

A new method of calculating charged deep level defects density in doped semiconductors from the band offsets of MIS device interfaces

Ravi Kumar Chanana

Department of Electrical and Electronics Engineering, Galgotia's College of Engineering and Technology, Affiliated to Uttar Pradesh Technical University, Lucknow, 1, Institutional Area, Knowledge Park-II, Greater Noida – 201306 India.

Abstract: Band offsets of the semiconductor/Insulator interfaces are utilized to determine charged deep level defects density in doped single and compound semiconductors. This method is new and is able to determine very low defects densities, which are not possible to be determined by other existing techniques. A modified equation for the intrinsic Fermi level in semiconductors is formulated by including the term due to defects density.

Keywords: Deep-level defects, metal-insulator-semiconductor, charge neutrality, Diamond

I. Introduction

Point defects are zero-dimensional defects in semiconductor crystals. They can physically be a vacancy (Schottky defect), an interstitial, a vacancy-interstitial pair (Frenkel), extrinsic point defect as an impurity atom, or a split interstitial defect. In a compound semiconductor such as GaAs, the presence of two types of atoms opens the possibility of having a Ga atom in place of an As atom. This type of defect is called a Ga antisite defect. There could also be complexes of this defect with other native or extrinsic point defects such as a antisite-vacancy complex. Point defects are electrically active defects as they can be in more than one charge state as a donor or acceptor defect. As a donor, the defect is neutral when occupied by the electron and is positive after donating an electron. In the same way, the acceptor is negative when occupied by electron and becomes neutral when empty. Thus, the point defects can be classified as shallow level defects with their energy levels close to the CB or VB, or deep level defects with their energy levels away from the CB or VB edges. An understanding of point defect physics can be gained by combining theory and experiment [1].

In this article, the density of charged intrinsic defects, N_{id} , is determined by identifying the position of the intrinsic Fermi level in a semiconductor having defects from the band offset measurements of a Metal-Insulator-Semiconductor (MIS) device interface. The intrinsic defects are charged deep level defects in a doped semiconductor. The method presented utilizes the physics of charge neutrality in a semiconductor leading to formulating the intrinsic Fermi level with an additional term due to N_{id} . Defect density calculations have been performed on Si, SiC, Diamond, and some compound semiconductors. The method is particularly able to determine very low defect density in Diamond, which otherwise is not possible by the existing techniques [1]. A limitation of this method is that in semiconductors like GaAs, where EL2 amphoteric defects pin the Fermi level to the middle of the bandgap, N_{id} determination is not possible.

II. Theory

In general, the charge neutrality equation for a semiconductor material can be written as:

$$n - p + N_A^- - N_D^+ + N_{id} = 0; \quad (1)$$

where, n is the density of conduction electrons, p is the density of valence holes, N_A^- is the density of shallow acceptors, N_D^+ is the density of shallow donors, and N_{id} is the intrinsic defects density of charged acceptor/donor deep traps that compensate the shallow donors/acceptors in a semiconductor. For an n-doped semiconductor, the equation will reduce to:

$$n - p - N_D^+ + N_{id} = 0; \quad (2)$$

and further if the semiconductor is made intrinsic by removing N_D^+ , then the equation will reduce to:

$$n - p + N_{id} = 0; \quad (3)$$

This gives the equation:

$$n + N_{id} = p. \quad (4)$$

Solving the equation further,

$$\ln(1 + N_{id}/n) = \ln(p/n). \quad (5)$$

The hole concentration p in a semiconductor is given as:

$$p = N_V \exp\left(-\frac{E_F - E_V}{kT}\right), \quad (6)$$

and the electron concentration n is given as:

$$n = N_C \exp\left(-\frac{E_C - E_F}{kT}\right). \quad (7)$$

In equations (6) and (7), N_C is the density of states in the conduction band, N_V is the density of states in the valence band, E_C is the bottom of the conduction band, E_V is the top of the valence band, E_F is the Fermi level in a semiconductor, k is the Boltzmann constant, and T is the temperature in Kelvin. Substituting equations (6) and (7) for p and n in equation (5) gives:

$$\ln\left(1 + \frac{N_{id}}{n}\right) = \ln\left(\frac{N_V}{N_C}\right) + \frac{-E_F + E_V + E_C - E_F}{kT} \quad (8)$$

