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Pressure induced phase transformation and electronic properties of AlAs

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ABSTRACT

We have performed the first-principle study to analyze the structural and electronic properties of aluminum arsenide under the application of pressure. The computations have been carried out using the ground state total energy calculation approach of the system. The first-principle approach has been used to compute the stability of various phases of AlAs, like original zinc blende (B3), intermediate NiAs (B8), NaCl (B1) and CsCl (B2) type as a function of pressure. The study observes a B3–B8, B3–B1 and B3–B2 transitions at 6.99 GPa, 8.18 GPa and 73.43 GPa. The computed phase transition pressures, lattice parameters, bulk modulus, and energy gaps are in good agreement with their experimental as well as theoretical counterparts. Band structure and density of states analysis have also been performed and results have been discussed in detail.

1. Introduction

The operating characteristics of the electronic and optoelectronic devices not only talks about the materials engineering at a practical level but they are also required for better understanding of the properties of materials and associated fundamental science behind them. Theoretical investigations as well as experimental researches are therefore of vital interest to all those working in this area of research. The electronic and structural properties of the complex systems have attracted considerable interest in both fundamental and applied physics. A large amount of work has been focused on theoretical understanding of a variety of compound semiconductors and their related properties. These compounds play an important role in microelectronics, for example, in the development of light emitting diodes and high frequency low noise devices for mobile telephones and advanced materials for spintronics [1–13]. The most remarkable aspect of tetrahedrally coordinated structures is their low density. The openness of these semiconductors is highlighted by the fact that for the homopolar members, the ratio of the volume of touching atom spheres to that of the unit cell is 0.34 which is less than half for the close-packed element structure (0.74). It is not surprising, because under pressure tetrahedrally coordinated semiconductors can be transformed to the structure with higher density [14]. Froyen and Cohen [15] and Martin [16] reported first on the phase transition in AlAs which was based on ab initio pseudopotential calculation and suggested that the high pressure structure could be either rocksalt (B1) or NiAs (B8). Weinstein et al. [17] reported the pressure induced structural transition by microscopic examination at 12.3 GPa on loading but the structure was unknown. Greene et al. [18] have performed an EDXD study on AlAs up to 46 GPa and found that AlAs transforms to NiAs structure. This was the first experimental observation of III–V compound transforming into the NiAs structure. The equilibrium transformation pressure was found to be 7 ± 5 GPa, averaging the large hysteresis. Onodera et al. [19] have reported B3–B8 phase transition in AlAs at 14.2 GPa by high pressure X-ray diffraction and electrical resistivity measurements.

Many methods of calculations have been used to confirm these results. One of them is to relate the high pressure behavior of these semiconductors to the type of chemical bonding between the nearest atoms by examining the electronic charge density evolution, which has been correlated to the empirical qualitative concept as ionicity [20,21]. The first-principles electronic structure calculations have allowed detailed studies of the energetics of the group IVA elements and the groups IIIA–VA and IIB–VIA compounds under high pressures [22]. Theoretically, III-arsenide

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compounds have been studied by employing different approaches; from phenomenological methods such as k.p. theory or empirical pseudo-potentials methods [23] to atomistic ab initio methods, such as the full-potential linear augmented plane wave (FP-LAPW) method within local density approximation (LDA) or generalized gradient approximation (GGA) and pseudopotential methods [24]. Recently, Wang et al. [25] have reported the first-principle study of the phase transition of AlAs in three crystallographic structures, *i.e.*, B3 (zinc blende), B8 (nickel arsenide) and B1 (rock salt) at high pressures using the full-potential linearized muffin-tin orbital (FP-LMTO) scheme within the generalized gradient approximation (GGA) correction in the framework of the density functional theory (DFT) and based on the condition of equal enthalpies.

Singh et al. [26–28] have successfully applied three-body-potential approach to describe the high pressure phase transition and other properties of Al based compound semiconductors. The effect of pressure on the structural stability of some III–V and IV–VI compound semiconductor based alloys has also been investigated successfully with three-body-potential (TBP) approach [29,30].

Cai and Chen [31] have reported a possible mechanism for B3–B8 transition, characterized by the space group of $C222_1$, and observed that there are relatively small values of activation enthalpy and strain anisotropy for B3–B8 transition of *AlAs* in comparison to the B3–B1 case. The calculated transition pressure from B3 to B8 ranges from 6.1 GPa [32] to 9.15 GPa [31], and B3 to B1 phase, from 7.4 GPa [32] to 11.88 GPa [31]. Not much information is available on B3–B2 transition in this compound. Looking to the technological importance of this material and success of first-principle methods, we thought it pertinent to analyze the transitions due to the application of pressure and thereby its material characteristics. Particularly three transitions B3–B8, B3–B1 and B3–B2 have been studied. Further the present work also computes lattice constant, bulk modulus and its pressure derivative, band structure and density of state in different phases of AlAs. These calculations provide a one stop shop for fundamental understanding of the structural and electronic properties of the aluminum arsenide.

2. Computational details

The present computations of the structural and electronic properties of aluminum arsenide have been performed using ATK tool [33]. Atomistix ToolKit (ATK) is a further development of TranSIESTA-C [34,35] which, in turn, is based on the technology, models and algorithms developed in the academic code TranSIESTA and, in part, McDCal [36], employing localized basis sets as developed in SIESTA [37]. The density functional theory (DFT) is, in principle a very good theory to predict ground state properties (e.g. total energy, atomic structure, Bulk modulus, etc.). However, DFT is not a theory to address efficiently the excited state properties and hence DFT typically underestimates the band gap of semiconductors and insulators by 20–30%. The ATK has been proved to be a very efficient tool in predicting the transport properties [38–40] of variety of bulk as well as nanostructured materials, where the electronic properties have also been discussed in detail. The norm-conserving pseudopotential is used in density function theory for total energy calculation of polyatomic systems. The electronic configuration of AlAs is Al: Ne $3s^2 3p^1$, and As: Ar $3d^{10} 4s^2 4p^3$. In the calculation of pseudopotential, the inner-cell configurations for Al ($1s^2 2s^2 2p^6$), and As ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$) have been distinguished from the valence electrons of Al ($3s^2 3p^1$) and As ($4s^2 4p^3$) shells, respectively. The Perdew Zunger (PZ) type parameterized local density approximation (LDA) exchange correlation functional (LDA-PZ) [41], Perdew, Burke and Ernzerhof (PBE) [42] type parameterized generalized gradient approximation (GGA-PBE) and Zhang and Yang revised PBE (rev PBE) [43,44] type GGA have been used for the present computations. In self-consistent manner, the calculation is performed using steepest descent geometric optimization technique with Pulay algorithm [45] for iteration mixing. The mesh cut-off is taken as 150Ryd with a k-mesh of $5 \times 5 \times 5$. LDA-PZ type potential computes total energy much lower than that of GGA-revPBE and GGA-PBE approaches. The total energy for original B3 type AlAs using LDA-PZ potential is −469.39 eV and with GGA rev PBE potential −324.49 eV, which indicates that LDA-PZ potential, is quite good for the calculation of energies of AlAs in different structural phases like B3, B1, B2 and B8. To get better understanding of fundamental physics associated with different phases of AlAs, the Fermi energies, binding energies and band energies have also been computed using LDA-PZ potential and given in Table 3.

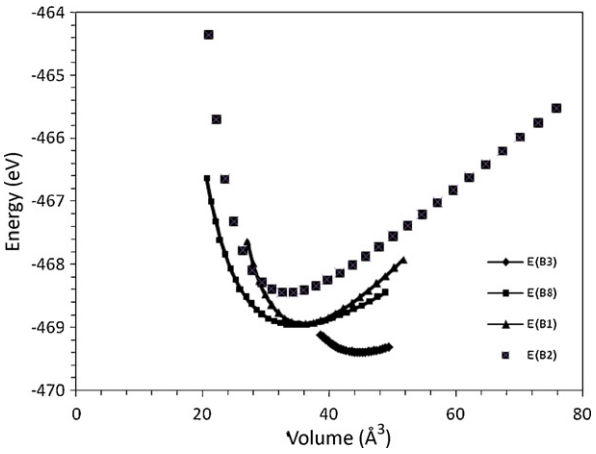

Fig. 1. Energy vs volume curve for B3, B8, B1 and B2 type phases of AlAs.

Classical understanding on the phase stability of solids suggests that as the pressure is applied, a particular phase of the solid becomes unstable and causes a change in the density and the volume, which in turn leads to the overlapping of the electron shells (charge transfer mechanism) and thus the phase transition takes place. Under the application of pressure, the B3 type III–V semiconductors are expected to transform into the NaCl (B1) structure and there is possibility of some intermediate NiAs (B8) type phase and further increase in pressure may cause stability of CsCl (B2) type structure. The stability of the phase of the solid can be defined in terms of its Gibbs free energy ($G = U + PV - TS$). This free energy at $T = 0$ K corresponds to the cohesive energy due to the mutual interaction of the ions. S is the vibrational entropy at absolute temperature T and V is the volume of the unit cell at pressure P.

3. Results and discussions

3.1. Energy vs volume (E–V) curve, lattice parameter and bulk modulus

To test the stability of various phases of AlAs, like B3, B8, B1 and B2 under the ambient condition as well as under compression, the calculated total energies have been plotted as a function of volume in Fig. 1. In ambient condition B3 structure has been found to be with minimum energy and same under compression first stabilizes in B8 type, then B1 and finally to the CsCl (B2) type with the lowest energy. The positive lattice energy difference of the two competitive structures at zero pressure very well explains the relative stability criterion given by Sangster et al. [46]. The lattice parameter corresponding to minima of the *E–V* curves corresponds to zero pressure, termed as the equilibrium or theoretical lattice constant.