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Pressure and Temperature Dependence of Energy Gap in SiC and $Si_{1-x}Ge_x$

Adnan M. Al-sheikh
Department of Physics\ College of Science\ University of Mosul
Mumtaz M. Hussien
Department of Physics\ College of Education for Pure Science \ University of Mosul
Siham J. Abdullah
Department of Radiology\ Alnoor University College

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ABSTRACT

The effect of pressure on energy gap for IV-IV compound SiC and $Si_{1-x}Ge_x$ alloy have been investigated and evaluated by using Birch-Murnaghan equation of state (EOS) and Bardeen equation of state. Ambiguity in the effect of pressure and temperature on E_g of different SiC polytypes (3C, 4H, 6H) have been investigated and attributed.

Variation of E_g in $Si_{1-x}Ge_x$ evaluated and an interpretation, for it, has been suggested.

Keywords: IV-IV compounds, energy gap, high pressure, $Si_{1-x}Ge_x$ alloy, SiC pollytypes.

اعتماد فجوة الطاقة E_g في SiC و $Si_{1-x}Ge_x$ على الضغط و درجة الحرارة

الملخص

تأثيرالضغط على فجوة الطاقة لمركب الزمرة IV-IV(SiC) وسبيكة $Si_{1-x}Ge_x$ قد تمت دراسته وحسابه باستخدام معادلة الحالة بيرخ-مرنكهان ومعادلة الحالة لباردين. الغموض لتأثير الضغط في الأنواع المتعددة (3C, 4H, 6H) للمركب SiC قد تمت دراسته وتفسيره.

تغير E_g في سبيكة $Si_{1-x}Ge_x$ مع نسب المكونات تم حسابه واقتراح تفسير له.

الكلمات الدالة: مركبات IV-IV، فجوة الطاقة، الضغط العالي، سبيكة $Si_{1-x}Ge_x$، الأنواع المتعددة لـ SiC .

INTRODUCTION

The electronic band structure is the significant key to understand the electrons behavior in crystalline solids,and their interaction with the lattice vibrations. It is very difficult to predict the properties of solid which contain a huge number of atoms, of the order of 10^{23} atoms/cm^3, It is necessary to use a suitable approximations. There are several methods to solve this problem were present in the past to calculate the band structure such as k.p, tight binding or linear combination of atomic orbital's (LCAO), pseudo-potentials, etc (Reparaz, 2008).

The electronic and optical properties has been altered due to hydrostatic pressure, these changes provides an important information on the band structure for vast variety of semiconductors (Engelbrecht *et al.*, 1997-II).

Group IV semiconductors Si, and Ge have the diamond structure. In this each atom is surrounded by four atoms,nearest neighbors atoms, which lies with equal distances at the corners of tetrahedron. (Otfried, 2004).

The origin of the semiconductivity of pure germanium is briefly explained using linear combination of atomic orbital's (LCAO) model as follows:

An isolated germanium atom has four electrons in the n=4 outer shell which are represented by the spectroscopic notation $4s^2 4p^2$. In order to form bonds with other germanium atoms, one s electron is promoted to p-shell, giving the bonding electrons a $4s\ 4p^3$ configuration. These orbital's directed to the corners of regular tetrahedron, with the result that in solid germanium, each atom is bounded to four others in tetrahedral coordination. Similarly, silicon has the electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$ simulate, in outer shell n=3, the configuration $3s\ 3p^3$.

Semiconducting phases also occur in silicon carbide (SiC), where Si in outer shell has the configuration $3s\ 3p^3$ while C^6 has the electronic configuration in outer shell n=2, $2s\ 2p^3$. In this binary compound the differences between cubic, hexagonal and rhombohedric structure are so small, that a large number of polymorphic modifications occur. More than hundred different polytypes exist. In all polytypes every atom is surrounded by four atoms of the other species.

The group IV Silicon-Germanium random alloy differs in several respects from SiC. One of the most characteristic features of this material composition concerns bulk $Si_{1-x}Ge_x$: Si and Ge are miscible over the complete range of composition (Levinshtein *et al.*, 2001).

