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Opto-Electronic Applications of Advanced Electronic Materials: InSe System

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Abstract: *Indium Selenide (InSe) is a complex system with many co-existing crystallographic phases. Extensive research has been done on identification of these phases but still there is a lot of scope in clarification of such structural modifications. This manuscript aims to highlight the phase transformation mechanism and synthesis of various layered structures of InSe. By compiling the recent advancements on examining InSe as opto-electronic material, our work attempts to emphasize the performance enhancement of this material.*

Keywords: Indium Selenide, Opto-Electronic, Performance enhancement.

INTRODUCTION

Chalcogenide glasses: The primary elements of chalcogenide glasses are chalcogens (Sulphur (S), Selenium (Se) and Tellurium (Te)). The word chalcogen is composed of two greek words (chalco+gen) which means ore-generating. These glasses are synthesized by formation of alloys with other group elements like indium (In), germanium (Ge), antimony (Sb) etc. Chalcogenide glasses are responsive to the absorption of electromagnetic radiation and show a diversity of light-actuated effects as a result of irradiation. Consequently, significant amount of research has been done on active opto-electronic devices using these materials. Doped chalcogenide glasses are novel contender for active utilizations such as amplifiers, FETs and buffers. There are plentiful papers on exploration of optical, electronic and physical properties of chalcogenide glasses [1]. Some chalcogenide alloys have two structural states (amorphous and crystalline). The resistance and reflectance contrast between these states makes them profitable in PCRAM and optical data storage applications. InSe is a layer structured chalcogenide glass. The two dimensional system is capable of forming multi-phase films in view of the inherent polymorphism. This binary compound is pure state has hexagonal structure with direct band gap of 1.7 eV [2]. Indium selenium system crystallizes in many compositions and many phases may co-occur in a particular proportion of the system. This is why the analysis of such materials becomes confusing and there is an urge to develop single phase InSe compounds [3]. γ- In_2Se_3 is the most stable and researched phase so far. It has also been found to be a promising candidate for opto-electronic applications. In this manuscript, we represent a review of the accessible literature on indium-selenium system. Various compositions are studied and compared on the basis of structure, synthesis, characterization and applications.

INDIUM-SELENIUM SYSTEM

Indium selenium is a binary III-VI 2D semiconductor which has a family of crystallographic modifications with different stoichiometric ratios. The In-Se phase diagram illustrate many compositions that co-exist in equilibrium such as InSe, In_2Se_3, In_4Se_3, In_6Se_7, In_3Se_4 etc. for a particular stoichiometry, many phases may exist together. For example, InSe has a β and γ phases whereas In_2Se_3 has 5 phases: α, β, γ, δ, κ.

InSe

InSe monolayer consists of a sequence of 4 atoms: Se-In-In-Se linked with covalent bonding with tetravalent indium locus.
The possible crystal structures in which it can crystallize are

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1) β -InSe with hexagonal structure.
2) γ-InSe with rhombohedral structure.

In_2Se_3

In_2Se_3 has a single layer of thickness of 5 atoms arranged in the sequence Se-In-Se-In-Se with each layer terminated with Se atoms by virtue of which the layers have weak van der waals interactions with each other [4]. This is probably the most complex known structures.

α- In_2Se_3 crystallizes in the stacking sequence Se-In-Se-In-Se in which there exists covalent bonding between the atoms and van der waals interactions within the layers. Both α and β have similar semiconducting layer composition and both can exist in hexagonal as well as rhombohedral forms. On the other hand, α is stable at room temperature but β is metastable and switches back to α unless it is doped with antimony (Sb). By heating α we obtain α-β transformation at 200°C and it remains β till 650°C [5].

γ- In_2Se_3 is a stable polycrystalline phase with defect wurtzite structure. This structure is basically NaCl type but has Indium vacancy on $1/3^{rd}$ of its cationic sites. This structure is achieved at 650°C and is stable upto 750°C. on further annealing, we obtain κ-In_2Se_3 (a metastable anisotropic phase) which transforms to δ-In_2Se_3 above 750°C [6].

The electrical, optical and structural properties of Indium-Selenide films rely on the following factors:

1) The growth technique.
2) The annealing temperature.
3) The stoichiometry or III-VI ratio.

