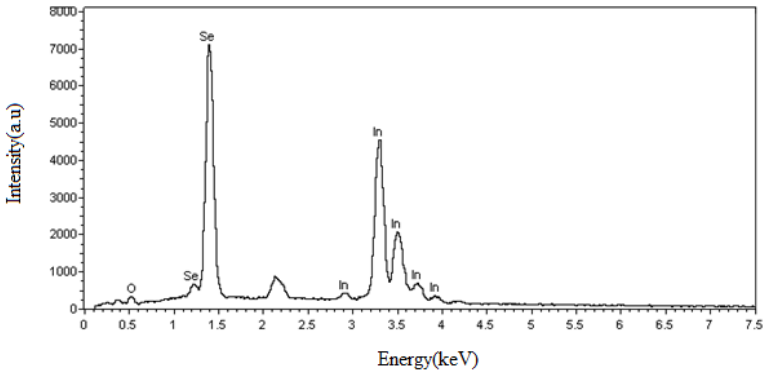

Figure 2: EDX spectra for InSe crystals.

In and Se elements have been taken as 61.17% and 38.83% in order to obtain the stoichiometric ratio being an important issue for the constituent of InSe compound, respectively. However, according to the EDX results, InSe contains In=57.04 %, Se =38.46% and O= 4.50%, respectively. These values are quite close to the expected ones and a little amount of In has been got bonding with O. The surface morphology images of the crystal were obtained by scanning electron microscope (SEM) technique at 15 kV with a 25.000 magnification. The surface of the InSe was coated with Au for SEM image enhancement. Figure 3 shows the SEM images of undoped InSe crystal.

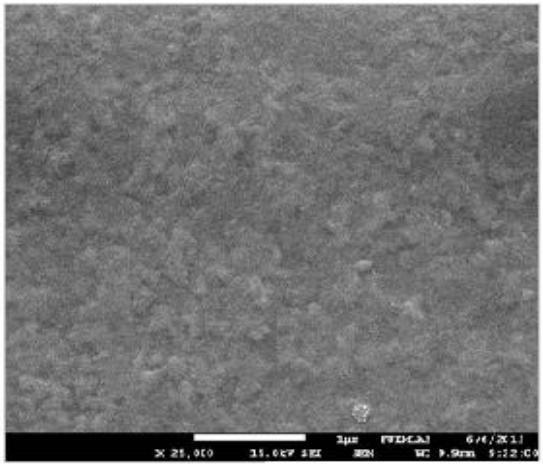

Figure 3: SEM images taken at 15 kV with a 25.000 magnification for undoped InSe crystals

It can clearly be seen that crystal has smooth and homogeneous surfaces. It has been found that the has a novel hexagonal form and the crystallite size, being quite close to each other, have been calculated to be 42-155 nm for InSe.

4 CONCLUSION

InSe single crystal used in this research were grown by using the Bridgman/Stockbarger method. The ingots have no cracks and voids on the surface in ingots. There is no process to polish and clean treatments at cleavage faces of these samples because of the natural mirror-like cleavage faces. InSe has specific impurities arising from its crystal structure. When transition element is doped in to InSe single crystals, these impurities which are transition elements are eliminated from the crystal during the growth process. Samples were cleaved along the cleavage planes (001). The freshly cleaved crystals had mirror-like surfaces even before using mechanical treatment.

We have reported the characterization of the InSe compound semiconductor by the XRD and EDX. It is found that the InSe crystal has hexagonal structure, quite close 2θ peak values. The calculated lattice constants were found to be a=4.005 Å and c=16.660 Å for InSe. The crystallite size (355.3 Å), residual strain ($10.19x10^{-4}$ lin^{-2} m^{-4}) and dislocation density ($7.92x10^{14}$ lin m^{-2}) values has been calculated using powder XRD results (004), respectively. It has been observed that InSe contains In=57.04 %, Se =38.46% and O= 4.50%. These results are in a good agreement with the ones obtained from EDX analysis.

