

Discussion on the Electron and Hole Effective Masses in Thermal Silicon Dioxide

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Abstract: This review and research study provides conclusive discussion on the electron and hole effective masses in thermal silicon dioxide placing their values at $0.42m$ and $0.58m$, where m is the free electron mass, correct to two decimal places. Only one of the masses needs to be determined as the electron and hole masses in materials add up to be equal to free electron mass with the hole effective mass being larger than the electron effective mass. The review also convinces the reader that the CBO (conduction band offset) or the Si-SiO₂ barrier height at the oxide/silicon interface of a Si MOS (metal-oxide-semiconductor) device is 3.20 eV.

Key words: Band offsets, effective masses, MOS device, materials, tunnelling.

1. Introduction

The characterization of a MIS (metal-insulator-semiconductor) device is important as it unravels the physics of the device and materials for the application of a reliable MISFET (metal-insulator-semiconductor-field-effect-transistor). An n -channel Si MOSFET (Metal-Oxide-Semiconductor-Field-Effect-Transistor) was demonstrated in early 1960, where grown thermal SiO₂ was utilized as the insulator. A Si MOS (metal-oxide-semiconductor) device has band offsets at the oxide/semiconductor interface along with the electron and hole effective mass values in the thermal SiO₂. The band offset values inform us about the amount of electron or hole current tunnelling through the oxide in the MOS device at low and high electric fields. This characterization has been in doubt ever since the invention of the transistor. One of the main reasons for this doubt has been that the hole effective mass in the Si-MOS device could not be found because the direct measurement and observation of FN hole tunnelling was not possible due to a large hole barrier at the anode of the Si-pMOS device of 4.6 eV which was higher than the electron barrier at the cathode causing electron

current to be dominant in the two-terminal MOS device. Carrier separation method using a MOSFET device resulted in the observation of hole current but the polysilicon depletion in the MOSFET prevented from accurate measurement of the hole tunnelling current in the oxide. Also, it was not known then that the flatband voltage has to be added to the applied voltage to give the oxide voltage for hole tunnelling, meaning that the science was also unknown for hole tunnelling calculations. The advent of 4H-SiC eliminated this problem and direct measurement and observation of FN hole tunnelling current was possible because of a low hole barrier of 2.91-2.92 eV in the pMOS device on 4H-SiC in accumulation [1, 2]. This paper puts to rest any doubts about the electron and hole effective masses in the thermal SiO₂ and the band offsets at the oxide/semiconductor interface of a Si or 4H-SiC MOS device by reviewing past research and providing corroborative evidence and science of a MOS device.

2. Theory

MIS characterization of a MOS device can be done easily in an Electronics laboratory of a University or

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College or at an Industry setting. The study of this device reveals the properties of the device that can make the transistor efficient and reliable. Some of the main properties are: interface states at the oxide/semiconductor interface and in the oxide near the interface, charge densities in the oxide, electrical breakdown strength of the oxide, leakage current in the oxide, the onset field for electron and hole tunnelling current, the carrier effective masses in the oxide and many others. An excellent 900-page book on the MOS physics and technology is available from Wiley and Sons publishers, written by E. H. Nicollian and J. R. Brews [3] that can provide detailed knowledge on the MOS device. This book can be supplemented with books on solid-state physics and solid-state device electronics [3]. Now, the science of the MOS device through author's recent studies has revealed that the character of a MOS device can be obtained theoretically on all parabolic semiconductors given the longitudinal electron and hole effective masses in the semiconductors and insulators and the bandgap of the materials without even fabricating the device [4-6]. Theoretical results are a sure shot based on the universal mass-energy equivalence relation, $dE/E = dm/m$. The problems would lie in experiments if a mismatch is found.

