CHAPTER 1: INTRODUCTION AND REVIEW OF LITERATURE

1.1. General Introduction to Compound Semiconductors

A compound semiconductor is a semiconductor composed of elements from two or more different groups of the periodic table. Compound semiconductors which consist of various elements have widely ranging physical properties. They play an important role in the development of science and technology and constitutes today's basic building blocks of emitters and receivers in cellular, satellite and fibreglass communication. Semiconductors have attracted much attention in recent years to their great potential for technological importance and have aroused considerably scientific interest. In the early days Silicon (Si) and Germanium (Ge) were the most important semiconductors which were widely used for developments of various kinds of applications. But the limitations of these semiconductors in high speed devices and devices requiring emission and absorption of light led to the development of other semiconductors like the III-V and the II-VI compound semiconductors since last three decades. The III-V and II-VI compound semiconductors are able to determine the wavelengths of light which it can absorb or emit and because of this property they are widely used in LEDs and construction of lasers with a wide range of visible and infrared portion of the spectrum. They have also been successfully used as sensors, detectors, modulators and in many other scientific applications. Among the III-V and II-VI compound semiconductors, Gallium phosphide (GaP), Gallium Arsenide (GaAs), Indium Arsenide (InAs), Indium Phosphide (InP), Zinc Sulfide (ZnS), Cadmium Telluride (CdTe) and Zinc Selenide (ZnSe) are extensively studied because of their useful physical, electro-optical and other distinctive properties. They are widely used in construction of infrared detectors and diode lasers [1]. They have been utilized in the electronics and telecommunications industries, in the military science and device applications such as top junction solar cells and multi junction solar cell system [2-6].

It has therefore become important to understand the electronic structure, elastic properties and phase transition under induced pressure. The energy band gap is the most important characteristics of semiconductors which distinguish it from metals and insulators. The electronic structure calculation will give the information regarding energy band diagram, total density of states, and partial density of states of the constituent atoms, hence enabling us to understand the contributions of the atomic orbital in the band diagram. Thus one can have the opportunity theoretically to engineer the structure of the material with desire band gap which is an extremely important parameter in technical point of view. It helps in determining the wavelength of light which it can absorb or emit and hence is widely used in many optical and optoelectronic devices. Thus understanding of the basic electronic properties of semiconductors has become important in order to appreciate how semiconductors can be used to create devices.

Understanding of elastic properties of materials is also important as elasticity describes the response of a compound to a very small loading which causes reversible deformation. Elastic constant is the fundamental material parameters which characterises the elastic behaviour of a solid. It gives us important information about the nature of force operation in solids and provides a link between the mechanical and dynamical behaviour of solids. It also provides important information about anisotropic features and structural stability of a material.

Generally compound semiconductors (binary compound) crystallises both in zinc blende (ZB) and rock salt (RS) structure. Therefore, it is interesting to study the structural phase transformation under induced pressure. In view of this, the investigations on band gap, elastic constants under induced pressure and their variation at different pressure can be done and it will provide insight properties under extreme induced pressure.

In recent years, the advancement of compound semiconductors in technological applications has resulted in search for new semiconductor materials and the improvement of existing materials has become an important field of study in materials science. The potential of compound semiconductor to be doped with other atoms that alter its electronic properties in a controllable manner is its important characteristic. The knowledge of the variation of electronic structure with doping for the bulk material is essential to improve the thin film study which is a potential material for solar cell studies. Thus by performing appropriate doping, materials can be engineered with desirable basic properties such as the electronic properties.

1.2. Review of literature

In the early 1960s, Jameson performed the structural phase transition studies in Si and Ge [7] as well as other III-V compound semiconductors [8]. A fist principle electronic structure calculation on III-V and II-VI compound semiconductors was done in 1981 by Wang and Kleein [9]. The phase transition of III-V compound semiconductors was studied by Chelikowsky in 1987 [10]. In 1990 the pressure dependence of the electronic properties of cubic III-V Indium compounds was studied by Van Camp and his co-workers [11]. A. Mujica and R. J. Needs [12] in 1996 found that the simple cubic phase of GaP should be stable between 14.7 GPa and 20.3 GPa. In 2008, A.R. Rashid et al. [13] have studied the structural and electronic properties of GaP and compared the lattice parameters, bulk modulus, and pressure derivative of the bulk modulus with earlier data. The High-pressure properties of the zinc blende structure have been determined by Raman scattering, ultrasonic measurements, fundamental absorption, and refractive-index measurements [14-16]. Froyen and Cohen [17] first reported the structural phase of GaAs in 1983. The structural transformation in GaAs was also investigated by Besson et al [18] and Weir et al [19] using the single-crystal x-ray absorption spectroscopy and elastic neutron scattering. Studies on electronic structures, high-