Since this is an intrinsic material, therefore $n = n_i$ and E_F is E_i . So the intrinsic Fermi level equation is given by:

$$E_i = \frac{kT}{2} \ln\left(\frac{N_V}{N_C}\right) + \frac{E_V + E_C}{2} - \frac{kT}{2} \ln\left(1 + \frac{N_{id}}{n_i}\right). \quad (9)$$

Usually, $N_V \cong N_C$, and $\frac{E_V + E_C}{2}$ is the middle of the bandgap for a semiconductor. Therefore,

$$E_i = \frac{E_g}{2} - \frac{kT}{2} \ln\left(1 + \frac{N_{id}}{n_i}\right). \quad (10)$$

Equation (9) is the equation for the intrinsic Fermi level in a doped semiconductor having charged defects. The second term on the right hand side of equation (10) is the additional term due to the density N_{id} of charged deep donor or acceptor traps in a doped semiconductor. The negative sign indicates that the energy due to N_{id} is above the midgap. It can be observed from this equation, that if the position of the intrinsic Fermi level in a semiconductor having defects is identified, then with the known bandgap of the semiconductor, the density of charged deep bulk defects in a doped semiconductor, N_{id} can be determined. These bulk defects will also show up on the surface of the semiconductor sample, such that, if N_{id} is high, then the surface density of defects will also be high, leading to pinning of the Fermi level at the interface with an insulator or metal as the case may be. Fermi level pinning would mean that the charge density at the interface cannot be changed by the application of bias.

III. Results and Discussion

The identification of E_i from semiconductor/insulator band offsets and calculation results of charged defect density is discussed first. MIS characterization has been performed on n^+ polysilicon gated n-channel silicon MOSFETs giving the Si/SiO₂ CBO and VBO as 3.2 eV and 4.6 eV respectively. The bandgap of SiO₂ is determined to be 8.9 eV and the electron and hole conductivity effective masses in SiO₂ are found to be 0.42m and 0.58m, where m is the free electron mass [2]. For an effective electron mass of 0.42m, the Si/SiO₂ band offset from the intrinsic Fermi level is given as $8.9 \times 0.421 \cong 3.75$ eV. The CBO of 3.2 eV added to 0.55 eV gives 3.75 eV. This 0.55 eV addition brings the CBO relative to the intrinsic Fermi level in silicon. This is also 0.01 eV less than midgap value for Si, meaning that the CBO of the Si/SiO₂ interface relative to intrinsic Fermi level of silicon, which is nearly at midgap, is 3.75 eV. The band offset for all the semiconductor/SiO₂ interfaces of 3.75 eV will thus identify the intrinsic Fermi level position in any semiconductor. Table I below gives the band offsets at the interfaces of Si, SiC and Diamond with SiO₂ in columns 4 and 5. ΔE_c in column 4 is determined by subtracting E_g from Φ_e , and Φ_e is determined by the internal photoemission of electrons from the semiconductor valence band to the oxide conduction band. ΔE_c subtracted from 3.75 eV gives $E_c - E_i$ in column 6, which is the position of the intrinsic Fermi level in that semiconductor.

