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Study of the high pressure and temperature response of silicon, germanium and gallium arsenide electronic energy bands

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In this study we investigate the different temperature electronic energy band structure responses of silicon, germanium and gallium arsenide at various applied hydrostatic pressures within a range that does not exceed their structural phase transition pressure. The pressure coefficients for each material have been determined. An atomistic insight was presented into the question of how much of the electronic band structure deformation, due to hydrostatic pressure, originates from the valence or the conduction bands. It was observed that the rate of increase in energy of the conduction band minimum with an increase in pressure is greater than that of the valence band maximum for Ge and GaAs, while it is less than that of the valence band maximum for silicon. The origin of this negative value of the first order pressure coefficient of silicon was explained in terms of *p* and *d* conduction band orbitals coupling at the X_c high symmetry point of the Brillouin zone, hence exhibiting quantum level repulsion between them, thus forcing the conduction band edge downwards in energy relative to the maximum of the valence band at Γ_c. The hydrostatic volume deformation potential, a_g is found to be constant for Ge and GaAs. Our results agree with the "empirical rules of pressure coefficients" for inter-band electronic transitions of types $\Gamma_v \rightarrow \Gamma_c$ in gallium arsenide, $\Gamma_v \rightarrow L_c$ in germanium and $\Gamma_v \rightarrow X_c$ in silicon.

Key words: Hydrostatic deformation potential; pressure coefficients; inter-band electronic transitions; orbital coupling; quantum level repulsion.

INTRODUCTION

The optical and electronic properties of semiconductors are fundamentally dependent on their electronic band structures. Modification of the electronic band structure of semiconductors using external pressure leads to optoelectronic properties that can be tuned for various applications such as quantum dot lasers, bioengineering, high-density memory, etc. (Ouyang et al., 2009). The most commonly used semiconductors in device fabrication are silicon, germanium, and gallium arsenide. The implementation of high-pressure electronic technology in Si, Ge, and GaAs- based devices requires a thorough understanding of the pressure responses of

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the energy band structures of the constituent semiconductor materials. Device integrity requires this understanding to foresee and avoid problems that may be encountered during the operation of the devices. Fabricators can then provide accurate specifications for the use of the devices. Silicon and germanium have the tetrahedral coordinated diamond crystal structure with each atom being at the center of a tetrahedron having four neighboring atoms (coordination number) at each corner of the tetrahedron. Their lattice parameters are 0.543 and 0.566 nm respectively (Streetman, 1990; Virginia-Semiconductor, 2002). Gallium arsenide is a III–V semiconductor with the zinc-blende structure having four nearest neighbor bonds to each atom separated by the tetrahedral angle of 109.47º (Feenstra and Stroscio, 1993). These four covalent bonds are provided by eight outer shell electrons, five of which are from As atoms and the other three from the Ga atoms. Unlike in silicon and germanium crystals where the bonds are centered at the midpoint between the ion cores, in GaAs the bonds are centered slightly closer to the As atoms (Feenstra and Stroscio, 1993). The lattice parameter for GaAs is 0.565 nm (Feenstra and Stroscio, 1993).

The value of the energy band gap for Si at 0 K and 300 K is 1.17 and 1.12 eV respectively (Levinshtein et al., 2001). It is an indirect band gap semiconductor (Levinshtein et al., 2001); therefore, an inter-band electronic transition can only conserve momentum with the absorption or creation of a quantum particle such as a phonon. For Ge, the band gap values at Ge at 0 K and 300 K is 0.74 and 0.70 eV respectively (Levinshtein et al., 2001). It is also an indirect band gap semiconductor, but the difference between its indirect and closest direct band gap is only 0.14 eV (Levinshtein et al., 2001). The band gap values for GaAs at 0 K and 300 K is 1.52 and 1.42 eV respectively (Bhojani et al., 2016). Unlike Si and Ge, GaAs is a direct band gap semiconductor (Bhojani et al., 2016).

All matter should ultimately transition into a metallic phase at sufficiently high pressure due to the electron delocalization induced by electron orbitals being forced to overlap. Thermodynamically, the most energetically stable structural phase has the lowest value of the Gibbs free energy *G*,

$$G = E + PV - TS \tag{1}$$

for a system of volume, *V* with an entropy, *S* at temperature, *T* and *P* is the pressure. A pressure induced phase transformation takes place when an increase in pressure causes a different structural phase of the system to have a lower Gibbs free energy, hence making it more energetically favorable. When silicon and germanium are compressed, they undergo a similar sequence of structural transitions because of their chemical similarity. Upon compression to above 70 kbar, Ge undergoes a sluggish transition into a tetragonal being complete at 120 kbar (Holzapfel, 1984; Habanyama et al., 2022; Habanyama and Samukonga, 2021).

Studies have shown that a similar transition in Si occurs in the pressure range 90 to 160 kbar (Holzapfel, 1984). Yu et al. (2006), found that the phase transition pressure for GaAs was around 163 kbar, using first principle calculations. In the current study we investigate the energy band structure responses of Si, Ge and GaAs, to applied high pressure within a range that does not exceed the transition pressure at which the materials would undergo a lattice structural phase change.

Paul (1998) introduced the so called, "empirical rules of pressure coefficients" which apply to semiconductors having crystal structures of the diamond and zinc-blende types. In a modified form, the rule states that for a fixed inter-band transition (excitation across the band gap), the pressure coefficient is almost constant for tetrahedral coordinated semiconductors and the dependence is mainly on the type of transition. For a transition type, $\Gamma_v \to \Gamma_c$ the pressure coefficient is around 10 meV/kbar, for a transition, $\Gamma_v \to L_c$ it is of the order of 5 meV/kbar and for a transition, $\Gamma_v \to X_c$ it is between -1 to -2 meV/kbar. Here, Γ, L and X represent high symmetry points in the first Brillouin zone while the subscripts 'v' and 'c' stand for the top edge of the valance band and the bottom edge of the conduction band, respectively. The validity of this ''empirical rule'' is tested in this work, for the materials studied. We also determine the comparative amount of the hydrostatic pressure induced deformation in the electronic band structure that originates from the valence or conduction bands. In heterostructures, quantum confinement of electrons and holes cannot be properly assessed without this information (Wei and Zunger, 1999).

Some quantum mechanical concepts have been used to explain our results, including known results from works executed using crystal symmetry based analysis. However, the quantum mechanical concepts of symmetry of Brillouin zones and the change of zonal structure have not been discussed in this work; these concepts are competently discussed by Bir and Pikus (1974).