pressure properties have been reported by various groups [10,20-22]. An ab initio simulation of high pressure phases of GaAs was done by Durandurdu and Drabold in 2002 [21]. The pressure induced phase transition to metallic state of InAs was first reported by Minomura and Drickamer [23] at 8.46 GPa pressure from high pressure resistivity measurements. Pitt and Vyas [4] in 1973 reported the phase transition of InAs from the ZB to RS through resistivity measurements. In 2014, Wang et al. [5] also studied the electronic transport properties of InAs using the non-equilibrium Green's function combined with density functional theory. S. Massidda and his group studied the structural and electronic properties of InAs and InP in 1990 [24]. In 2010, Lukacevic and his co-workers performed a density functional theory study of the phase stability of high pressure phases in InAs and InP [25]. The semiconductor-to-metallic phase transition from ZB to RS structure of InP is found to occur between 8.5 and 13.3 GPa pressure [8, 23, 26,27]. The phase stability of group III phosphide has been studied by Arbouche et al. [28] and reported the phase transition of InP occurring at about 7.35 GPa pressure. Branicio et al. [29] also investigated phase transition of InP at around 10.2 GPa pressure.

The first structural phase transformation of the II-VI compound semiconductors was studied experimentally by Edwards and Drickamer in 1960 [30]. Marino and Warekois in 1963 studied the high pressure phases of II-VI compound semiconductors [31]. Studies on the structures of the high pressure phases of II-VI compound semiconductors were also done in 1963 by Rooymans [32] and Owen and his group [33]. Thermoelectric properties and phase transitions of II-VI compound semiconductors at high pressure was studied by Shchennikov and Ovsyannikov in 2007 [34]. Richard M. Martin in 1970 studied the elastic properties of ZnS [35]. A quasi-particle band structure study of II-VI compound semiconductors was done by Zakharov and his co-workers in 1994 [36]. In 1990 E. Ves and his group studied the effect of pressure on the energy of the direct optical absorption edge and phase transition of cubic ZnS [37]. Desgreniers and his group in 2000 studied the pressure induced structural changes in ZnS [38]. In 2009, M.

Cardona and his group studied the electronic, vibrational and thermodynamic properties of ZnS [39] Energy dispersive X-ray diffraction technique has been used to perform high pressure studies of ZnS by Pan et al. [40]. In 2013, Jun and his co-workers performed XAFS investigation on the zinc belnde structure of ZnS [41]. Lee and Chang in 1995 studied the structural properties of ZnS and ZnSe [42]. In 1993, Mc Mahon and his group found out that with increasing pressure, the ZB structure of CdTe underwent a transition to cinnabar structure which was stable for only a short pressure interval and later changed to RS structure on further increasing pressure [43]. Earlier studies also confirmed the phase transition of CdTe from the ZB to RS structure at 3.8 GPa pressure [44]. In 2000, Kanoun and his co-workers investigated the structural, elastic and electronic properties of cadmium telluride using the molecular dynamic simulation [45]. The structural stability of cadmium chalcogenides under high pressure was studied by Benkhettou and his group in 2006 [46]. In 1998, R. J. Nelmes and Mc Mohan using the X-ray diffraction method confirmed the phase transformation from ZB to RS phase of ZnSe occurring at 13.5 GPa pressure [47]. The ZB to RS phase transition of ZnSe was also found to occur at 18 GPa pressure by Varshney and his co-workers from Slater-Kirkwood variational method [48]. In 2002, M. Jin, Q. Cui, E. Mukhar and D. Ding monitored the structural phase transformation from ZB to RS phase using a second harmonic generation (SHG) measurement [49]. The structural phase transformation of ZnSe under high pressure was also studied by Qteish and Munoz in 2000 using the first principle pseudopotential method [50]. In 2003 Gangadharan and his co-workers studied the structural phase transformation of ZnS and ZnSe compound semiconductors using TB-LMTO method [51]. Bilal and his co-workers in 2014 performed a first principle studies of the structural, elastic electronic and optical properties of Zn-chalcogenides under pressure [52].

1.3 Motivations

The prediction and synthesis of III-V and II-VI compound semiconductors has already been successfully performed by many researchers but still there is great need to exhaustively determine the structural properties, phase transition, elastic properties and electronic structure of these materials under induced pressures. The study of these properties under induced pressure will enable us to understand the behaviour of the materials under extreme conditions of pressures. This kind of information will helps us to understand thermal expansion, atomic bonding and their structural properties at higher pressures. But study of these properties experimentally under high pressure is very difficult. Therefore we can generate the structure of the materials computationally and predict the properties of the desired materials using well established solid state theories. In this thesis we have therefore calculated the structural properties, phase transition, elastic properties and electronic structure of III-V (GaP, GaAs, InP, InAs) and II-VI (ZnS, CdTe, ZnSe) compound semiconductors computationally based on the Density Functional Theory (DFT).

1.4. Research Objectives

The objectives of the thesis work are:

1. To study the structural properties and electronic properties of binary compound semiconductors. This includes the structural studies, Density of states (DOS) and energy band diagram.
2. Investigating the elastic properties of the compound semiconductors such as Elastic constants, Poisson's ratio, Young modulus, and Debye's temperature.
3. To study phase transition and thus study the electronic & elastic properties under induced pressure.
4. To study the effect of doping on the compound semiconductors and thus study its structural phase transformation.