Some work related to this has been recapitulated in the following section:
D. Y. Lyu et al. examined the In-Se system by preparing 3 samples :

1) IS400- In_2Se_3 annealed at 400°C.
2) IS425- In_2Se_3 annealed at 425°C.
3) IS450- In_2Se_3 annealed at 450°C.

All the samples were characterized for structural analysis and the results are different for all the samples. IS400 shows a mixed α and γ phase with energy band gap of 1.943 eV. IS425 and IS450 were both single phase γ-In_2Se_3 with E_g values 1.942 and 1.946 respectively [3].

Aytunc Ates et al. exhibited that by augmenting the growth temperature the diffraction peak intensities in the XRD diffractograms were increased. This implies that the crystallinity of sample is enhanced due the formation of γ-In_2Se_3 for temperature greater than 400°C. The optical band gap values of annealed films were also observed to be greater than as grown films. This is because γ-In_2Se_3 has higher energy band gap. The photocurrent has been discovered to be directly proportional to temperature which implies an improvement in conductivity [7].

T.Kato et al. has also demonstrated results for varying VI-III ratio and deposition temperature in α-In_2Se_3 compound [8]. Other compositions like In_3Se_4 (rhombohedral structure), In_4Se_3 (orthorhombic) and In_6Se_7 (monoclinic) are also present side by side in the In-Se phase diagram.

GROWTH TECHNIQUES

With the help of binary alloy phase diagram of Indium Selenium system, bulk samples are prepared with various methods like melt-quench and solid-state reaction. Pure In and Se in powdered form are used as precursors in these methods.
Indium selenium thin films can be prepared with various growth techniques:

1) Vacuum evaporation
2) Molecular beam epitaxy (MBE)
3) Metalorganic chemical vapour deposition (MOCVD)
4) Mechanical alloying
5) Electro deposition
6) Flash evaporation

Though electro-deposition is a simple, economical and low temperature technique, it is problematic to obtain high efficiency solar cells with this technique. Dual source MOCVD is by far the best known technique to grow high quality buffer layers in solar cell applications. There are many advantages of MOCVD over other techniques like large scale production, homogeneity, high quality films can be tailored by modulating the flow rate of precursors in dual source MOCVD which is an edge over single source MOCVD. Weak crystallinity and multiple phases are two major issues with these films which are of great concern nowadays.

APPLICATIONS

In-Se is a binary source for formation of ternary and higher order materials which are highly sensitive to light and have innumerous applications like photo-diodes, photo-detectors, CIS and CIGS solar cells, switching devices, heterojunction devices, photovoltaic cells, data storage and nano-photonic applications.

Photovoltaic applications

InSe compounds are relevant for photovoltaic cell fabrication because of the following properties.

1) Low density of dangling bonds resulting in very low recombination rate.
2) High absorption coefficient which is directly proportional to temperature and photon energy [9]
3) A band gap of 1.9 eV which is suitable for solar energy conversion.
4) It has appraised photoconductivity which makes it competent absorber in photocells.
5) It has low resistivity which is essential to minimize the series resistance of the cell.

In semiconductor, the threshold for absorption of photons is determined by band gap and transparency to incident spectral radiation is measured by refractive index. That is why a pre-knowledge of these primary prospects is important for the characterization of opto-electronic properties of semiconductors.

CIGS

Copper indium gallium selenide is a I-III-VI chalcopyrite compound with Cd free buffer layer made up of In_2Se_3 because of this incorporation of an active layer it has many utilities over commercial CdTe and a-Si solar cells. A direct band gap of this layer steers to high absorption coefficient. This minimizes the photocell dimensions fulfilling the requirements of miniaturization, because of the absence of any Pb or Cd content it is a much more environment friendly approach with an efficiency of 20%, higher than other widespread solar cells in the market. Moreover, by adjusting the Ga to In and S to Se ratio, the band gap can be monitored in the realm (1.0 eV to 2.4 eV). As a result, definitely graded band gap can be attained [10]. A schematic diagram of CIGS based solar cell is shown in Fig. 1.

V. N. Katerinchuk et al. has deviced uniform p-n InSe photodiode and investigated that it has a wide spectral response in the incident radiation range of 1.2-3.2 eV [11]. Jian Jung Wang et al. has fabricated a photosensitive switch with InSe nanowires. It has swift and reversible switching with on/off ratio as high as 50 [12].

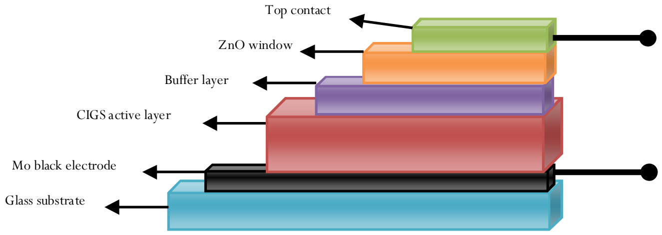

Figure 1. CIGS based solar cell

Nano-applications

Flawless optical and electrical devices can be achieved by varying the proportion, architecture and phases of nano In-Se. Large bonding and structural anisotropy of layered In_2Se_3 is the reason for their potential applications in nanophotonics, biosensors, thermo-electronics and energy conversion. Therefore, due to the incalculable demand of high scale integrated opto-electronics devices, the development of photodetectors with interdisciplinary nanomaterials is essential. Anurag and hailin peng et al. have individually prepared In_2Se_3 nanowires bearing two growth directions. One is along the z-axis and the other is perpendicular to it. The parallel component has a superlattice structure comprising Se atoms on the adjacent layers linked by vander waal forces. This layer depicts metallic nature with very high conductivity. The reason of this is unfolded in terms of conducting lines crossing the Fermi level from the valence band to conduction band and from conduction band to valence band. The perpendicular part is composed of Se atoms bound with covalent bonds. It exhibits n-type semiconducting behavior with lesser conductivity. Interestingly, by scaling down from bulk to nano the conductivity of In_2Se_3 elevates by 3 order of magnitude [13,4]. Wei Feng et al. has demonstrated multilayer nanosheet InSe (1:1) transistors and phototransistors whose thickness dependent photo response is a key factor for constructing ultra thin layered device. The performance panorama of this transistor surpasses the commercially established photodetectors because of its high sensitivity, fast on/off speed and broad spectal response from UV to NIR (Near infrared) [14].

PCRAM (Phase Change Random Access Memory)

The resistivity of InSe can be varied by a factor of 10^5 which is exceptionally superior than conventional non-volatile memories. That is why nano InSe is a promising candidate for PCRAM applications. This resistance depends on the degree of crystallinity. The reset current desired for phase transformation from crystalline to amorphous is lowered in highly resistive In_2Se_3 nanowire based PRAM

[15]. This can also be attributed to low melting temperature of nanoscale InSe cells. Moreover, when we are handling nano dimensions the heat dissipation of nanowires is suppressed and as a consequence the thermal conductivity also abates. Therefore, by utilizing this material we can design a high speed, low power, and non-volatile and nanoscale data storage device [16].

CONCLUSION

This review illustrates a thorough summary on the present understanding of InSe structural morphology. Various phases of In2Se3 have been identified but oftenly α and γ phases are synthesized, whereas other phases are still in the darker side. Out of all the growth techniques, MOCVD has succeeded in quality and stability. By virtue of high absorption coefficient, optimum band gap and wide spectral response, CIGS solar cells with cadmium free In_2Se_3 active layer have produced the most efficient and eco-friendly photovoltaic cells. Nanostructuring of the material enhances the properties of phase change memory devices by augmenting the switching speed and curtailing the input power. Apart from all this, phase controlled synthesis of InSe with proper experimental conditions should be further probed.

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REFERENCES

[1] Zakery and R. S. Elliott, *Optical Nonlinearities in Chalcogenide Glasses and their Applications*, 135 ed., Springer Series in Optical Sciences, Springer Berlin Heidelberg, 2007.

[2] Herrero J, Ortega, " Electrochemical synthesis of photoactive In_2Se_3 thin films", *J.Sol Energy Mater*, Vol. 16, pp. 477, 1987.