Computational methods

Our computation is based on total energy minimization using a plane-wave basis in the density functional theory (DFT) formalism (Kohn and Sham, 1965; Hohenberg and Kohn, 1964), which was applied self-consistently to the valence electrons. Crystal structures and pseudopotentials of the constituent elements were the only inputs in our calculations. Structural optimization procedures and the determination of electronic properties were simulated using the Quantum Espresso software (Giannozzi et al., 2009). The interaction between electrons and the ion cores were calculated using the Andrea Dal Corso-type ultra-soft pseudo-potentials (USPP) for Si, Ge, Ga and As, which have the valence electronic configurations, $3s^23p^2$, $3d^{10}4s^24p^2$, $3d^{10}4s^24p^1$ and $3d^{10}4s^24p^3$, respectively. The correlation between electrons and their exchange interaction were modelled using the Generalized Gradient Approximation (GGA-PBE) (Perdew et al., 1996). A 16×16×16 Monkhorst Pack (Monkhorst and Pack, 1976) ***k***-point mesh sampling was used in the Brillouin zone with a 70 Ry plane-wave cut-off energy. The convergence of the self-consistent field (SCF) threshold was within 10^{-3} eV/atom.

We initially made the assumption that the crystal structures were being studied at absolute zero of temperature. The pressure in this ground state can be determined by varying,

$$P = -\frac{\partial E}{\partial V} \qquad (2)$$

the volume of the unit-cell and computing the rate of change of the internal energy, following Murnaghan's equation of state (Murnaghan, 1944),

$$p = \left[B_0 /(dB_0 / dp)\right]\left[(a_0 / a)^{3dB_0 / dp} - 1\right] \qquad (3)$$

is used to convert the pressure dependence to a relative change in the lattice constant a, where B_0 is the bulk modulus while a_0 is the equilibrium lattice constant at zero hydrostatic pressure. It was then proceed to determine how the band gap energy, E_g varies with increasing pressure. This is done by first looking at how the band gap energy varies with the logarithm of the unit-cell volume, V. A common definition of the hydrostatic volume deformation potential, a_g is (Bouhafs et al., 2000; Dridi et al., 2002).

$$a_g = \frac{dE_g}{d \ln V} \qquad (4)$$

This is in fact a relative deformation potential between the conduction and valance bands but the absolute deformation potential at an energy state E_i is,

$$a_i = \frac{dE_i}{d \ln V} \qquad (5)$$

It is the dependence on pressure of the energy gap that is usually measured experimentally as opposed to the values of the deformation potential a_g. However, the hydrostatic pressure coefficient, d*Eg*/d*P* is related to a_g by (Bouhafs et al., 2000; Dridi et al., 2002),

$$a_g = -B\frac{dE_g}{dP} \qquad (6)$$

Where B is the bulk modulus. Since the hydrostatic pressure coefficient, α = d*Eg*/d*P* (in eV/kbar) is a first-order derivative, we can extend this definition to a second-order hydrostatic pressure coefficient, $\beta = d^2Eg/dP^2$ (eV/kbar^2) such that the band gap energy, $E_g(0)$ with no applied hydrostatic pressure is related to that at any pressure, $E_g(P)$ through the quadratic pressure function (Bouhafs et al., 2000; Dridi et al., 2002),

$$E_g(P) = E_g(0) + \alpha P + \beta P^2 \qquad (7)$$

Finally, we look at the variation of the band gap energy with respect to both pressure and temperature changes. The relationship was then used (Rodríguez, et al., 2009))

$$E_g(P,T) = E_g(0,0) + \alpha P - \frac{kT^2}{T + c} \qquad (8)$$

Where T is the temperature, while k (eV/K) and c (K) are temperature coefficients. We can include temperature dependence at T = 0 K in Equation (7) as follows,

$$E_g(P,0) = E_g(0,0) + \alpha P + \beta P^2 \qquad (9)$$

Where, $E_g(0,0)$ is the energy band gap in eV at P = 0 kbar and T = 0 K. We combine Equations (8) and (9) to get,

$$E_g(P,T) = E_g(0,0) + \alpha P + \beta P^2 - \frac{kT^2}{T + c} \qquad (10)$$

It is well known that the band gaps with no pressure applied at absolute zero of temperature, that is $E_g(0,0)$, of the semiconductors Si, Ge and GaAs are underestimated by the Generalized Gradient Approximation. This error was corrected in our calculation by introducing a constant off-set in each DFT calculation, similar to the addition of a Hubbard *U* factor in the GGA+*U* method (Dudarev et al., 2008; Liechtenstein et al., 1995). It should be pointed out that the addition of a constant factor to the initial band gap energy, $E_g(0,0)$ does not affect the values of the energy derivatives, $\alpha = dEg/dP$ and $\beta = d^2 Eg/dP^2$. Our presented approach does not study the symmetry of Brillouin zones. Symmetry methods in similar work were used by by Bir and Pikus (1974).

RESULTS

Lattice structures of silicon, germanium and gallium arsenide were simulated, and the visualization of various aspects of the structure was done using the Xcrysden software package (Kokalj, 2003), as shown for GaAs in Figure 1. Electronic band structures were simulated for silicon, germanium and gallium arsenide at various hydrostatic pressures below their respective structural phase transition pressures. Figures 2a and b show the band structures simulated for Si and Ge.

It is seen in Figure 2a that the indirect band gap of Si is along the path between the high-symmetry points Γ and X of the Brillouin zone. The valence band maximum is at Γ and although the conduction band minimum is not exactly at X, the inter-band (band gap) transition is along the ***k***-path from Γ to X. We will therefore classify silicon as having an inter-band electronic transition of the type, $\Gamma_v \rightarrow X_c$. Figure 2b shows the valence-band maximum at Γ and the conduction band minimum at L signifying a $\Gamma_v \rightarrow L_c$ inter-band transition type across the indirect band gap of Ge. Figures 3a and b show the band structures simulated for GaAs at pressures of 0.01 and 105.02 kbar respectively.

Figure 3a shows that the valence-band maximum and conduction band minimum both occurs at Γ, which is indicative of a $\Gamma_v \rightarrow \Gamma_c$ inter-band transition type. It is observed in Figure 3b that the valence-band maximum