5 HIGHLIGHTS

1. Undoped InSe single crystal has been grown by using the Bridgman/Stockbarger method.
2. The structural was studied by employing the techniques of XRD and EDX
3. XRD studies revealed that the prepared bulks were crystalline in nature.
4. A little amount of In has been got bonding with O. A low amount of oxygen element is determined that binds with indium.
5. In and Se elements have been taken as 61.17% and 38.83% in order to obtain the stoichiometric ratio being an important issue for the constituent of InSe compound, respectively. However, according to the EDX results, InSe contains In=57.04 %, Se =38.46% and O= 4.50%, respectively.

6 ACKNOWLEDGEMENTS

This work was supported by the Atatürk University Research Fund, Project No: 2013/300

REFERENCES

[1] Balitskii O. A., Lutsiv R. V., Savchyn V. P. and Stakhira J. M.(1998). Materials Science and Engineering, 56, 5–10.

[2] Kobbi B., Ouadjaout D. and Kesri N. (2001). Vacuum, 62, 321-324.

[3] Siciliano T., Tepore A., Micocci G., Genga A., Siciliano M. and Filippo E.(2011). Synthesis and characterization of indium monoselenide (InSe) nanowires, 22, 649–653.

[4] Cullity B.(1972). Elements of X-Ray Diffraction, Addison Wesley, Reading, MA, 102

[5] Abdullah M. M., Bhagavannarayana G. and Waha M. (2010). Journal of Crystal Growth, 312,1534–37.

[6] Hirohata A., Moodera J. S.and Berera G.(2006). Structural and electrical properties of InSe polycrystalline films and diode fabrication. Thin Solid Films, 510, 247-250.

[7] Gysling H. J., Wernberg A. A. and Blanton T. N.(1992). Molecular Design of Single- Source Precursors for 3-6 Semiconductor Films, Control of Phase and Stoichiometry in In_xSe_y Films Deposited by a Spray MOCVD Process Using Single-Source Reagent, 4, 900-905.

[8] Choi I. and Yu P. Y. (2003) Properties of phase-pure InSe films prepared by metalorganic chemical vapor deposition with a single-source precursor. Journal of Applied Physics,93 (8), 4673-4677

[9] Siciliano T., Tepore A., Micocci G., Genga A., Siciliano M. and Filippo E. (2011). Synthesis and characterization of indium monoselenide (InSe) nanowires. J Mater Sci Mater Electron,22, 649–653.

[10] Viswanathan C., Gopal S., Thamilselvan M., Premnazeer K., Mangalaraj D., Narayandass S. K., Yi J. and Ingram D.C.(2004). Space charge limited current, variable range hopping and mobility gap in thermally evaporatedamorphous InSe thin films. Journal of Materials Science: Materials in Electronics, 15, 787-792.

[11] Viswanathan C., Senthilkumar V., Sriranjini R., Mangalaraj D., Narayandass S. K. and Yi J.(2005). Effect of substrate temperature on the properties of vacuum evaporated indium selenide thin films, Cryst. Res. Technol 40 (7), 658 – 664.

[12] Ateş A. , Kundakçı M., Astam A. and Yıldırım M. (2008). Annealing and ligth effect on optical and electrical properties of evaporatedindium selenide thin films. Physica E, 40, 2709-2713.

[13] Siciliano T., Tepore A., Micocci G., Genga A., Siciliano M. and Filippo E.(2011). Formation of In_2O_3 Microrods in Thermal Treated InSe Single Crystal. Crystal Growth Design, 11, 1924-1929.

[14] Mosca D. H., Mattoso N., Lepienski C.M., Veiga W., Mazzaro I., Etgens V.H. and Eddrief M.(2002). Mechanical properties of layered InSe and GaSe single crystals. Journal of Applied Physıcs, 91 (1), 140-144

[15] Mustafa F. I., Gupta S.N., Goyal S. and Tripathi k.(2010). Effect of indium concentration on the electrical properties of InSe alloy. Physica,405, 4087–4091.

[16] Gürbulak B., Yıldırım M., Ateş A., Doğan S. and Yoğurtçu Y.K. (1999). Jpn. J. Appl. Phys.38, 5133-36.

[17] Zolfaghari M., Jain K. P., Mavi M. S., Balkanski M., Julien C. and Chevy A.(1996). Materials Science Enginering, 38, 161-70.

[18] Ravichandran K., Sakthivel B. And Philominathan P.(2010). Cryst. Res. Technol 45, 2