Chapter 1:

Introduction

1.1. Introduction

In recent years, the semiconductor manufacturing industries not only focus on the production of high-performance devices but also continuous efforts are being delivered to reduce the production expenses without harming the environment. Limitations in the optical and electronic behavior of the conventional semiconductors, Si and Ge, due to their indirect nature of optical transition, failed to fulfill the basic requirements for the fabrication of efficient optoelectronic devices. Consequently, evaluation of new compound semiconductors and also different multi-layered hetero-structure devices have been going on. As a replacement of Si and Ge, compound semiconductors such as GaAs [1, 2], Cu(In, Ge)Se_2 [3, 4], ZnO [5, 6], etc belonging to the different groups in the periodic table have attracted huge research attention owing to their interesting optoelectronic properties. The constituent elements of the III-V compound semiconductors, are not earth-abundant and as well as toxic. Furthermore, extremely complicated and expensive techniques namely metal-organic chemical vapor deposition (MOCVD), and molecular beam epitaxy (MBE) are typically employed for the fabrication of the III-V compound semiconductors restricting their application for day to day uses. Among all the II-VI materials utilized for optoelectronic application, ZnO is the most widely studied semiconductor material. Although ZnO thin film and nano-structured devices have been used extensively to fabricate UV sensors and laser, the high bandgap of ZnO (~3 eV) makes it incompatible for photovoltaic applications. As an alternative, now a day two-dimensional layered materials (WS_2 [7, 8], MoS_2, [9, 10] black phosphorus [11, 12], etc), organic semiconductor [13] and perovskite materials [14] are also applied to fabricate photodetectors and solar cells. Even though organic semiconductors can be synthesized using simple chemical processes, their open atmospheric stability is very poor. Organic semiconductor-based devices typically have a lifetime of only a few hours [15]. On the other hand, all the high-performance devices fabricated using perovskite materials contain lead (Pb) as a constituent element. The toxicity of Pb limits their large scale industrial production. It is well proven that the multi-layered heterostructures optoelectronic devices fabricated using variable bandgap semiconductors can considerably improve the efficiency and bandwidth compared to the single-layer structure [16-19]. The layers must be grown in such a way that at first, the incident radiation will fall on the highest bandgap material in the structure. However, the defect states originated due to the in-plane lattice mismatch and the structural anomaly between two successive layers significantly hindered the flow of photocarriers which in turn reduce the performance parameters. Last few years, the scientific communities predominantly concentrate on the development of novel, abundant and eco-friendly semiconducting materials with desirable optical properties.

1.2. Motivation

In view of the above, a compound direct bandgap semiconductor $ZnSnP_2$ nowadays is getting considerable research attention due to its unique optical and electronic properties. It can be a good alternative to overcome the typical issues which plagued the use of conventional semiconductors as mentioned in the previous section. $ZnSnP_2$ exists in two distinct phases viz, one is ordered chalcopyrite and the other one is disordered sphalerite. This transformation from ordered to disordered state takes place at 720 ºC where the cations (Zn & Sn) can occupy random positions at the lattice site i.e, the occupying probability of Zn and Sn atoms are same for a specific position [22-25]. However, the position of the anion (P) remains unaltered. Chalcopyrite $ZnSnP_2$ exhibits a bandgap of 1.70 eV whereas for the sphalerite phase it is 0.75 eV, as predicted by the Scanlon et al. from a density functional theory (DFT) calculation [20]. They have further shown that by preciously introducing the amount of disorder in the sample the value of the bandgap can be varied continuously within the above-mentioned range. It is worthwhile to mention that during the transformation from ordered to disordered phase the value of the in-plane lattice constant (a) remains unaffected. Since the value of the in-plane lattice constant (a) does not change with bandgap, thus in a multi-layered structure of $ZnSnP_2$ with varying bandgap, the contribution of defect states generated due to lattice mismatching could be neglected. Interestingly, an optical band gap of 1.70 eV, which is close to the optimum bandgap (~ 1.50 eV) at the Schockley-Quisser limit, has been reported [20, 24]. Moreover, other advantages such as ternary $ZnSnP_2$ is non-toxic, the constituent elements for the preparation of $ZnSnP_2$ are earth-abundant and inexpensive. The high absorption coefficient (> 10^4 cm^{-1}) above 1.60 eV, find $ZnSnP_2$ a potential alternative for optoelectronic device applications. It also has excellent lattice matching with GaAs substrates.

1.3. Objective

In this work, we would like to develop semiconductor devices based on $ZnSnP_2$ and investigate their suitability for applications in optoelectronic devices such as Photodetector and solar cells by using various optical, structural, electrical and morphological characterization techniques. We will perform the bulk growth of $ZnSnP_2$ using the pristine ingredients of Zn, Sn, and P by solution growth (SG) technique. The ordered chalcopyrite and disordered sphalerite structure can be obtained by changing the growth conditions. Thin films of $ZnSnP_2$ can be deposited on different substrates by Physical Vapour Deposition (PVD) technique. Information about the composition, crystallinity, grain size and generated a strain of both the bulk and the thin film will be extracted with the help of X-ray diffraction analysis, Scanning & Transmission electron microscopy. UV-Vis spectroscopy will be used for the estimation of the optical bandgap. Photoluminescence (PL) spectroscopy with temperature variation starting from room temperature down to a low temperature of 15 K reveals information about different optical transitions including defects in materials. The PL spectroscopy will be further used to study the free-to-bound transitions in $ZnSnP_2$. These results will be the first step towards realizing the novel functional optical device as a photodetector and solar cell using $ZnSnP_2$. Further, we will grow heterojunction solar cells using wide bandgap material as a window layer on top of $ZnSnP_2$ as a main absorbing layer.

