Journal of Ovonic Research Vol. 6, No. 4, July-August 2010, p. 173 – 180

SYNTHESIS OF $GeTe_{0.1}Se_{0.9}$ SINGLE CRYSTALS AND ITS STRUCTURAL AND OPTICAL CHARACTERIZATION

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This paper represents the investigation on growth of single crystals of $GeTe_{0.1}Se_{0.9}$ using Chemical Vapour Transport (CVT) technique using Iodine as a transporting agent. Photographs of Energy Dispersive Analysis of X- ray (EDAX) reveals that $GeTe_{0.1}Se_{0.9}$ single crystals are nearly stoichiometrically perfect. Structural confirmation of these crystals was accomplished by X- ray diffraction and it shows that $GeTe_{0.1}Se_{0.9}$ has hexagonal closed packed crystal structure and lattice parameters have been calculated. The electron diffraction pattern/photograph confirms the single crystallinity of the grown crystal. A study of microstructures on this crystal has been made and its layered pattern is found. The characterization of optical band gap has been calculated at room temperature throughout the wavelength 200 – 2500 nm near the fundamental absorption edge. It shows that grown crystals have direct and indirect energy gaps of 1.08 eV and 0.8 eV respectively.

(Received July 3, 2010; accepted July 16, 2010)

Keywords: Ge-Te-Se, Single crystal, CVT method, EDAX, Optical characterization

1. Introduction

Chalcogenides are materials composed of S, Se, Te or Sb and these are under wide investigation for applications in the field of optical and electrical storage due to their fast reversible crystalline to amorphous phase transition in application with laser or electrical pulses. Phase change materials are now successfully employed in the optical data storage and are becoming promising candidates for the future electronic storage applications. Chalcogenide based Phase Change Random Access Memory PC RAM) is being investigated as the next generation non volatile memory (NVM) technology. The use of chalcogenides as a potential memory material was first described by Stanford Ovshinskys. Binary constituents i.e. GeTe and Sb_2Te_3 may be used for the phase change recording [1]. In the chalcogenides material, application of heat induces a change in their internal structure resulting in a phase transformation when the material is heated up to its melting temperature and quenched quickly, the bonds within have no times to rearrange themselves resulting in the creation of a disordered mass which represents the amorphous state (i.e. RESET state, memory bit 0). When the material is heated between glass transition temperature and melting temperature and then cooled slowly, the phase becomes crystalline (i.e. SET state, memory bit 1. For those 50 – 100 ns is the switching time for the crystalline/ amorphous transition [2].

In order to study the crystallization behavior of the GeTeSe ternary systems, a novel multipulse laser techniques has been used. Optical and structural properties are responsible for the dependence of the nucleation and growth rates on composition. It is found that Se content is dominant in determining both the nucleation rates and the amorphous optical constants, while the single or multiphase nature of the resultant crystalline state determines the crystal growth speed

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[3]. Based on this, compositions on the GeTe – GeSe line are unique in that they are single phase for Se content up to 25 % thus, crystallization and optical characterization allowed to use materials for the phase change principles as discussed earlier.

The structural, optical and crystallization effects of the addition of Se are added to GeTe is represented by A. P. J. M. Jongenelis et al in [3]. They also show that why both crystallization properties and optical constants change when more Se is added to GeTe. Finally they found that very narrow range of material compositions can simultaneously satisfy the optical and crystallization requirements for a CD compatible erasable disc.

The layer like orthorhombic chalcogenides, i.e. GeTeSe have found application in holography, high temperature lubricants, TV tubes, electronic devise fabrication and PEC solar cells. Further, metal chalcogenides offer a range of optical band gaps, which is suitable for various optical and optoelectronic applications. The semiconducting layered metal chalcogenides form a major class of new material that have been investigated for energy conversion in photoelectrochemical (PEC) solar cells and in solid state (p- n Schottky) solar cells[4].