3. Results and Discussion

Since the advent of 4H-SiC semiconductor material for the design and development of high voltage power electronics devices such as MOSFETs, direct measurement and observation of FN (Fowler-Nordheim) hole tunnelling current through the MOS device is possible. The Au-SiO₂-p-4H-SiC-Si faced MOS device with Au as the cathode causes accumulation of holes at the semiconductor surface. The smaller hole barrier of 2.91-2.92 eV at the oxide/semiconductor interface as compared to the larger electron barrier at the Au cathode of 4.2 to 4.4 eV brings about the observation of FN hole tunnelling as the dominant current in the two-terminal MOS

device. The hole effective mass in thermal SiO₂ is calculated to be $0.58m$ and is confirmed by a Japanese research group, Nemoto et al. [7]. The CBO (conduction band offset) in a 4H-SiC MOS device oxidized on the C-face of a (000-1) oriented surface has been independently characterized by the author to be 2.914-2.915 eV approximated to 2.92 eV. Here, the CBO is the VBO (valence band offset) on the Si-faced 4H-SiC MOS device [8]. If 2.915 eV VBO is utilized with the slope constant of 258 MV/cm in the author's earlier study [2], then the hole effective mass comes out to be $0.576m$ which can be rounded to $0.58m$. The raw data of the author's earlier study [2] increase the slope constant to 259 MV/cm if two lower field data points are included in the FN plot. This slope constant of 259 MV/cm will give the hole effective mass of $0.5806m$ for a VBO of 2.915 eV on the Si-faced 4H-SiC MOS device [2]. If the 2.915 eV VBO is approximated to 2.92 eV, then with the slope constant of 259 MV/cm, the hole effective mass becomes $0.577m$ or nearly equal to $0.58m$. All possibilities lead to $0.58m$ as the hole effective mass in thermal SiO₂. It has also been shown by the author that the longitudinal electron and hole effective masses in parabolic semiconductors such as Si and 4H-SiC are related to the intrinsic Fermi energy level E_i in the semiconductors by the universal mass-energy equivalence relation $dE/E = dm/m$, where dE is the differential potential energy of electrons from E_i to the CB (conduction band) of the semiconductor, E is the semiconductor bandgap as the total potential energy of electrons relative to the valence band, dm is the differential mass as the longitudinal electron effective mass in the material, and m is the free electron mass. This universal relation is obtained by differentiating the mass-energy equivalence relation of Einstein, who first found that intrinsic energy E is equivalent to rest mass m_0 by the relation $E = m_0c^2$. The same relation holds for E as the total relativistic energy of a moving mass m , and c is the speed of light, given as $E = mc^2$, where $m = m_0/(\sqrt{1-v^2/c^2})$ with v as the velocity of the moving mass m . This relation is differentiable in the velocity

interval $[0, c]$, giving $dE/E = dm/m$ as the above equation for the mass m is a continuously increasing function with velocity v . Applying this universal mass-energy equivalence principle to the thermal oxide as an insulator which is modelled as a wide bandgap semiconductor, gives the electron effective mass in the oxide as $0.42m$, given that the hole effective mass in the oxide is confirmed to be $0.58m$, and the differential energy of holes from the intrinsic Fermi energy level E_i in SiO_2 to the oxide VB (valence band) is $E-dE$ [4-6]. The universal mass-energy equivalence relation is also applicable to other energy transformations such as nuclear and chemical energies.

The above paragraph assures that the electron effective mass in thermal SiO_2 is $0.42m$, where m is the free electron mass. The original establishment of this value is from the research study of Lenzlinger and Snow in 1969 [9]. The FN characteristics in Fig. 6 of the research paper for Si gives the slope constant of the plot as 258 MV/cm and the reported Si- SiO_2 barrier height by photoemission is 3.25 eV. The equation for the slope constant of the FN characteristics of a MOS device is given as [10, 11]:

$$B = 68.3 \times \left(\frac{m_{ox}}{m}\right)^{1/2} \times (\phi_0)^{3/2} \dots \dots \text{MV/cm}$$

Here, B is the slope constant at 258 MV/cm, m_{ox} is the electron effective mass in SiO_2 , and ϕ_0 is the Si- SiO_2 barrier height at 3.25 eV. The calculation by substituting the above values in the equation for the slope constant gives m_{ox} as $0.4156m$ which is reported as $0.42m$ in the graph for Si. Shifting the line of the slope a bit to the right from the bottom only, so as to properly fit the bottom most point on the graph reduces the slope to 254 MV/cm, which is also obtained for an 8.5 nm thermal oxide in another study [10, 11]. