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On the variation of bandgap of semiconductors with temperature

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Abstract: *This article derives a simple linear model for semiconductor bandgap variation with temperature. The model is based on the theorem of equipartition of energy for the electrons and holes at thermal equilibrium which gives the average kinetic energy of an electron or hole to be (3/2)kT. The calculated bandgaps at temperatures of 100K to 600K of Silicon matches with the observed experimental values to within ±1%. The model is applicable to bandgaps of all covalently bonded semiconductors at high temperatures and is possibly valid for the electron work functions of metals and the oxide/semiconductor band offsets as well.*

Keywords: *Bandgap, Semiconductors, Silicon, Silicon Carbide, Temperature*

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I. Introduction

The study of the variation of semiconductor bandgap with temperature has pertinent applications of quantum computers that operate at very low temperatures of less than 100K, and the high temperature electronics using compound semiconductors such as Silicon Carbide, Gallium Nitride, Boron Nitride, Germanium Carbide and Diamond for power and high frequency applications. Pearson and Bardeen in their research paper of March 1949 assumed a linear variation of semiconductor bandgap, E_G with temperature. They obtained a value for dE_G/dT as -3.0 x 10^{-4} eV/K experimentally for Silicon with E_G (0K) as 1.115 eV [1]. Just to mention, Late John Bardeen was a two-time Nobel Laureate for Physics. H.Y. Fan in 1951 calculated the effect of lattice vibrations in producing shift of the energy levels in Silicon which results in a temperature variation of the energy gap in semiconductors. He found dE_G/dT for Silicon to be -3.58 x 10^{-4} eV/K close to the experimentally obtained value of Pearson and Bardeen given above [2]. The research paper by Thurmond in 1975 gives the variation of E_G of Si with temperature in Kelvin based on Varshni's equation of 1967 [3-4]. Varshni's equation is developed around the experimentally measured absorption edge spectrum of Si and Ge by G.G. Macfarlane et al. in 1958-59 up to 4.2 K temperature [5-6]. The present article shows that while the Varshni's non-linear equation accurately describes the temperature variation of semiconductor bandgap, the simpler linear model describes the temperature variation of the semiconductor bandgap for high temperatures greater than 100K and up to 600K within ±1% of the experimental values obtained from the Varshni's equation. This temperature range is pertinent to the high temperature electronic applications. It also describes the behaviour of the Fowler-Nordheim (FN) temperature model as shown with the example of 4H-SiC MOS device in an earlier study where the SiO_2/4H-SiC conduction band offset (CBO) varies as -2.8 x 10^{-4} eV/K in the 100K to 600K temperature range [7].

II. Theory

If one considers a parabolic band structure of a semiconductor, then the electrons in the conduction band are described by the energy equation:

$$E(p) = E_c + \frac{p^2}{2m_n^*} = E_c + \frac{1}{2}m_n^* v_{th}^2 \quad (1);$$

and the holes in the valence band are described by the energy equation:

$$E(p) = E_v - \frac{p^2}{2m_p^*} = E_v - \frac{1}{2}m_p^* v_{th}^2 \quad (2).$$

Subtracting equation (1) from (2) and applying the theorem for equipartition of energy of electrons and holes at thermal equilibrium, gives [8]:

$$E_G(T) = E_G(0K) - 3kT \quad (3).$$

$$E_G(T) = E_G(300K) + 3k(300 - T)/q \quad in\ eV \quad (4).$$

This linear model of the semiconductor bandgap variation with temperature is mentioned in words in Macfarlane et al., but the above equation derivation and calculations of bandgap variation with temperature based on this model are not presented [5]. In this model, $E_G(T)$ is taken as a positive number. Actually, the bandgap should represent a negative potential energy of the electrons in the conduction band relative to the valence band at zero energy. The bandgap increases in magnitude at lower temperatures than 300K and reduces at higher temperatures. The change in bandgap at any temperature T from the value at 300K will be the same