2. Experimental

2.1 Growth of Crystals

In this investigation, single crystals of $GeTe_{0.1}Se_{0.9}$ have been grown by CVT technique using Iodine as transporting agent. In this technique, we have to set temperature gradients between two zones in order to enhance the transport of material in vapour form. This is done with the help of a two zone horizontal furnace having a special sillimanite threaded tube (grade KR 80 GA HG) closed at one end, 450 mm in length, 70 mm outer diameter, 56 mm inner diameter with threaded pitch of 3 mm. The cleaned ampoule was filled with stoichiometric proportion of Ge (99.999%), Te (99.99%) and Se (99.99%) pure of about 5 g for growth and compound preparation. This ampoule was sealed at a pressure of 10^{-5} torr. The sealed ampoule was then kept into a two zone furnace at constant reaction temperature up to desired temperature and maintained at that temperature for 7 days, as shown in the growth condition for $GeTe_{0.1}Se_{0.9}$. Finally, the furnace was cooled off at the room temperature with the rate of 20 K/ h. Here two zone horizontal furnace provides an appropriate temperature over the entire ampoule. Figure 1 shows that how the ampoule is subjected to the temperature profile along two zone furnace. Figure 2 shows the photographs of grown crystals.

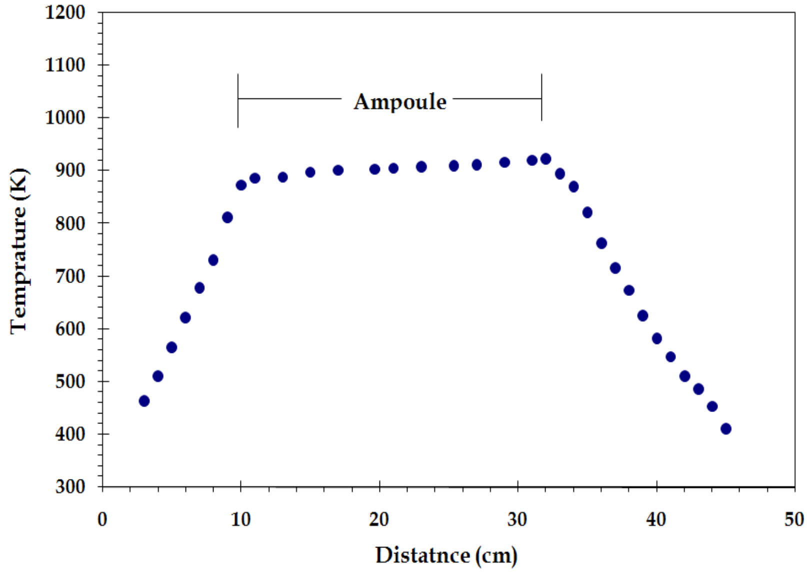

Fig. 1. Temperature profile along two zone furnace showing the position of the ampoule.

Table 1. Growth condition for $GeTe_{0.1}Se_{0.9}$ (I_2) single crystals using Chemical Vapour Transport (CVT) technique.

Crystal	Temperature		Crystal size	Crystal thickness	Shape and color
	Hot Zone (^{0}K)	Cold Zone (^{0}K)	(cm x cm)	(μm)	
$GeTe_{0.1}Se_{0.9}$ (I_2)	923	898	0.5 X 0.8	35	Needle type and shiny black opaque

2.2 Structural Characterization

Single crystals of $GeTe_{0.1}Se_{0.9}$ were directly used for obtaining the photograph of EDAX. But one should know that the photograph of EDAX may be obtained using the powder form of single crystal. The composition of the specimen was verified through Energy Dispersive Analysis of X-rays (EDAX), using it quantitative elemental data can obtain from an analysis of this photograph as shown in Fig. 3.