THEORETICAL DETAILS

The behavior of the semiconductors under pressure has been a topic of experimental and theoretical study for sometimes (Wei and Zunger,1999-II; Angilella *et al.*, 2008).

The pressure coefficient

$$\alpha_P = \frac{dE_g}{dP} \qquad (1)$$

where E_g is the energy gap, P is the pressure.

Interband transition in a semiconductor is related to the volume deformation potential

$$\alpha_V = \frac{dE_g}{d\ln V} \qquad (2)$$

Via the bulk modules (B=-dP/d(lnV)) through the relation.

$$\alpha_P = -\left(\frac{1}{B}\right)\alpha_V \qquad (3)$$

The pressure-volume-temperature equation of state (EOS) is fundamental to high pressure science because of its widespread use as internal pressure standard (Shim *et al.*, 2002; Sanditov and Belomestnykh, 2011).

This work presents the effect of high pressure on energy gap by using α_P and three different EOSs which are

Murnaghan EOS (Murnaghan, 1937)

$$\frac{V_P}{V_o} = \left(1 + \frac{PB'}{B_s}\right)^{\frac{-1}{B'}} \qquad (4)$$

B_s adiabatic bulk modulus, B'first pressure derivative of B_s, $V_o$volume at atmospheric pressure, Vvolume at pressure p.

and (Radi *et al.*, 2007)

$$a_P = a_o\left(1 + \frac{PB'}{B_s}\right)^{\frac{-1}{3B'}} \qquad (5)$$

a_p lattice constant at pressure p, a_o lattice constant at atmospheric pressure.

Birch-Murnaghan EOS (Birch, 1952)

$$P_{BM} = \frac{3B_o}{2}\left[\left(\frac{V}{V_o}\right)^{-7/3} - \left(\frac{V}{V_o}\right)^{-5/3}\right]\left[1 + \frac{3}{4}(B_o' - 4)\left(\left(\frac{V}{V_o}\right)^{-2/3} - 1\right)\right] \qquad (6)$$

Bardeen EOS(Bardeen, 1938)

$$P_B = 3B_o\left[\left(\frac{V}{V_o}\right)^{-5/3} - \left(\frac{V}{V_o}\right)^{-4/3}\right]\left[1+\frac{3}{2}(B_o'-3)\left(\left(\frac{V}{V_o}\right)^{-1/3}-1\right)\right] \qquad (7)$$

Where: B_o isothermal bulk modulus at atmospheric pressure,B'_ofirst pressure derivative of B_o.

Energy gap in SiC, polytypes (3C, 4H, and 6H), varies with pressure according to the fallowing relation (Levinshtein *et al.*, 2001).

$$E_g = E_g(0) + \propto_p p \qquad (8)$$

Where: P applied pressure in (Gpa), $E_g(0)$ energy gap at zero temperature.

While energy gap vary with temperature according to:

$$E_g = E_g(0) - \frac{KT^2}{T+\theta} \qquad (9)$$

Where: K temperature coefficient, θ constant, nearly equal to Debye temperature.

(Arezky *et al.*, 2009) shows that the variation of energy gap with both temperature and pressure expressed as:

$$E_g = E_g(0) + \alpha_p P - \frac{KT^2}{T+\theta} \qquad (10)$$

Variation of lattice parameter of $Si_{1-x}Ge_x$ system with composition can be evaluated by using the following quadratic expression (Dismukes *et al.*, 1964).

$$a(x) = 0.002733x^2 + 0.01992x + 0.5431(nm) \qquad (11)$$

(Herzog, 2000) determined variation of lattice parameter of $Si_{1-x}Ge_x$ system with composition by using Vergards rule.

$$a_{Si_{1-x}Ge_x} = a_{Si} + [a_{Ge} - a_{Si}]x \qquad (12)$$

As a consequent of lattice parameter changes, E_g will also be varied with composition.(Jaros,1985)expressed this variation by using the following quadric expression

$$E_g = E_{gSi} + (E_{gGe} - E_{gSi})x + cx^2 \qquad (13)$$

Where: c bowing parameter equal 0.22.