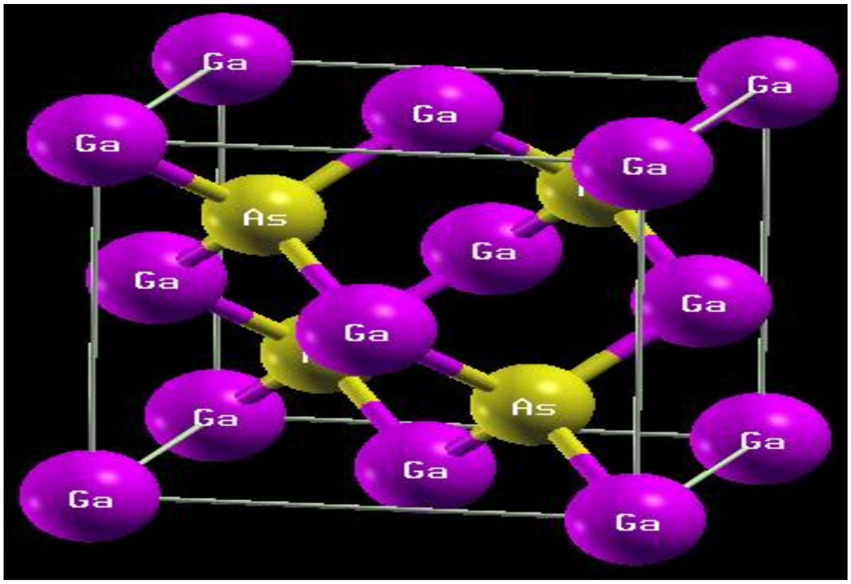
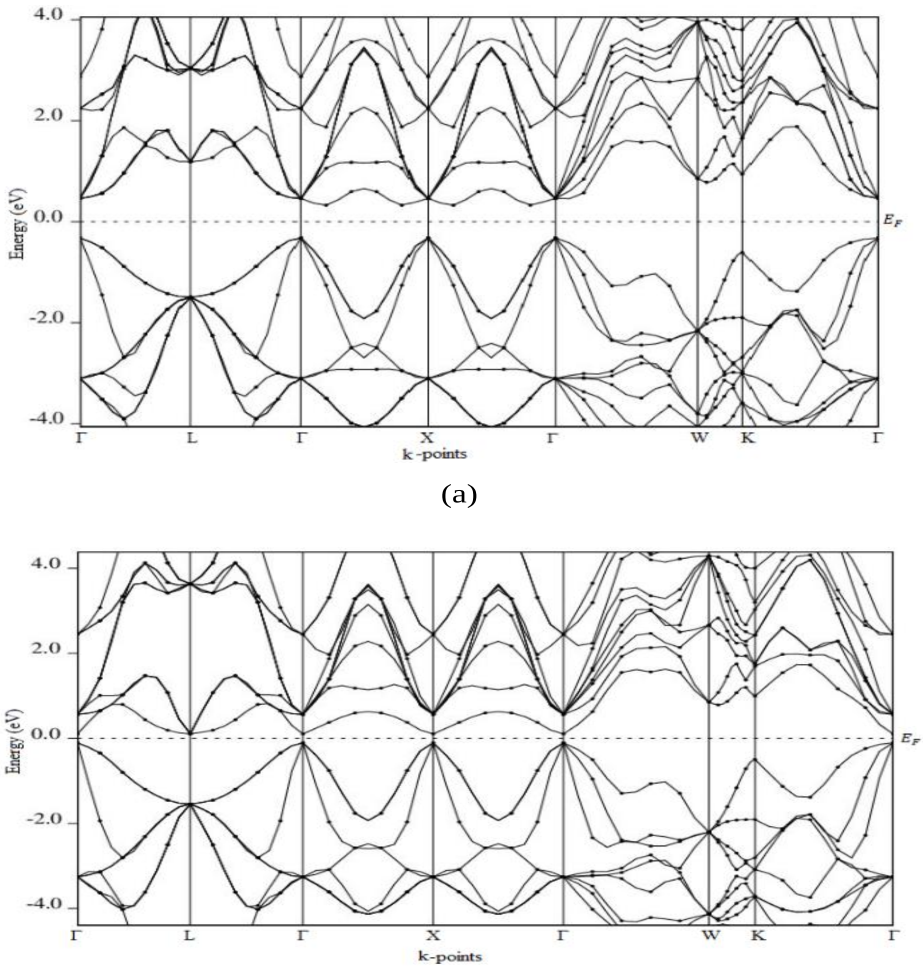


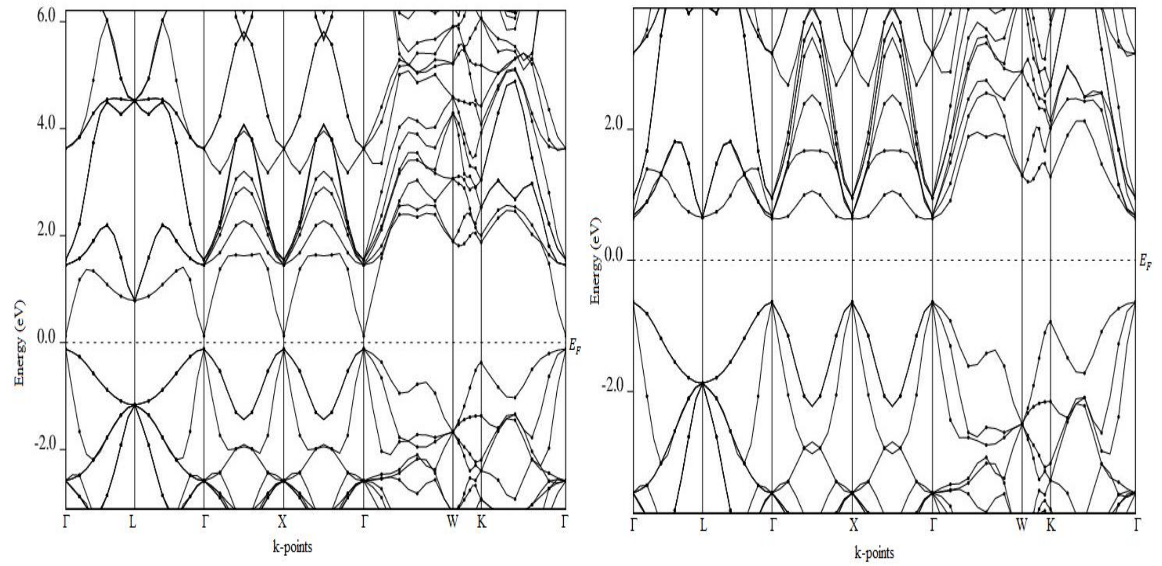
Figure 1. Simulation of the zinc blende crystal structure of GaAs.



(a)

(b)

Figure 2. a. Indirect electronic band structure for Si in the vicinity of the energy gap; **b.** Indirect Ge band gap structure throughout the first Brillouin zone.



(a) (b)

Figure 3. a. Direct electronic band structure for GaAs throughout the first Brillouin zone at 0.01 kbar; b. GaAs band structure at 105.02 kbar.

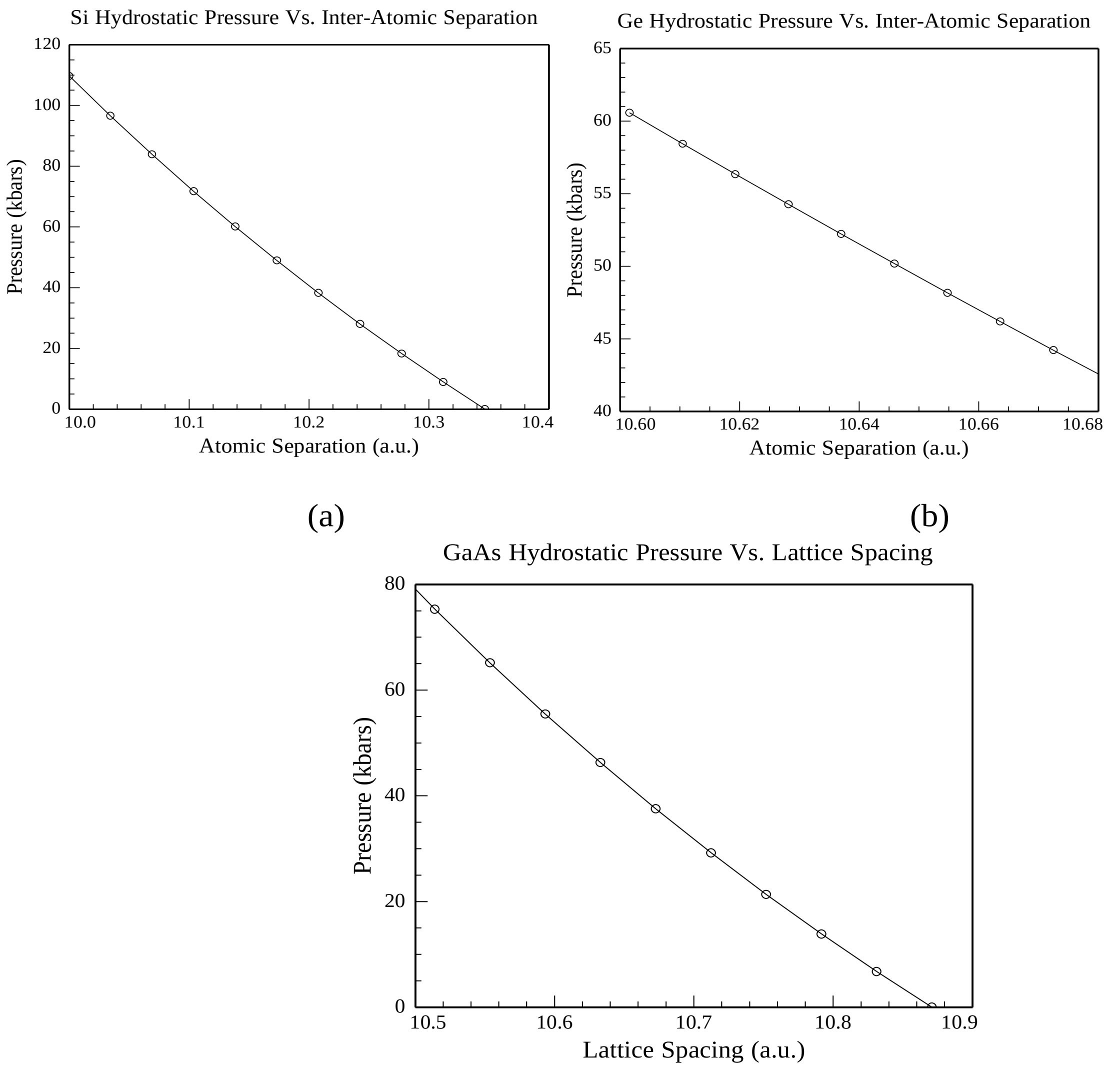
remains at the center of the Brillouin zone, that is, the Γ point, and maintains its curvature as pressure increases. However, as the pressure increases, the bottom of the conduction band, at the Γ point, significantly opens out in curvature and its minimum shifts slightly towards the X symmetry point, therefore making the band gap slightly indirect. We will, however, consider GaAs as having a $\Gamma_v \rightarrow \Gamma_c$ inter-band electronic transition type. Figures 4a, b and c show the relationship between the hydrostatic pressure and the lattice parameters as expressed by Equations 2 and 3 for Si, Ge and GaAs respectively.

The band gap energies for all the three semiconductors were plotted against the pressure and a quadratic fit to Equation (9) was drawn through the data points in order to obtain the values of, $E_g(0,0)$, α and β. Figures 5a, b and c show these respective plots for Si, Ge and GaAs The values was obtained, $E_g(0,0) = 1.170$ eV, $\alpha = -0.0018191$ eV/kbar and $\beta = 1.1263\times10^{-6}$ eV/kbar^2 from the quadratic fit to Equation (8) for silicon. The results for germanium are, $E_g(0,0) = 0.742$ eV, $\alpha = 0.013724$ eV/kbar and $\beta = -2.4445\times10^{-5}$ eV/kbar^2, while those for gallium arsenide are, $E_g(0,0) = 1.519$ eV, $\alpha = 0.011944$ eV/kbar and $\beta = -2.0745\times10^{-5}$ eV/kbar^2.

A C++ program was written and used to calculate the variation of the band gap energy with respect to both pressure and temperature changes using Equation 10. This was done for silicon using the temperature coefficients $k = 4.73\times10^{-4}$ eV/K (Levinshtein et al., 2001) and $c = 636.0$ K (Levinshtein et al., 2001). The temperature coefficients used for germanium were, $k = 4.8\times10^{-4}$ eV/K (Levinshtein et al., 2001) and $c = 235.0$ K (Levinshtein et al., 2001), while those for gallium arsenide. were, $k = 5.405\times10^{-4}$ eV/K (Bhojani et al., 2016) and $c = 204.0$ K (Bhojani et al., 2016). The results for Si, Ge and GaAs are plotted in Figures 6a, b and c respectively.

DISCUSSION

The authors result show that silicon and germanium remain as indirect band gap semiconductor at both low and high applied hydrostatic pressures below their structural phase transition pressures, with $\Gamma_v \rightarrow X_c$ and $\Gamma_v \rightarrow L_c$ inter-band electronic transition types respectively, as seen in Figures 2a and b. Figures 3a and b show that GaAs has a direct band gap with a $\Gamma_v \rightarrow \Gamma_c$ inter-band transition type at low pressure but as the pressure increases, the minimum of the conduction band at the Γ point, shifts slightly towards the X symmetry point, therefore making the band gap indirect. This reflects a weakening of the directional character of the Ga-As inter-atomic bonds held by the sp^3 hybridized orbitals as the pressure increases. Tetrahedral coordinated semiconductors in the zinc blende and diamond structures are characteristic of covalent inter-atomic bonding of sp^3 hybridized orbitals. Orbitals that have the same energy form shells in which the value of the principle quantum number, n, which takes the positive integer values, $n = 1, 2, 3$, e.t.c., is the same. The value of the angular momentum quantum number, l defines the subshells. The values of n and l are related by, $l = 0, 1, 2\ldots n-1$ and subshells are given the letters s, p, d, f, etc,