The X-ray diffraction measurement was recorded by the means of X- ray diffractometer (Philips, Model- X'PERT) for prepared single crystal of $GeTe_{0.1}Se_{0.9}$ (I_2). We can identify the crystal structure of the specimen with the help of it. CuK_α radiation was used for obtaining the XRD pattern. Figure 4 shows the XRD pattern of the grown crystal. We have calculated the value of lattice parameters a, b, and c, unit cell volume and densities are calculated.

The photograph of electron diffraction pattern of single crystal of $GeTe_{0.1}Se_{0.9}$ grown by CVT technique has been taken by Transmission Electron Microscope (TEM, Philips, Model TECNAI). This helps us to confirm the single crystallinity that whether the material shows single crystallinity or poly crystallinity.

2.3 Morphological Characterization

A study of microstructure of the as grown crystals of $GeTe_{0.1}Se_{0.9}$ by CVT technique is presented here. Morphological of grown surfaces of bulk single crystal consists of a variety of structures whose study leads to derive the condition and mechanism of growth.

2.4 Optical Characterization

The optical absorption data were taken by means of (Perkin Elmer Model: Lambda- 19) Spectrophotometer. The surfaces of this type of grown crystals were mirror like. The a and b- axes were confirmed in the plane of cleavage i.e. in the basal plane. Measurements were performed at room temperature with the incident light beam normal to the basal plane i.e. along the c- axis of the grown flakes. As the crystal structure did not permit cutting and polishing, so measurements were not performed along the c- axis [7]. Crystal flakes were pasted on a thick black paper with a cut exposing the crystal flake to the incident light. The reference used for this work was a replica of the black paper, having the cut in the exactly the same position as the crystal flake. This arrangement was necessary because the crystal size was smaller than that of the sample compartment. $GeTe_{0.1}Se_{0.9}$ (I_2) used in the present work since were in the form of thin platelets, as grown sample could be directly used for obtaining the absorption spectra [8]. In this present case, absorption spectrum taken over the spectral range 200- 2500 nm. The absorption coefficient 'α' were determined at every step of 5 nm with scanning speed 240 nm/min.

3. Results and discussion

3.1 Crystal Growth

The ampoule containing the crystals was broken and crystals having maximum size were removed carefully. We obtained black opaque shiny crystals in this grown process. The maximum size of the grown crystals and growth conditions of the crystals are given in the Table-1.

Fig. 2. Photograph of grown $GeTe_{0.1}Se_{0.9}(I_2)$ single crystals.

3.2 EDAX

A careful study of the data indicates that, the single crystals of $GeTe_{0.1}Se_{0.9}$ grown by CVT technique using Iodine transporting agent are nearly stoichiometrically perfect. EDAX analysis did not reveal the presence of secondary phase in them. EDAX spectra taken from representative sample is taken and with the help of it, quantitative elemental data obtain from an analysis of this photograph is shown in Table-2.

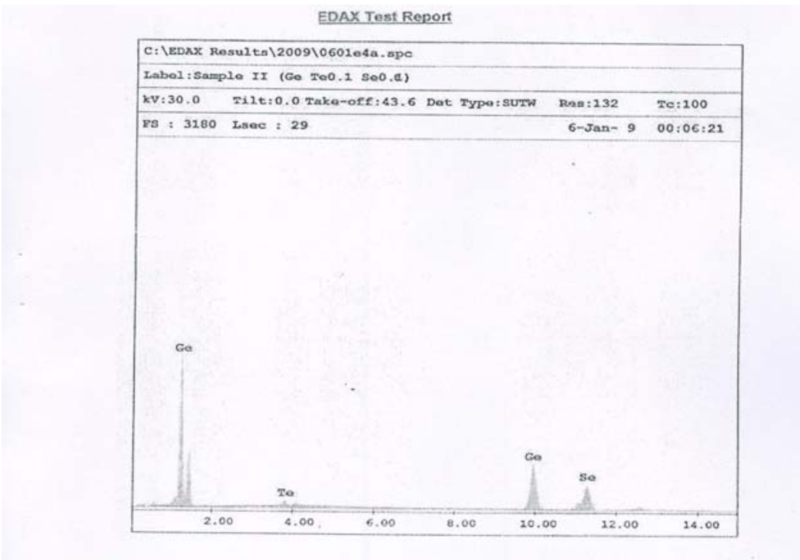

Fig. 3. EDAX Photograph of $GeTe_{0.1}Se_{0.9}$ (I_2) single crystal.