Table I. The semiconductor bandgap (E_g), the photoemission barrier (Φ_e), the CBO and VBO, the position of intrinsic Fermi level (E_i), the energy due to N_{id} , intrinsic carrier concentration (n_i) and the intrinsic defect density (N_{id}) for Si, SiC and diamond interfaces with amorphous SiO₂ ($E_g=8.9$ eV).

sc	$E_g(300K)$	Φ_e	ΔE_c	ΔE_v	$E_c - E_i$	$E_i - E_g/2$	n_i (cm ⁻³)	$N_{id}(cm^{-3})$
Si	1.12	4.27	3.2	4.6	0.55	0.01	1.5E10	1.5E10
4H-SiC	3.26	6.0	2.78	2.9	0.97	0.66	1.0E-08	1.1E14
6H-SiC	3.02	6.0	2.95	2.9	0.80	0.71	1.0E-6	5.2E17
3C-SiC	2.38	6.0	3.6	2.9	0.15	1.04	1.5E-1	1.8E33
15R-SiC	2.96	6.0	3.0	2.9	0.75	0.73	2.0E-6	4.8E18
Diamond	5.5	6.9	1.4	2.0	2.35	0.4	1.0E-26	2.3E-13

Thus, column 6 provides the position of the intrinsic Fermi level below the conduction band of the semiconductors Si, SiC, and Diamond. From equation (10) it can be seen that the energy due to N_{id} relative to n_i is given in column 7. Given the n_i values in column 8, the N_{id} concentrations in the semiconductors are calculated using equation (10) and presented in column 9. It can be observed that the key to finding the N_{id} volume density is identifying the intrinsic Fermi level position in a doped semiconductor/insulator interface. Here, Si and SiC samples are doped n-type and the diamond sample is doped p-type.

A literature survey of charged defect density calculations provides N_{id} data for three of the six semiconductors in Table I: Si [3], 4H-SiC [4-5], and 6H-SiC [6]. These data match very well to the calculations in the Table and hence the author has the confidence in the theory and method of calculating N_{id} presented in this article. Comparing the N_{id} values for Si, SiC, and Diamond, it can be observed that N_{id} in SiC is at least 10^4 times more than in Si and very small in Diamond. Since the bulk defect density will be reflected at the interface also therefore it can be inferred that SiC/SiO₂ interface will have more defect states than Si and Diamond. This is also established by the MOS device study of Si, SiC and Diamond. Si MOS study gives interface trap density (D_{it}) in the low 10^{11} order near conduction band (CB) [7], SiC MOS study gives D_{it} in the 10^{13} order near CB [8], and Diamond MOS has D_{it} in the low 10^{10} order near CB [9], and these values are all without any kind of interface passivation. It needs to be mentioned here that near conduction band means physically near the semiconductor/oxide interface on the semiconductor side. SiC is thus definitely more defective than Si and Diamond, although research efforts are underway to reduce D_{it} in SiC MOS device to the level of Si MOS device [8]. It can be observed that Diamond has the best interface with the SiO₂ having the least N_{id} .

In a charged semiconductor/SiO₂ interface, band offset measurements by photoemission techniques could be in error. This problem and its simple solution is discussed next. Thermal SiO₂ grown on Si has small D_{it} of 10^{10} cm⁻² eV⁻¹ after Hydrogen passivation, and a fixed positive charge density near the interface in the oxide of 10^{10} /cm². These values of densities are small and do not affect the internal photoemission measurements, even for ultrathin oxide of 2-4 nm [10]. Thin oxides with large charge density can cause band bending in the semiconductor of the semiconductor/oxide interfaces of SiC/SiO₂ [11] or Diamond/CVD SiO₂ [9]. Fixed positive charge can cause band bending inwards so as to cause accumulation in n-semiconductor and the VBO will be less than actual and the CBO will be more than actual. Fixed negative charge in the oxide will cause depletion in the n-semiconductor and the CB will bend upwards giving less than actual CBO and more than actual VBO. A similar analysis can be performed for the p-type semiconductor, where the fixed positive charge will cause depletion in the p-semiconductor and the fixed negative charge will cause accumulation in the p-semiconductor. A good review on internal photoemission explains this problem [12]. The remedy for this is to have a thick oxide of 20 nm or more such that the voltage required at the gate of the MIS device to compensate the fixed charges fall more across the oxide due to its higher resistance and less across the semiconductor, thus causing almost no band bending at the semiconductor surface. The literature provides support for this method on SiC/SiO₂ interfaces, where oxide thickness of greater than 20 nm [13], and 40 nm [11, 14] were taken in the samples.