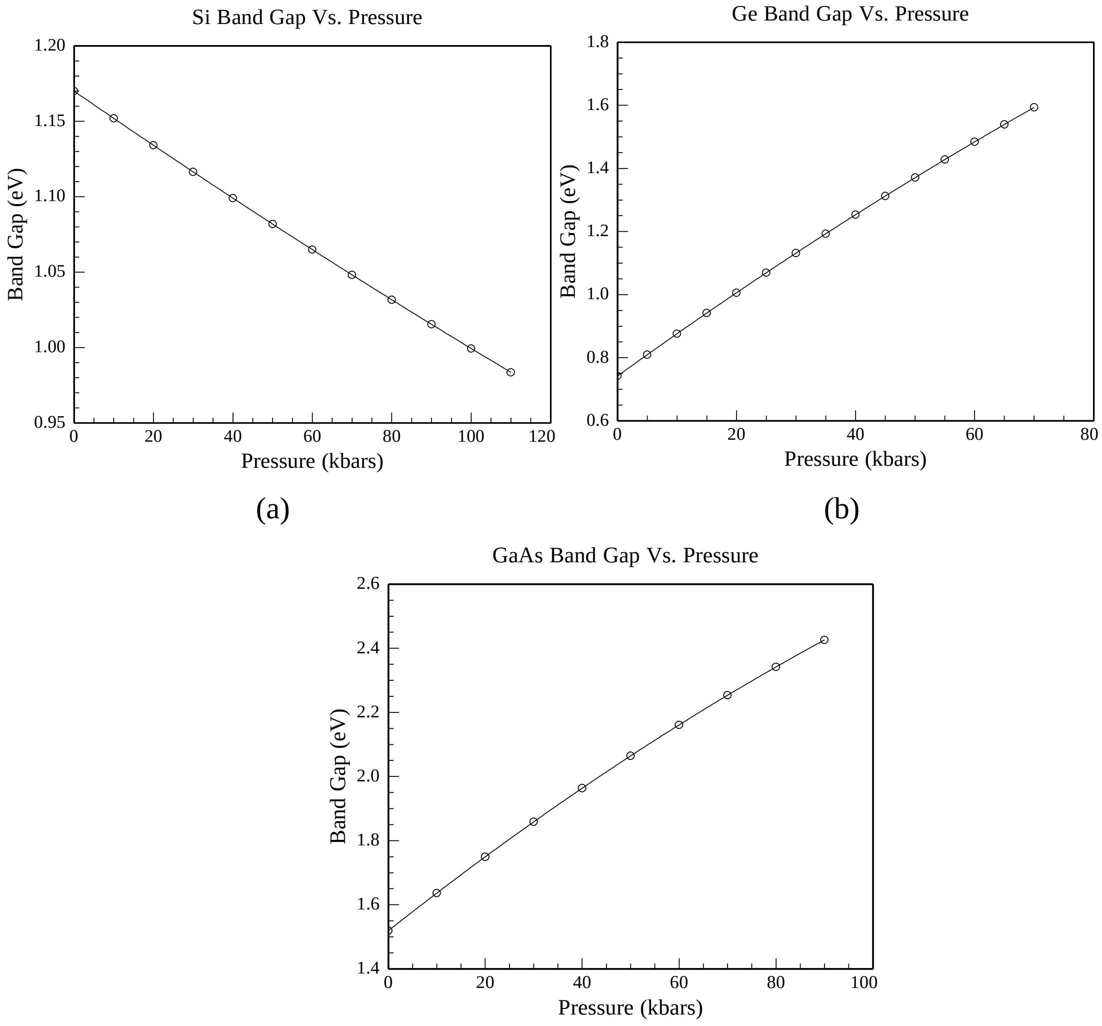
(a) (b)

(c)

Figure 4. Graphs of the hydrostatic pressure as a function of the lattice parameters for (a) silicon, (b) germanium and (c) gallium arsenide.

respectively. The electronic configurations of Si, Ge, Ga and As are, [Ne]$3s^2 3p^2$, [Ar]$3d^{10} 4s^2 4p^2$, [Ar]$3d^{10} 4s^2 4p^1$ and [Ar]$3d^{10} 4s^2 4p^3$ respectively, where [Ne] and [Ar] are the configurations of neon and argon respectively. These three semiconductors all have *s* and *p* outer shell or valance electrons which lead to the diamond structure-type, sp^3 hybridized. The diamond structure-type of covalent bonding can be explained, using Figure 7a which shows two paired electrons of opposite spins in both the 1*s* and 2*s* states of free carbon atoms. On the other hand, the 2*p* electrons in the $2p_x$ and $2p_y$ states are not paired.

During the formation of a diamond crystal, a 2*s* electron is excited to the $2p_z$ state, meaning that the 2*s*, $2p_x$, $2p_y$ and $2p_z$ states then have one unpaired electron each. These states with the same shell energy ($n = 2$) undergo hybridization, meaning that they form four similar hybrid or mixed sp^3 orbitals as shown in Figure 7b. The four tetrahedral coordinated covalent bonds between neighboring atoms in the diamond crystal are formed by these hybrid orbitals. Figure 5 shows that the bandgap energy reduces with an increase in pressure for Si whereas for Ge and GaAs it increases with pressure. In order to explain these results, an illustration was made in Figure 8, where we image isolated silicon atoms coming together to form a crystal. The atoms have an electronic configuration [Ne] $3s^2 3p^2$ in the ground state. The outer shell electrons are in the $n = 3$ shell. This shell contains *s* ($l = 1$), *p* ($l = 2$) and *d* ($l = 2$) subshells. The *d* levels are not indicated in the electronic configuration because they



(a) (b)