Table 2. Chemical composition (Wt %) of grown $GeTe_{0.1}Se_{0.9}$ (I_2) crystal by EDAX analysis.

Crystal	Wt (%) of elements from EDAX			Wt % of elements taken for growth experiment		
	Ge	Te	Se	Ge	Te	Se
$GeTe_{0.1}Se_{0.9}$ (I_2)	23.17	3.95	24.85	22.196	3.901	23.902

3.3 X- Ray Diffraction

A well resolved X-ray peak corresponding to the (0017) and (0014) planes are observed. It reveals that the $GeTe_{0.1}Se_{0.9}$ (I_2) single crystal has a strong preferred orientation and their crystallites are perpendicular to (0017) and (0014) planes. Hexagonal crystal structure was found for dichalcogenide semiconductor materials in the references [5] for single crystal layered semiconductor $ZrS_{1.5}Se_{0.5}$ and $ZrS_{0.5}Se_{1.5}$ of CdI_2 type structure. XRD reveals that the specimen has hexagonal closed packed structure and contains six chalcogenide atoms per unit cell. The intensity of all other reflections is weak as compared to this (0017) and (0014) reflection plane. The lattice parameters used for indexing the XRD peaks in its pattern are matched perfectly with lattice parameters/constants at different composition of $GeTe_{1-x}Se_x$ (x = 0.60, 0.64, to 0.88). [6] shows that $GeTe_{1-x}Se_x$ has hexagonal crystal structure. The values of lattice parameters, unit cell volume and the density were found by X- ray diffraction, as listed in Table- 3.

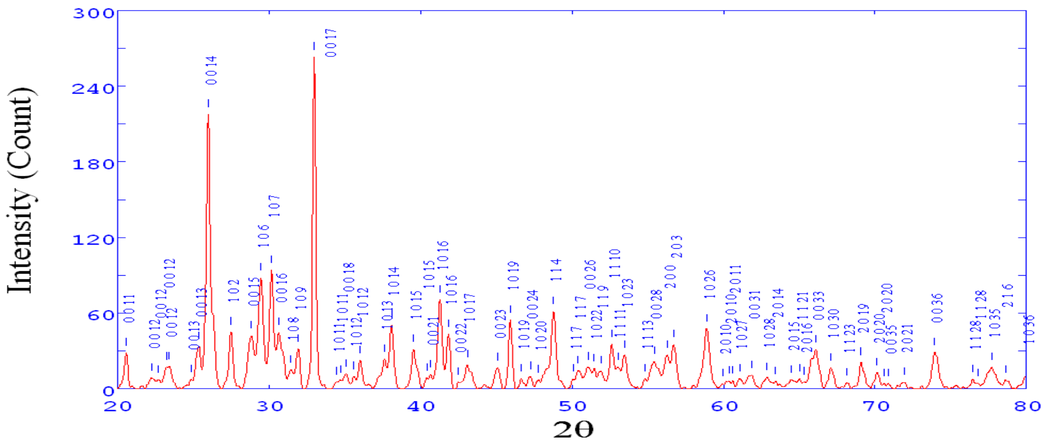

Fig. 4. XRD pattern of $GeTe_{0.1}Te_{0.9}$ (I_2) single crystals.

Table 3. Lattice parameters, Unit cell volumes and X-ray density for $GeTe_{0.1}Se_{0.9}$ (I_2) single crystals.