Another review article by Afanasev [15] provides band offset data for various compound semiconductors relevant to the electronic industry with amorphous Al₂O₃, given in Table 1 of reference [15]. The bandgap of Al₂O₃ is 6.1 eV and the MIS structures utilize a thickness of 20nm to eliminate the problems of band bending in charged semiconductor/insulator interfaces. The CBO of Si/Al₂O₃ interface from the intrinsic Fermi level of Si is 2.65 eV forming the control data for identifying the intrinsic Fermi level in other semiconductors. The Table II below provides the calculated N_{id} values for the compound semiconductors and Ge, excluding GaAs and GaSb which exhibit Fermi level pinning and is indicated by FLP in the table. Once again, column 6 provides the position of intrinsic Fermi level below the CB by subtracting ΔE_c in column 4 from 2.65 eV. It can be noticed that the intrinsic Fermi level for InGaAs, InAs, and InSb lie in the CB and have very large N_{id} values. This indicates that electron mobility will be severely degraded in devices made from these semiconductors. K. Xu et al [16] have performed band offset measurements of InP with atomic layer deposited Al₂O₃ in 2013. Their work provides the photoemission barrier (Φ_c) of 3.5 eV, thus correcting the CBO data of Afanasev [15] to 2.15 eV in column 4. The N_{id} value for GaP matches very well to the calculations performed by DLTS measurements in the literature [17]. This provides confidence in the calculated N_{id} values for other compound semiconductors and Ge in Table II by the new method in this article. It can be observed in the table below that $E_i - E_g/2$ is negative for Ge indicating that energy due to N_{id} in equation (10) becomes positive and is thus in the lower half of the bandgap.

Table II. The semiconductor bandgap (E_g), the photoemission barrier (Φ_c), the CBO and VBO, the position of intrinsic Fermi level (E_i), the energy due to N_{id} , intrinsic carrier concentration (n_i) and the intrinsic defect density (N_{id}) for several compound semiconductor interfaces with a-Al₂O₃ ($E_g=6.1$ eV).

sc	$E_g(300K)$	Φ_c	ΔE_c	ΔE_v	$E_c - E_i$	$E_i - E_g/2$	n_i (cm ⁻³)	N_{id} (cm ⁻³)
Si	1.12	3.25	2.1	2.9	0.55	0.01	1.5E10	1.5E10
Ge	0.67	2.85	2.2	3.3	0.45	-0.11	2.0E13	9.5E16
GaAs	1.42	3.45	2.0	2.7	0.65	0.06	2.1E06	FLP
In _{0.53} Ga _{0.47} As	0.74	3.45	2.7	2.7	-0.05	0.42	6.3E11	6.7E25
InAs	0.35	3.45	3.1	2.7	-0.45	0.625	1.0E15	7.5E35
GaP	2.24	4.1	1.8	2.0	0.85	0.27	2.7E06	2.8E15
InP	1.35	3.5	2.15	2.6	0.50	0.175	1.3E07	9.1E12
GaSb	0.73	3.05	2.3	3.05	0.35	0.015	1.5E12	FLP
InSb	0.17	3.05	2.9	3.05	-0.25	0.335	2.0E16	3.1E27

IV. Conclusions

The present article gives a new method of calculating the density of charged deep level defects in the doped semiconductors by identifying the intrinsic Fermi level in any semiconductor from the band offset measurements of MIS devices. The method is able to give very low defect densities that are not possible by the existing methods, such as in Diamond, Si, and InP. A limitation of this method is that it cannot be used in semiconductors whose Fermi level is pinned to the middle of the bandgap such as in GaAs or GaSb. The article also gives a new equation of the intrinsic Fermi level in semiconductors with an added term due to the density of charged intrinsic defects.

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