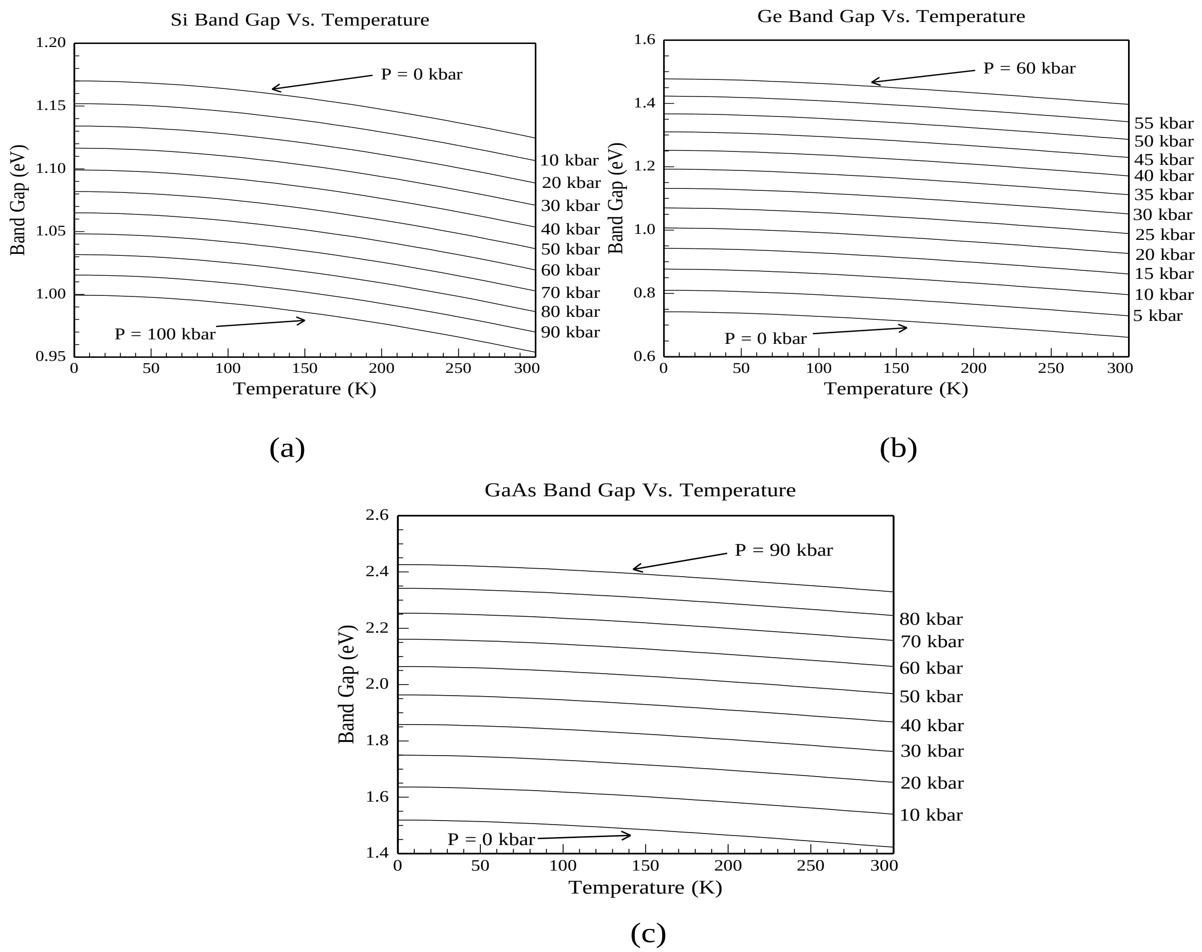
(c)

Figures 5. a. Plot of the silicon band gap energy against pressure with a quadratic fit drawn through the data points; b. Germanium band gap energy plot against pressure; c. Plot of the gallium arsenide band gap energy against pressure.

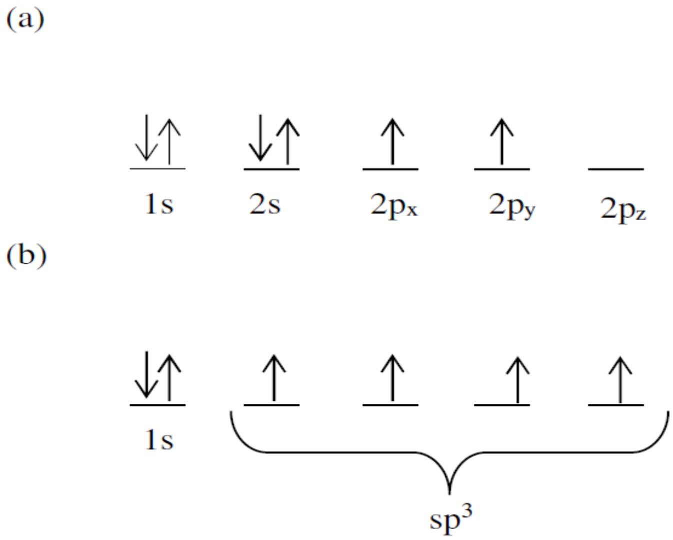
are not occupied by any electrons in the ground state of a free silicon atom but they are present in the n = 3 shell and have a large pressure induced effect on the electronic band structure of silicon.

If the number of silicon atoms is N, then there are 4N electrons in the original isolated atomic n = 3 shell, with 2N in the 3s states and 2N in the 3p states. Figure 8 shows that as the interatomic distance is decreased, the discrete 3p and 3s levels broaden out into bands and eventually they merge into a single band of mixed 3s-3p energy levels at the ‘cross over point’, containing 8N states. As the atomic spacing becomes closer to the equilibrium interatomic separation, r_0 of a silicon crystal, this band divides into two giving rise to the conduction and valence bands, with an energy gap, E_g separating them. This band splitting also separated the 8N electronic states such that 4N of them go up to the conduction band while the other 4N remain in the lower the valence band. The 2N electrons which were in the 3s subshell and the 2N electrons which were in the 3p subshells undergo sp^3 hybridization and all end up in the 4N states of the valence band; the 4N states in the conduction band remain empty.

The d states which were in the same n = 3 shell as the s and p states of the free atoms are still present above the s and p states in the conduction band of the silicon crystal. In tetrahedral coordinated crystals like silicon, the p orbitals and d orbitals have similar representations at certain high symmetry points in the Brillouin zone, such as the X points. These similarly represented orbitals can therefore couple and repel each other with a quantum mechanism similar to that expressed by the Pauli



Figures 6. Variation of the band gap energy with temperature at different pressures using Equation (10) for, (a) silicon, (b) germanium and (c) gallium arsenide.



Figures 7. (a) Two paired electrons of opposite spins in the 1*s* and 2*s* states. The 2*p* electrons in the $2p_x$ and $2p_y$ states are not paired. (b) The 2*s*, $2p_x$, $2p_y$ and $2p_z$ states have one unpaired electron each and undergo hybridization to form four similar sp^3 hybrid orbitals.

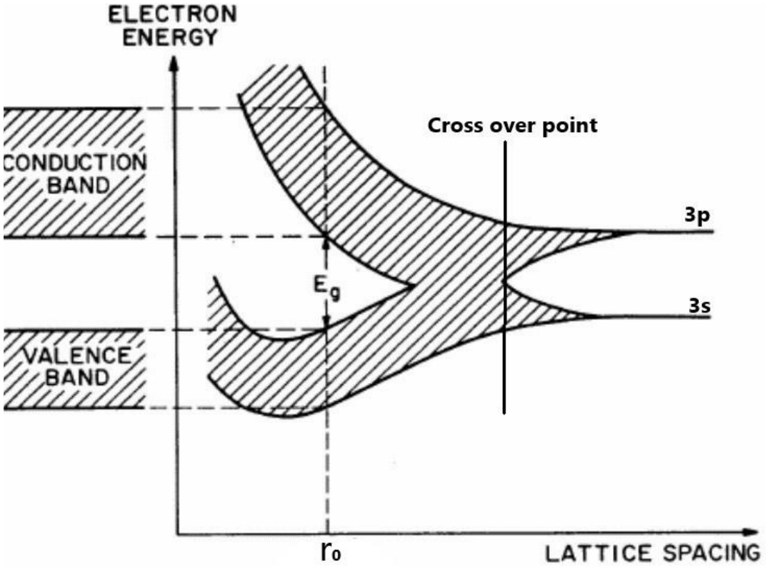


Figure 8. Isolated silicon atomic 3*s* and 3*p* states forming energy bands as a function of interatomic separation, in crystal formation.

exclusion principle; this is the *p-d* coupling effect (Wei and Zunger, 1999; Lee et al., 1985).