Crystal	a=b (Å)	c (Å)	Unit cell volume $(Å)^3$	Density (g cm^{-3})
$GeTe_{0.1}Se_{0.9}$ (I_2)	3.77	46.4	571.108	2.728

3.4 Electron Diffraction

Figure 5 shows the photograph of electron diffraction pattern of grown crystal was obtained by Transmission Electron Microscope (TEM, Philips, Model TECNAI) and it contains sharp white spot image in a particular manner with the scale of 200 nm. This is the main evidence of single crystallinity of material.

Fig. 5. Electron diffraction pattern of single crystal $GeTe_{0.1}Te_{0.9}$ (I_2) semiconductor.

3.5 Microstructures

Fig. 6 show the photographs of growth layers on an otherwise homogeneously flat surface of $GeTe_{0.1}Te_{0.9}$ (I_2) single crystal. One is inclined to conjecture that layer mechanism is operative during the crystal growth. The growth layers on the surfaces of these crystals are seen in Figure 6 to initiate from crystal periphery and result into a flat surface along with growth layers and a flat surface surrounded by growth layers. It shows that surface of a $GeTe_{0.1}Se_{0.9}$ crystal in which the growth layers are seen to initiate from edges or boundaries.

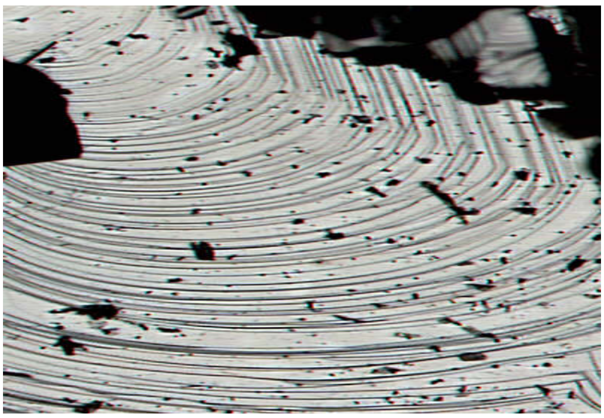

Fig. 6. Micrograph showing the initiation of growth layers from crystal edges on a $GeTe_{0.1}Se_{0.9}$ (I_2) single crystal.

3.6 UV VIS NIR Optical Absorption Spectrum

Fig. 7 shows the absorption spectrum taken from $GeTe_{0.1}Se_{0.9}$ single crystal in the form of thin platelet/flake over the spectral range 200 to 2500 nm. After study we found that the absorption edge is presence in the spectral range 300 to 950 nm. In order to analyze the results from this spectrum, values of absorption coefficient 'α' were determined at every step of 5 nm.

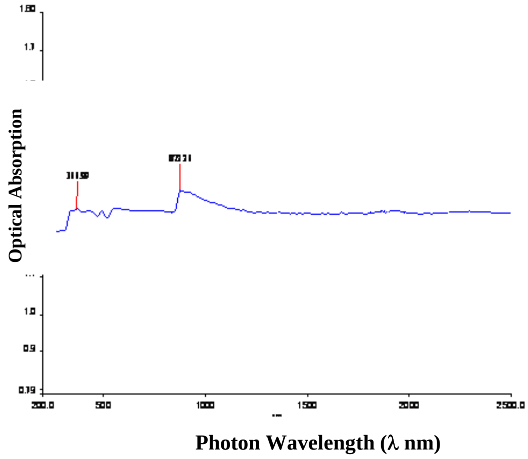

Fig. 7. Optical absorption spectrum from a CVT grown $GeTe_{0.1}Se_{0.9}$ (I_2) single crystal.