1.4. Chapter Overview

Entire work has been arranged and represented in several chapters. An overview of all those chapters, in a nutshell, is given below.

Chapter 2: This chapter is containing different growth techniques, structural, optical and electrical properties of $ZnSnP_2$ ingot and thin film. Furthermore, the key parameters of the photodetector and solar cell are defined.

Chapter 3: This chapter contains an overview of various growth dynamics and thermodynamic processes usually involved during physical vapor deposition. Moreover, the basic principle of different characterization techniques like x-ray diffraction, x-ray reflectivity, scanning electron microscopy, transmission electron microscopy, optical absorption spectroscopy, photoluminescence measurement and details of several device-specific characterization techniques have also been included.

Chapter 4: This chapter represents the deposition of $ZnSnP_2$ thin film on multiple substrates by electron beam evaporation and its structural and optical characterization. It further contains detailed temperature-dependent photoluminescence measurements were performed for identifying the energy position of the inter-band defects.

Chapter 5: This chapter describes the photodetection behavior of the $ZnSnP_2$ epilayer grown on the p-Si substrate by thermal evaporation technique for photodetector application in the visible to near-infrared region of the electromagnetic spectra. The current-voltage curves are fitted using Lambert W function to obtain the barrier heights, and ideality factors under dark and also illuminating the device. It also contains the performance of the structure as a solar cell.

Chapter 6: This chapter represents the bias and power dependency of a metal-semiconductor-metal broadband photodetector, formed using the $ZnSnP_2$ epilayer. Two Schottky junctions were analyzed independently. Moreover, their performance in self-powered configuration and application of bias has also been tested.

References

[1] S. Moon, K. Kim, Y. Kim, J. Heo and J. Lee, Sci Rep, (2016) 6, 30107.

[2] M. Iiegems, B. Schwartz, L. A. Koszi and R. C. Miller, Appl. Phys. Lett, (1978), 33, 629.

[3] T. Negami, Y. Hashimoto and S. Nishiwaki, Sol. Energy Mater. Sol. Cells, (2001), 67, 331.

[4] P. Jackson, R. Wuerz, D. Hariskos, E. Lotter and W. Witte, Phys. Status Solid RRL, (2016), 8, 583.

[5] D. Kim, I. Yun and H. Kim, Curr. Appl. Phys., (2010), 10, S459.

[6] C. Lin, Y. Hsuan, H. Chen, J. Chen, C. Kung, R. Vittal and K. Ho, Energy Environ. Sci., (2011), 4, 3448.

[7] S. Li, Z. Chen and W. Zhang, Mater. Lett., (2012), 72, 22.

[8] C. Lan, C. Li, S. Wang, T. He, T. Jiao, D. Wei, W. Jing, L. Li and Y. Liu, ACS Appl. Mater. Interfaces. (2016), 8, 18375.

[9] M. Tsai, S. Su, J. Chang, D. Tsai, C. Chen, C. Wu, L. Chen and H. He, ACS Nano, (2014), 8, 8317.

[10] W. Wang, A. Klots, D. Prasai, Y. Yang, K. Bolotin and J. valentine, Nano Lett., (2015), 15, 7440.

[11] M. Huang, M. Wang, C. Chen, Z. Ma, X. Li, J. Han and Y. Wu, Adv. Mater., (2016), 28, 3481.

[12] M. Buscema, D. J. Groenendijk, G. A. Steele, H. S. J. V. D. Zant and A. C. Gomez, Nat. Commun., (2014), 5, 4651.

[13] C. K. Renshaw, X. Xu and S. R. Forrest, Organic Electronics, (2010), 11, 175.

[14] R. Dong, Y. Fang, J. Chae, J. Dai, Z. Xiao, Q. Dong, Y. Yuan, A. Centrone, X. C. Zeng and J. Huang, Adv. Mater. (2015), 27, 1912.

[15] H. Lee, S. Nam, H. Kwon, S. Lee, J. Kim, W. Lee, C. Lee, J. Jeong, H. Kim, T. J. Shin and Y. Kim, J. Mater. Chem. C, (2015), 3, 1513.

[16] X. Li, W. Chen, S. Zhang, Z. Wu, P. Wang, Z. Xu, H. Chen, W. Yin, H. Zhong and S. Lin, Neno Energy, (2015), 16, 310.

[17] G. Guerguerin, F. Elhordoy, C. J. Pereyra, R. E. Marotti, F. Martin, D. Leinen, J. R. Ramos-Barrado and E. A. Dalchiele, Nanotechnology, (2011), 22, 505401.

[18] H. Qiao, J. Yuan, Z. Xu, C. Chen, S. Lin, Y. Wang, J. Song, Y. Liu, Q. Khan, H. Y. Hoh, C. Pan, S. Li and Q. Bao, ACS Nano, (2015), 9, 1886.

[19] H. Pettersson, J. Tragardh, A. I. Persson, L. Landin, D. Hessman and L. Samuelson, Nano Lett., (2006), 6, 229.

[20] D. O. Scanlon and A. Walsh, Appl. Phys. Lett. (2012), 100, 251911.

[21] G. A. Seryogin, S. A. Nikishin and H. Temkin, Appl. Phys. Lett., (1999), 74, 2128.

[22] A. M. Mintairov, N. A. Sadchikov, T. sauncy and M. Holtz, Phys. Rev. B, (1999), 59, 197.

[23] S. Sahin, Y. O. Ciftci, K. Colakoglu and N. Korozlu, J. Alloys Compd., (2012), 529, 1.

[24] P. St-Jean, G.A. Seryogin and S. Francoeur, Appl. Phys. Lett., (2009), 96, 231913.