for all non-polar semiconductors given by the second term in the above equation. At 0K, the change is equal to 0.0775 eV. This gives a linear change of -2.59 x 10^{-4} eV/K. It is nearly the same as that obtained experimentally by Pearson and Bardeen [1]. The above equation can be further simplified as follows:

$$E_G(T) = E_G(300K) + 0.0775 - \frac{3k}{q}(T) \;\; in\; eV \qquad (5).$$

For Si, taking the value of E_G (300K) as 1.12 eV, the above equation will become:

$$E_G(T) = 1.1975 - (2.59\, x10^{-4})x\, T \qquad for\; Si. \qquad (6).$$

The non-linearity which exists at low temperatures does not show in the above linear equation (6), where the measured value of the Si bandgap at about 0K is 1.17 eV instead of 1.1975 eV calculated from the linear equation. The error at 0K because the non-linearity in the absorption data by Macfarlane is not expressed in the proposed linear equation. This can now be compared to the Varshni's equation for Silicon that fits the experimental data of Macfarlane et al., and is given as [3-5, 9]:

$$E_G(T) = 1.17 - \frac{(4.73\, x\, 10^{-4})T^2}{(T+636)} \qquad for\; Si \qquad (7).$$

Here, 1.17 eV is the measured bandgap of Si at about 0K [5]. The Debye temperature is 636K. Below a temperature of 63.6K, the equation is expected to be non-linear varying as T^2, and above a temperature of 63.6K, the equation is expected to be linear with T [3]. It has been demonstrated that the linear equation is within ±1% of the experimental values from the absorption edge spectrum of Si in the temperature range of 100K to 600K as presented in the Table below in the Results and Discussion section III. This temperature range is applicable to the FN temperature model also, which at very low temperatures may also follow the non-linear model, when the conduction band offset of the oxide/semiconductor interface may vary as T^2 [7]. The intrinsic carrier concentration for Si at 300K is improved to 1.01 x 10^{10}/cm^3 from an earlier value of 1.45 x 10^{10}/cm^3 [10]. The values of density of states in the conduction band N_c, and the density of states in the valence band N_v, for Si at 300K are 2.8 x 10^{19}/cm^3 and 1.04 x 10^{19}/cm^3 [9]. These values give the bandgap of Si at 300K as 1.10 eV when the formula below is used:

$$E_G = \frac{kT}{q} ln\left(\frac{N_C N_v}{n_i^2}\right) \quad in\; eV \qquad (8).$$

Here, k is the Boltzmann constant as 1.3806 x 10^{-23} Joules/Kelvin, T is the temperature in Kelvin so that kT is the energy in Joules and q is the energy of the electron as 1.602 x 10^{-19} Joules per eV. Another report of N_c and N_v values gives N_c as 3.2 x 10^{19}/cm^3 and N_v as 1.8 x 10^{19}/cm^3. These values along with the intrinsic carrier concentration value of 1.01x 10^{10}/cm^3 at 300K give the Si bandgap at 300K as 1.118 (or 1.12) eV. The measured value by G.G. Macfarlane et al. in 1958 from the absorption edge spectrum of Si is also 1.1209 to 1.1256 eV at 300K, given that the exciton dissociation energy varies from 10 meV to 14.7 meV [4-5]. A critical assessment of the relevant scientific literature by M. A. Green also places the value of Si bandgap at 300K as 1.1242 eV [11].

III. Results and Discussion

The calculated values for the Si bandgap at different temperatures in Kelvin based on the Varshni's non-linear equation (7) and the equation (6) from the linear model based on the theorem for equipartition of energy are tabulated below. The calculated bandgap from the linear model is within ±1% of those from the Varshni's non-linear equation in the 100K to 600K temperature range. The author has made a simple model for temperature variation of the Fowler-Nordheim electron tunnelling current in 4H-SiC MOS device from which the conduction band offset variation with temperature has been found to be -2.9 (-2.8 more precisely) x 10^{-4} eV/K. This is similar to the bandgap variation with temperature of Si found by Pearson and Bardeen

Table I. The calculated Silicon bandgaps at different temperatures from the non-linear and linear equations.