Energy gap determination

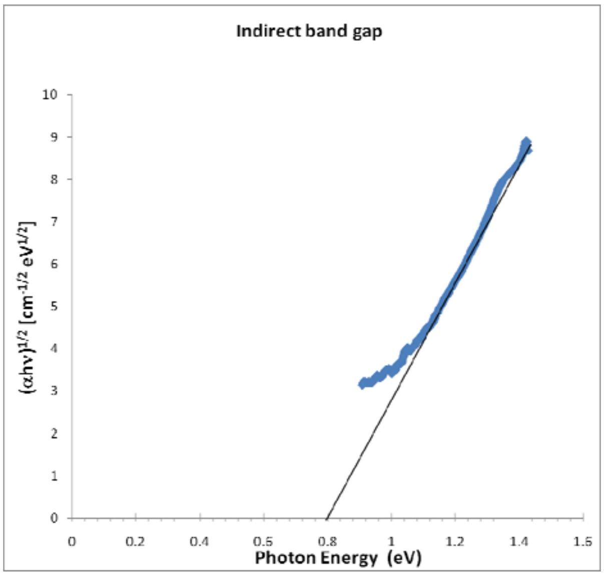

Fig. 8. $(\alpha h\nu)^{1/2}$ versus photon energy for $GeTe_{0.1}Se_{0.9}$ (I_2) single crystal.

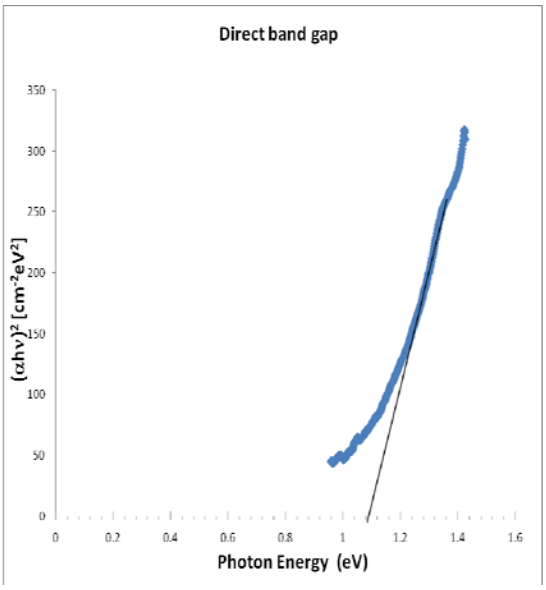

Fig. 9. $(\alpha h\nu)^2$ versus photon energy for $GeTe_{0.1}Se_{0.9}$ (I_2) single crystal.

The dependence of absorption coefficient 'α' in terms of direct and indirect transitions can be performed with the help of equation 1 and equation 2, i.e. derived for three dimensional crystals. Simplest form is as follows [8] (Pankov and Jaques 1975)

$$\alpha h\nu = A\left(h\nu - E_g\right)^r \qquad (1)$$

For direct transitions and

$$\alpha h\nu = \sum_j B_j \left(h\nu - E'_g \pm E_{pj}\right)^r \quad (2)$$

For indirect transitions.

Where, ‘α’ is the absorption coefficient, hv is the energy of the incident photon, E_g the energy of for the direct transition, $E_g^{'}$ the energy for the indirect transition, the energies of the phonons assisting at indirect transitions, A and B are parameters depending on temperature, photon energy and phonon energies E_{pj} . For the analysis of the experimental results obtained at constant temperature, equation 1 and equation 2 are sufficient and especially while we are interpreting results from semiconducting materials absorption spectra. The exponent ‘r’ in above two equations depends upon whether the transition is symmetry allowed or not and the constants A and B will assume different values for the allowed and forbidden transitions.

4. Conclusion

In this present work, we have grown single crystals of $GeTe_{0.1}Se_{0.9}$ successfully by CVT technique having fairly large size. X- Ray Diffraction shows its hexagonal crystal structure and it contains six atoms per unit cell. EDAX result shows that grown crystals are nearly stoichiometrically perfect. Electron diffraction pattern proves the single crystallinity nature of the crystals. Microstructures of crystals lead to derive the condition and mechanism of growth. Finally, these crystals possess both direct and indirect bandgap which shows its semiconducting nature.

Acknowledgement

Authors are thankful to UGC, New Delhi, India for the sanction of a major research project to G.K. Solanki which provided the necessary financial help for carrying out this work.

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