This *p-d* coupling increases with decreasing bond length between the atoms, which is what happens as the hydrostatic pressure is increased. In Si, where the *p-d* repulsion effect is large, the negative value of the pressure coefficient is as a result of the quantum level repulsion of the lowest states in the conduction band at the X symmetry point of the Brillouin zone by the unoccupied 3*d* states with the same principle quantum number.

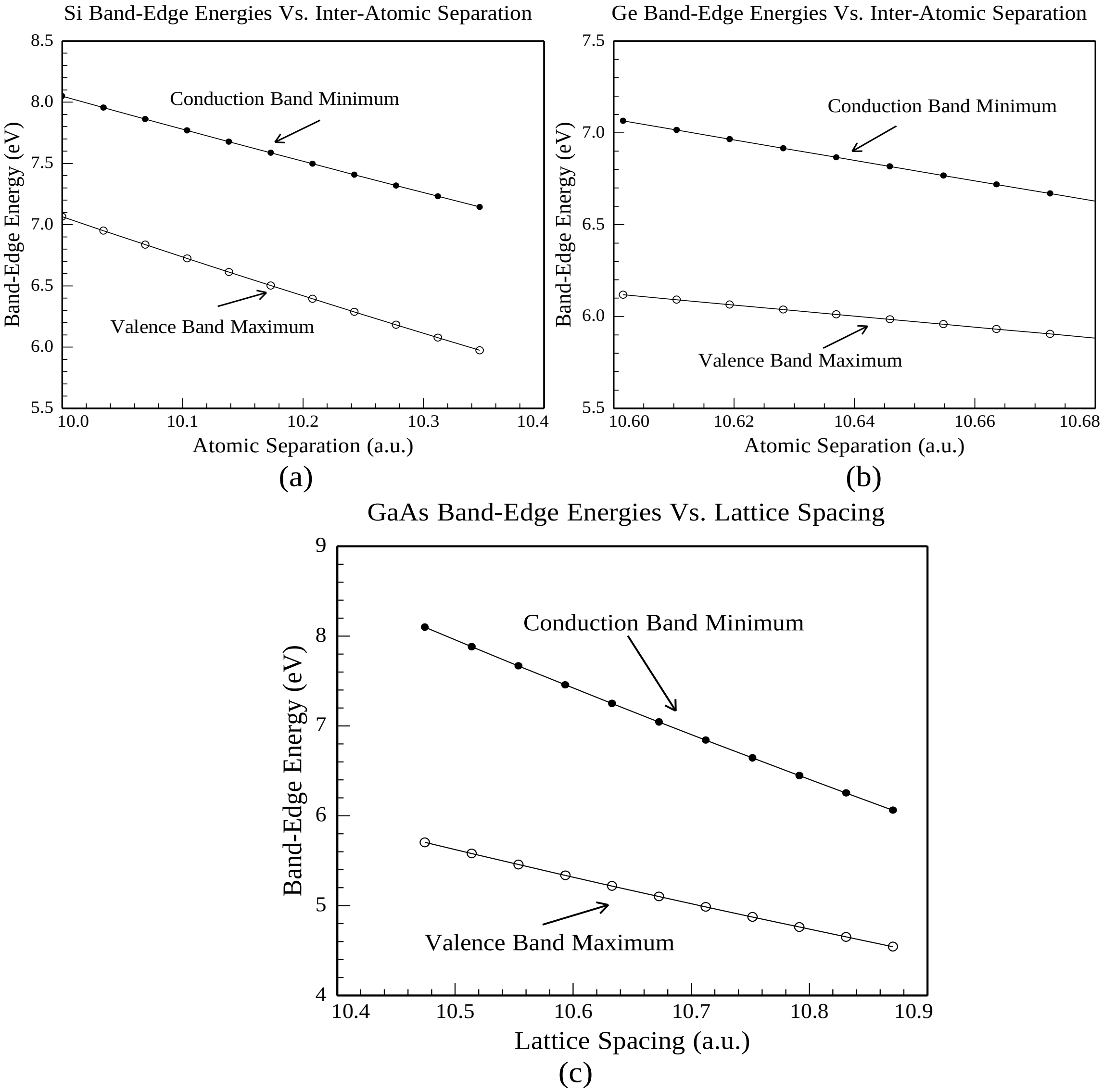
The fact that the bandgap energy does not reduce with an increase in pressure for Ge and GaAs indicates that the *p-d* coupling effect is not strong in Ge and GaAs. To explain why the bandgap energy actually increases with pressure in Ge and GaAs, if we drew diagrams like the one in Figure 8 for the bands arising from the free atomic states of Ge and GaAs as a function of interatomic distance, they would be similar to the ones for Si. As can be seen in Figure 8, the position of r_0 is such that any reduction in the atomic spacing due to increased pressure would shift r_0 to the left, hence increasing the separation between the valence and conduction bands, the origin of this effect is detailed in Figure 9, in terms of the relative energy shifts of the band edges with increased pressure.

The comparative amount of the hydrostatic pressure-induced deformation in the electronic band structure originating from the valence or conduction bands was determined. To accomplish this, Figures 9a, b, and c are presented with plots of the valence band maximum and the conduction band minimum as a function of atomic separation for Si, Ge, and GaAs, respectively.

It can be seen from Figure 9 that in all cases the valence band maximum energy increases with the reduction in the lattice separation, that is, it increases with pressure. It is also seen that the same applies to the conduction band minimum. However, the rate of increase (negative slope) in energy of the conduction band minimum with reduction in atomic separation (increase in pressure) is greater than that of the valence band maximum for Ge and GaAs, while it is less than that of the valence band maximum for silicon due to *p-d* coupling. An interesting question posed in the literature by Wei and Zunger (1999) is whether the band gap *Eg* depends linearly with pressure or with ln(*V*), where *V* is the unit cell volume. This is in view of the implications of Equations 4 and 6 through the bulk modulus, which is known to increase as volume decreases. Figure 10 shows our calculated values of the band gap energy in relation to ln(*V*) for Si, Ge and GaAs.

It was observed from Figure 10 that the band gap energy, *Eg* is, to a good approximation, a linear function of ln(*V*), for Ge and GaAs but not for Si. According to Equation 4, this implies that the hydrostatic volume deformation potential, a_g, is constant for Ge and GaAs. On the other hand, Figure 5 shows that *Eg* is, to a good approximation, a linear function of pressure for Si but not for Ge and GaAs. Our results are consistent with those reported by Wei and Zunger (1999), who carried out some related work on GaAs. They concluded further that for GaAs, dEg/dp decreases as the pressure increases, while $2dEg/d\ln(V)$ slightly increases with a decrease in volume.