COMPUTATION AND RESULTS

Variation of E_g for SiC with pressure

Using equation (8) with α_p data tabulated in Table-1.

Table 1: Pressure and temperature coefficients for SiC

SiC structures	α_p	Θ	K
3C	$-0.34*10^{-3}$	1200	$-6.0*10^{-4}$
6H	$-0.03*10^{-3}$	1200	$-6.5*10^{-4}$
4H	$0.08*10^{-3}$	1300	$-6.5*10^{-4}$

Fig. (1) shows the effect of pressure on energy gap of SiC in its different polytypes. Where E_g for 4H-SiC increases with pressure, while E_g for 3C-SiC and 6H-SiC decreases with pressure as these structures have a negative α_p value.

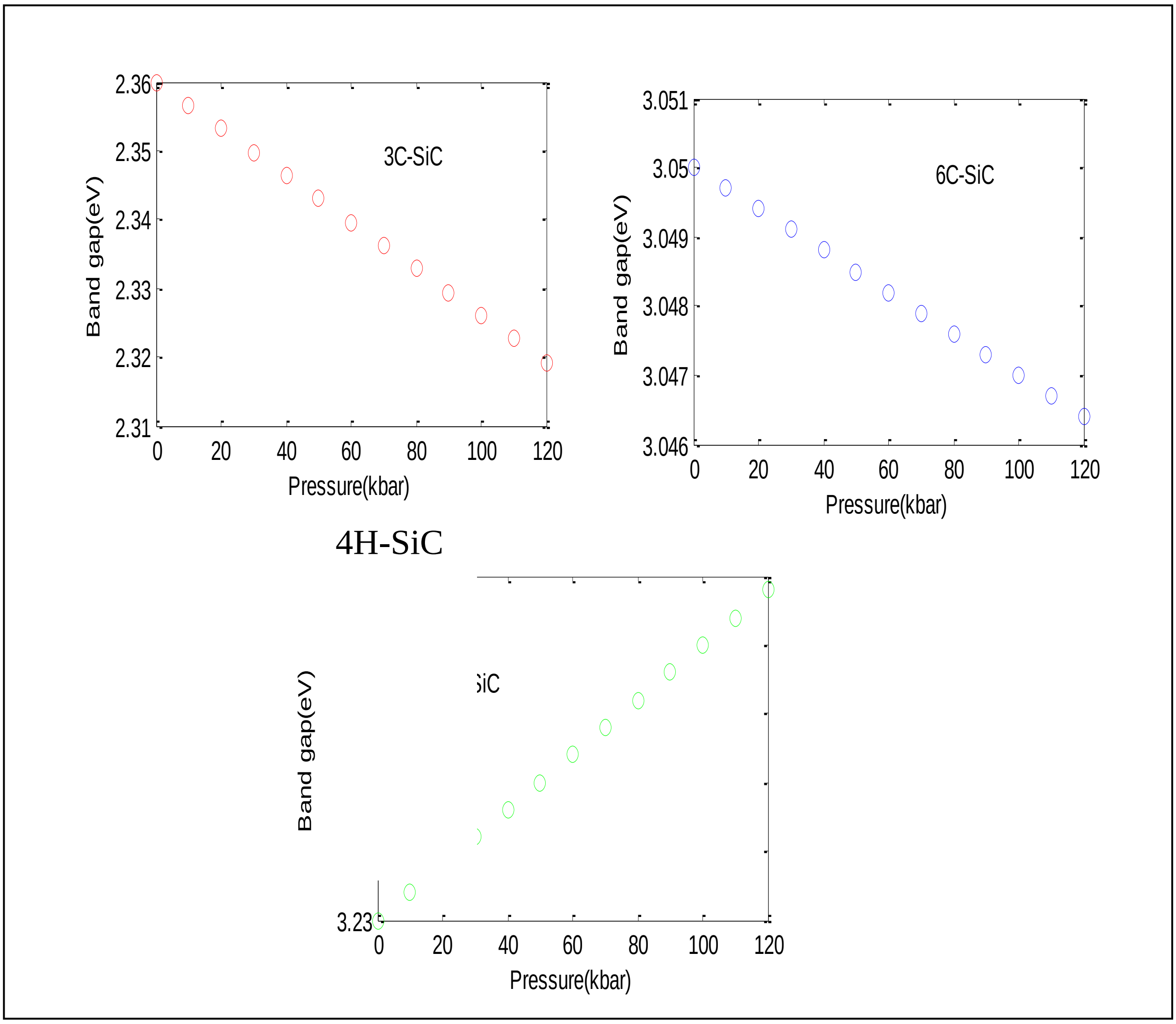

Fig. 1: The hydrostatic pressure dependences of energy gap for 3C-, 4H- and 6H-SiC polytypes