Temperature in Kelvin (K)	Si bandgap calculated from Varshni's equation , in eV	Si bandgap calculated by the linear equation suggested by the author, in eV	Percentage error from the values in column 2	Comments
0	1.17	1.1975	2.35	
100	1.1635	1.1716	0.70	The calculated bandgap from the linear model is within ±1% from 100K to 600K.
200	1.1473	1.1457	-0.14	
300	1.1245	1.1198	-0.42	
400	1.0969	1.0939	-0.27	
500	1.0659	1.0680	0.20	
600	1.0322	1.0421	0.96	
700	0.9965	1.0162	1.98	
800	0.9591	0.9903	3.25	

The change in bandgap with temperature in the linear model is valid for all covalently bonded semiconductor. Only the value of bandgap at 300K will be different for different semiconductors. If one

considers a metal semiconductor contact and find that the bandgap of the semiconductor varies as -2.59 x 10^{-4} eV/K and the metal Fermi level remains the same, then the vacuum level above the semiconductor will be shifted up or down by the same amount and so the electron work function of the metal will also vary as -2.59 x 10^{-4} eV/K. However, Mohamed Akbi has shown the variation as -4.58 x 10^{-4} eV/K by taking an example of Ag contact on ZnO [12].

This study is giving indications that the electron work function of metals, the semiconductor bandgaps and the oxide/semiconductor band offsets may vary with temperature by the same non-linear Varshni's equation at low temperatures below 100K and may vary linearly with temperature above 100K to at least up to 600K. The linear model gives a dE_G/dT value of about -2.59 x 10^{-4} eV/Kelvin for the semiconductor bandgap. The fact that the SiO_2/4H-SiC conduction band offset changes at nearly the same rate of -2.8 x 10^{-4} eV/K indicates that the change in the bandgap with temperature for the 4H-SiC is mainly in the conduction band [7]. This may be true for other semiconductors as well. The electron effective mass will increase with temperature [5]. The direct proportionality of energy and mass has been given by Einstein in his mass-energy equivalence equation $E=mc^2$. Here, E is the constant intrinsic energy for a constant rest mass m, which Einstein originally derived, and E is relativistic total energy for a moving relativistic mass m. Relativistic mass is the rest mass times the Lorentz factor. So, when the temperature increases, the average kinetic energy of the electron increases as (3/2)kT, and the effective mass of the electron also increases by showing a decrease in the drift velocity [13], demonstrating the same direct proportionality between energy and mass as in Einstein's equation. The bandgap of thermal SiO_2 at 300K is very large at 8.93 eV. A 0.0775 eV change in bandgap at 600K from the linear model will cause a less than 1 % change in the effective masses using the relation dE/E equals dm/m, where dE and dm are differential energy and mass. Thus, the electron and light hole effective masses in thermal SiO_2 will remain stable with temperature, although it can change by about 10% in Si [5]. The low temperatures are important for quantum computers and the high temperatures are important for high temperature electronics based on semiconductors such as Silicon Carbide, Gallium Nitride, Boron Nitride, Germanium Carbide and Diamond. The linear model is applicable to the high temperature electronics in the range of 100K to 600K, and so the average kinetic energy change of a conduction electron of (3/2)kT with temperature is appropriate for the FN temperature model [7].

IV. Conclusions

The linear model for the variation of semiconductor bandgap with temperature based on the theorem of equipartition of energy at thermal equilibrium is a simple model that is applicable for high temperature electronics in the range of 100K to 600K. In Si, the semiconductor bandgap calculated from the simple model is within ±1% of the observed experimental data and the calculated bandgaps from the non-linear Varshni's equation from 100K to 600K. The linear model appears to be applicable to electron work functions of metals and oxide/semiconductor band offsets also, apart from its applicability to the semiconductor bandgaps at high temperatures. The electron and hole effective masses in thermal SiO_2 have a negligible change with temperature due to its very wide bandgap of 8.93 eV at 300K.

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