Figures 6a, b, and c show that the band gap energy reduces with an increase in temperature at all values of the pressure for all three semiconductors. This is expected since the energy of electrons in a material is



(a) (b)

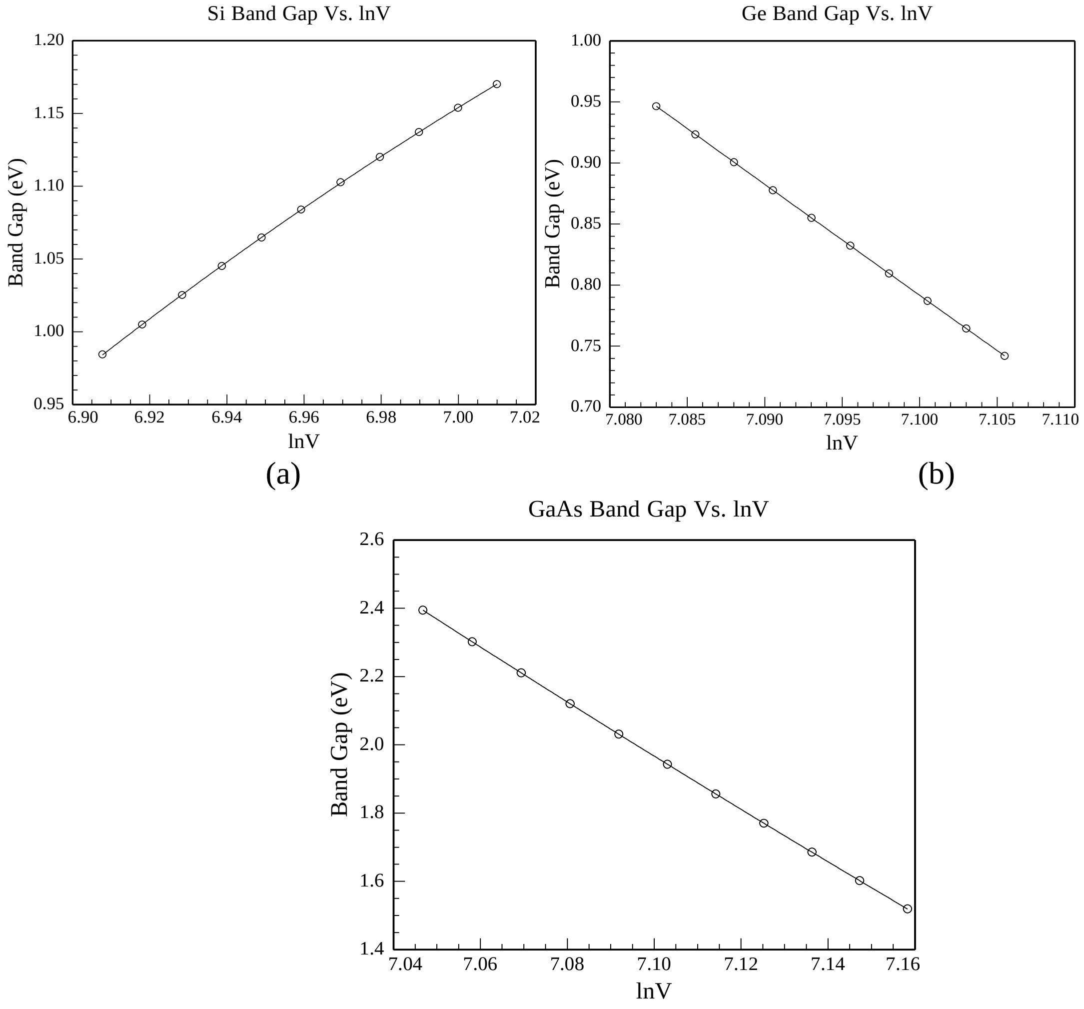
(c)

Figure 9. Plots of the of the valence band maximum and the conduction band minimum as a function of the atomic separation for, (a) Si, (b) Ge and (c) GaAs.

bound to rise with temperature, hence reducing the amount of extra energy required for inter-band transitions. The extra energy required to cross the band gap threshold represents the reduced band gap energy. The limitations of our method mainly arise from the non-incorporation of the symmetry of Brillouin zones in our analysis. Our method does not allow for the consideration of certain symmetry properties and changes of zonal structure. Such applications have been demonstrated by Sun et al. (2010).

Conclusion

The electronic energy band structures of silicon, germanium and gallium arsenide have been studied under high pressure and different temperatures. The pressure coefficients have been determined in their respective order as: α = -0.0018191 eV/kbar and β = 1.1263×10^{-6} eV/kbar^2; α = 0.013724 eV/kbar and β = -2.4445×10^{-5} eV/kbar^2; α = 0.011944 eV/kbar and β = -2.0745×10^{-5} eV/kbar^2. An atomistic insight was presented into the question of how much of the band gap deformation, due to hydrostatic pressure, originates from the valence or the conduction band. The rate of increase in energy of the conduction band minimum with an increase in pressure is greater than that of the valence band maximum for Ge and GaAs, while it is less than that of the maximum of the valence band for silicon. The negative value of the first-order pressure coefficient in Si



(a) (b)

(c)

Figure 10. Calculated values of the band gap energy in relation to ln(*V*) for, (a) Si, (b) Ge and (c) GaAs.

is unique among the Group IV elements (Hameed and AL-Sheikh, 2011). We explain this as being due to the presence of d states which are in the same shell as the s and p valence electron states of the silicon atom and are present above the s and p states in the conduction band of the crystal. The p and d orbitals have similar representation at the X high symmetry points in the Brillouin zone, and they therefore couple and exhibit quantum level repulsion between each other. The d levels hence repel the conduction band at Xc, forcing it downwards in energy relative to the maximum of the valence band at Γv, and this p-d coupling increases with hydrostatic pressure. The hydrostatic volume deformation potential, ag, is found to be constant for Ge and GaAs. Our results show that the bandgap energy reduces with an increase in temperature at all values of the pressure for all three semiconductors. These results are in good agreement with those reported in the literature (Hameed and AL-Sheikh, 2011). One of Paul's (1998) "empirical rules of pressure coefficients" states that for an inter-band transition of the type, $\Gamma_v \rightarrow \Gamma_c$ as is the case in GaAs, the pressure coefficient is around 10 meV/kbar, Our result for GaAs is 11.944 meV/kbar, which agrees with the rule. Another of the empirical rules states that for a transition of type, $\Gamma_v \rightarrow L_c$ as is the case in Ge, the pressure coefficient is around 5 meV/kbar. Our result for Ge is 13.724 meV/kbar, which is within an acceptable 10 meV/kbar order of magnitude above the generalised 5 meV/kbar predicted for all, $\Gamma_v \rightarrow L_c$ transitions. A third empirical rule states that for a transition, $\Gamma_v \rightarrow X_c$, as is the case in Si, the pressure coefficient is between -1 or -2 meV/kbar. Our result for Si is -1.8191 eV/kbar which agrees perfectly.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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