Variation of SiC energy gap with temperature

On substituting θ and K values from (Table 1) and energy gap values from (Table 2) into eq.9, Fig. (2) shows decreasing E_g, for SiC in its different polytypes, with temperature.

Table 2: The values of energy gap for SiC polytypes at (0 K)

SiC structures	$E_g(eV)$
3C	2.36
6H	3.05
4H	3.23

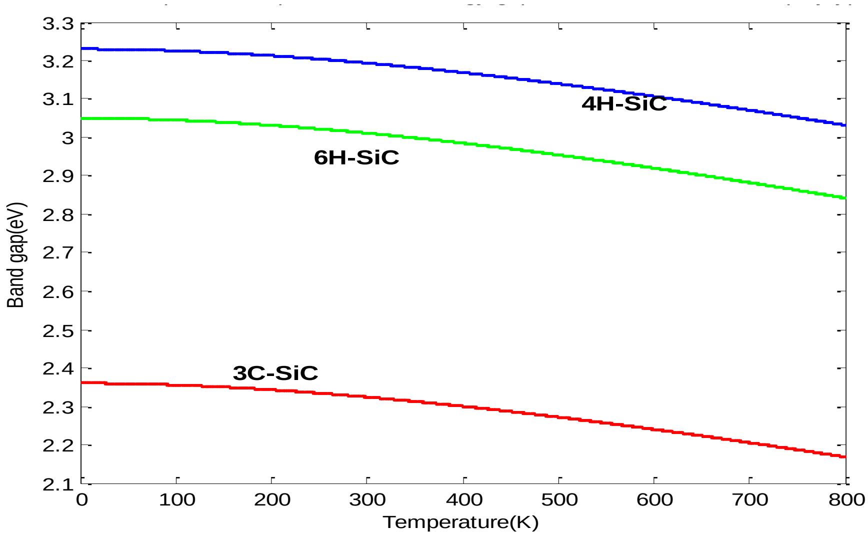

Fig. 2: Temperature dependence of energy gap for 3C-, 4H-, and 6H-SiC polytypes at atmospheric pressure

On comparing results shown in Fig. (1) and Fig. (2), it is clear that E_g for 4H-SiC structure increases with increasing pressure, Fig. (1), and decreases with raising temperature, Fig. (2), which represent, generally, an expected behavior for semiconductor martials.

But the ambiguity appear on comparing results, for 3C-SiC and 6H-SiC, shown in Fig.(1) with results shown in Fig. (2), where both figures show decreasing E_g values with increasing pressure, Fig. (1), or increasing temperature, Fig. (2). In other words that E_g for, 3C-SiC and 6H-SiC, decreases by raising temperature or increasing applied pressure. In contract to the behavior of 4H-SiC structure.

This discrepancy between results in Fig. (1) itself, further to contradiction between results in Fig. (1) and Fig. (2), still represent a research area.

Looking to 3C, 4H, and 6H structures may form a corner point in understanding this ambiguity.

SiC has equal parts of silicon and carbon, both of which are group IV elements. The carbon atom is situated at the center of mass of the tetragonal structure outlined by the four neighboring Si atoms as shown in, Fig. (3). The distance between neighboring silicon (a) or carbon atom is approximately 3.08 Å forall polytypes.