[3] D.Y. Lyua, T.Y. Lina, J.H. Lin, S.C. Tseng, J.S. Hwang, H.P. Chiang, C.C. Chiang, S.M. Lan, "Growth and properties of single-phase g-In_2Se_3 thin films on (1 1 1) Si substrate by AP-MOCVD using H2Se precursor", *Solar Energy Materials & Solar Cells*, Vol. 91, pp. 888–891, 2007.

[4] Hailin Peng, Chong Xie, David T. Schoen, and Yi Cui, "Large Anisotropy of Electrical Properties in Layer-Structured In2Se3 Nanowires", *Nano Letters*, Vol. 8, pp. 1511-1516, 2008.

[5] Yen-Chin Huang, Zhen-Yu Li, Wu-Yih Uen, Shan-Ming Lan, K.J. Chang, Zhi-Jay Xie, J.Y. Chang, Shing-Chung Wang, Ji-Lin Shen, "Growth of g-In2Se3 films on Si substrates by metal-organic chemical vapor deposition with different temperatures", *Journal of Crystal Growth* , Vol. 310, pp. 1679–1685 ,2008.

[6] D. Nithyaprakash, N. Punithavenia, J. Chandrasekaran, "The effect of annealing temperature on the structural and optical properties of In2Se3 thin films",

[7] *Optoelectronics And Advanced Materials –Rapid Communications*, Vol. 4, pp. 357 – 360, 2010.

[8] Aytunc- Ates, Mutlu Kundakc, Aykut Astam, Muhammet Yıldırım, "Annealing and light effect on optical and electrical properties of evaporated indium selenide thin films", *Physica E*, Vol. 40, pp. 2709–2713,2008.

[9] T.Kato, Y.Utsugi, T.Ohara, T.Muranaka, Y.Nabetani, T.Matsumoto, "Dependence of In2Se3 crystal structures grown on GaAs (001) substrates on growth temperature and VI/III ratio", *Journal of Crystal Growth*, Vol. 311, pp. 847–850, 2009.

[10] Tarrant, D. Ermer, J. Conference Record in *23rd IEEE Photovoltaic Specialists Conference*, 1993, p. 372.

[11] A.F. Qasrawi, "Temperature dependence of the band gap, refractive index and single-oscillator parameters of amorphous indium selenide thin films", *Optical Materials*, Vol. 29, pp. 1751–1755, 2007.

[12] V.N. Katerinchuk, M.Z. Kovalyuk, *Sov. Phys. Semicond.*, Vol. 25, pp. 577, 1991.

[13] Jian-Jun Wang, Fei-Fei Cao, Lang Jiang, Yu-Guo Guo, Wen-Ping Hu, Li-Jun Wan, "High Performance Photodetectors of Individual InSe Single Crystalline Nanowire", *J. AM. CHEM. SOC.*, Vol. 131, pp. 15602-15603, 2009.

[14] Anurag Srivastava, R. Chandiramouli, "Band structure and transport studies on impurity substituted InSe nanosheet – A first-principles investigation", *Superlattices and Microstructures*, Vol. 79, pp. 135-147, 2015.

[15] Wei Feng, Jing-Bin Wu, Xiaoli Li, Wei Zheng, Xin Zhou, Kai Xiao, Wenwu Cao, Bin Yang, Juan-Carlos Idrobo, Leonardo Basile, Weiquan Tian, PingHeng Tan, PingAn Hu, "Ultrahigh photo-responsivity and detectivity in multilayer InSe nanosheets phototransistors with broadband response", *J. Mater. Chem. C*, Vol. 3, pp. 7022, 2015.

[16] Xuhui Sun, Bin Yu, Garrick Ng, Thuc Dinh Nguyen, and M. Meyyappan, "III-VI compound semiconductor indium selenide (In_2Se_3) nanowires: Synthesis and Characterization", *Applied Physics Letters*, Vol. 89, pp. 1-3, 2006.

[17] Bin Yu, Sanghyun Ju, Xuhui Sun, Garrick Ng, Thuc Dinh Nguyen, and M. Meyyappan, David B. Janes, "Indium selenide nanowire phase-change memory", *Applied Physics Letters*, Vol. 91, pp. 1-2, 2007.

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