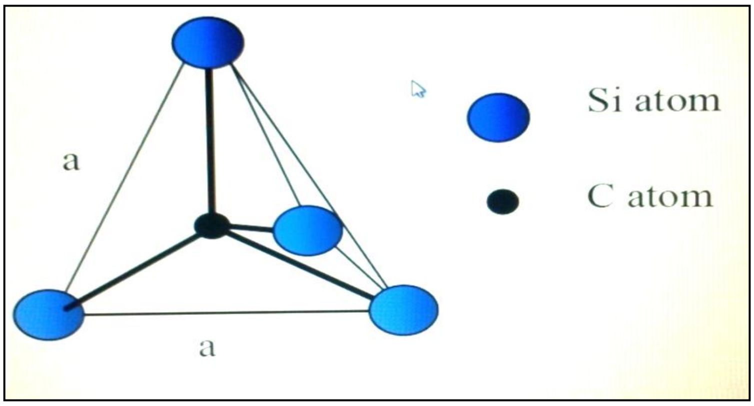

Fig. 3: The tetragonal bonding of a carbon atom with the four nearessilicon(Lee, 2002).

The distance between the C atom and each of the Si atoms is approximately 2.52 Å. The height of the unit cell, called c, varies between the different polytypes. Therefore, the ratio of c/a differs from polytype to polytype. This ratio is 3.271, and 4.908 for the 4H, and 6H SiC polytypes, respectively. The polytype is a variation of crystalline material in which the stacking order of planes in the unit cell is different.

Each SiC bilayer, while maintaining the tetrahedral binding scheme of the crystal, can be situated in one of three possible positions with respect to the lattice (A, B,or C), Fig. (4).

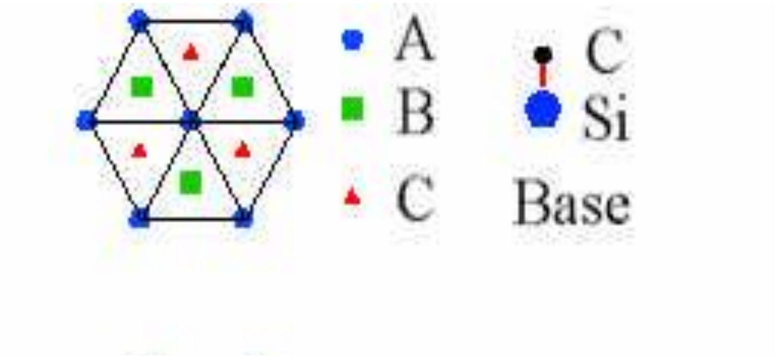

Fig. 4: The staking sequence of silicon carbide

The bonding between Si and C atoms in adjacent bilayer planes is either of a Zinc-blende (Cubic) or Wurtzite (Hexagonal) nature depending on the stacking order (Morkoc *et al.*, 1994). As shown in Fig. (5) (Knippenberg, 1963), if the stacking is ABCABC...the cubicpolytype commonly abbreviated as 3C-SiC.While 4H-SiC is (ABCB...) and 6H-SiC is (ABCACB...) (Lee, 2002**)**. These two types of SiC are the most common hexagonal polytypes. 4H-SiC consists of equal amounts cubic and hexagonal bonds, while 6H-SiC is two-thirds cubic, see (Table 3).

Table 3: Stacking sequences in the c-axis direction for different SiC polytypes

	Stacking sequence	**No. hexagonal**	**No. cubic**
3C	ABC	0	1
6H	ABCB	1	1
4H	ABCACB	1	2

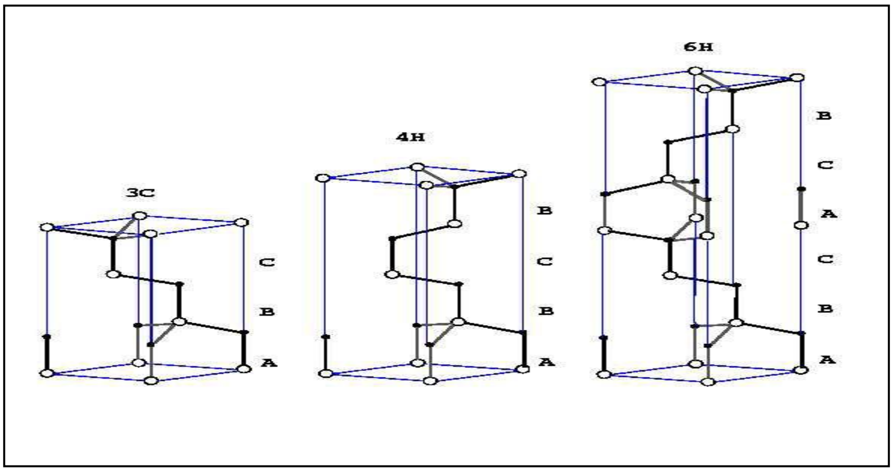

Fig. 5: The staking sequence of common 3C-,4H-, and 6H-SiC

Notifying (Table 3) and Fig. (5) indicate that 4H-SiC which have 2:1 Cubic:Hexagonal shows increases in E_g with increasing pressure and decreases in E_g with raising temperature, while the ambiguity appear in 3C-SiC which have Cubic structure only and 6H-SiC Cubic-Hexagonal structure in 50%, i.e. the, general, expected semiconductor behavior appear in 4H-SiC which have hyperdized Cubic-Hexagonal structure in 2:1 sequence.

Variation of E_g for $Si_{1-x}Ge_x$ with pressure

As Si^{14}, Ge^{32} atoms have different sizes, lattice parameters will varies with composition due to strain effect in the alloy. This change in lattice parameters might consequently cause variation in E_g with composition. Furthermore electronic structures for Si: $1s^2 2s^2 2p^6 3s^2 3p^2$ and Ge: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$. Filled $3d^{10}$ in Ge lies below 4s and away from it such that it cannot interact with 4s. But this situation does not allow $3d^{10}$ to be considered within the core electrons, consequently it does not take a role in construction of metallic bond, where 4s electrons has the fundamental role in bond construction (Altman,1991).

On substituting B_o and B'_o values, for Si and Ge from Table-IV, into eqs.6 and 7. (V_p/V_o) values, for Si and Ge, at different pressure has been evaluated.

Table 4: The values of lattice constant, energy gap, bulk modulus and it's first pressure derivative for Si and Ge

	Lattice constant a (Å)	Energy gap E_g (eV)	Bulk modules B_o (Gpa)	Firest pressure derivative B'_o
Si	5.4310	1.15	98	4.24
Ge	5.6575	0.65	77.2	4.55

as eq.5 can be rewritten in the form

$$a_p = a_o \left(\frac{V_p}{V_o}\right)^{1/3} \tag{14}$$

Then eq. 14 gives variation of lattice constant with pressure. On combining eqs.14 and 12. Fig. (6) shows variation of lattice constant, for $Si_{1-x}Ge_x$ at different compositions, with pressure.

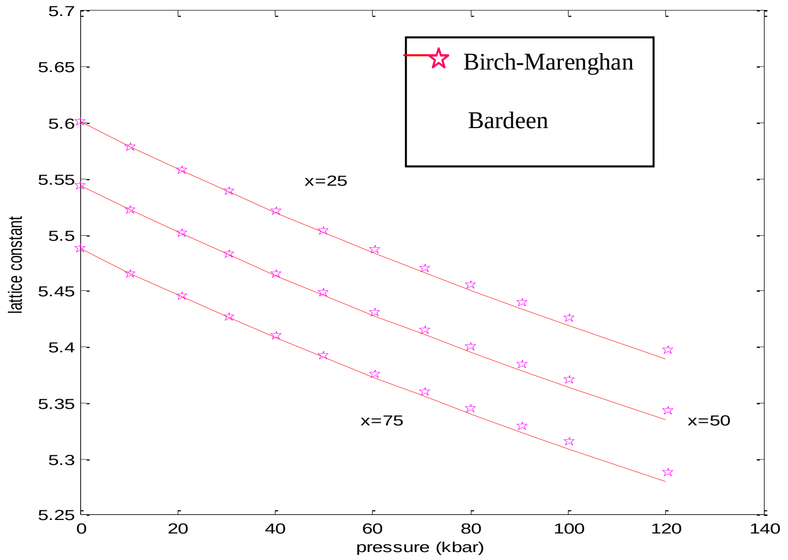

Fig. 6: Variation for, $Si_{1-x}Ge_x$ lattice constant with pressure at different composition, by using Birch-Muranghan and Bardeen EOSs

Substituting E_g values from (Table 4) into eq.13. Fig.(7) shows variation of E_g for $Si_{1-x}Ge_x$ with composition.

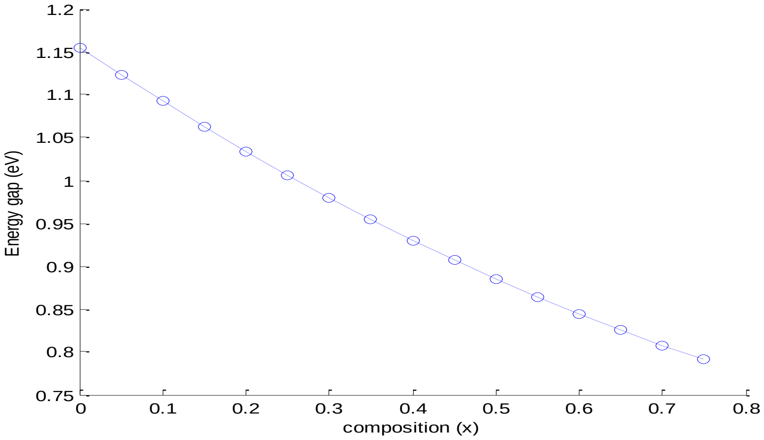

Fig. 7: Energy gap for $Si_{1-x}Ge_x$ at different composition at room temperature

(Adachi, 2009), express pressure coefficient for $Si_{1-x}Ge_x$ in the form

$$\propto_p = 7.8 - 1.6x \tag{15}$$

for x=0.5

$$\propto_p = 7 * 10^{-3}$$

On substituting α_p values into eq.8. Fig.8 show variation of E_g for SiGe with pressure.

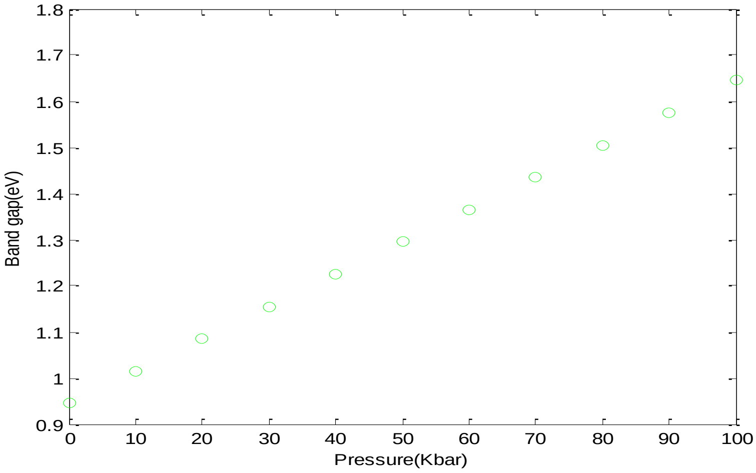

Fig. 8: Variation of E_g for SiGe with pressure

DISCUSSION

On comparing results for SiC in Fig. (1) and Fig. (2) it appear that E_g for 3C-SiC and 6H-SiC polytypes decreases with raising temperature and decreases, as well, with applied pressure, while E_g for 4H-SiC polytype decreases with raising temperature and increases with increasing applied pressure. The ambiguity in the results of 3C and 6H polytypes to have lower E_g with increasing pressure or raising temperature may be attributed by the stacking sequence for 3C and 6H where there are (0:1 and 1:1, hexagonal:cubic) stacking sequence. While for 4H-SiC there is (1:2, hexagonal: cubic) stacking sequence.

For $Si_{1-x}Ge_x$ Fig. (7) shows that E_g for this alloy decreases with composition as Ge increases. This could be interpreted by the effect of filled $3d^{10}$ in Ge electronic configuration. While increasing E_g for SiGe by increasing applied pressure, Fig. (8), agree, mostly, with the general properties of semiconductors.

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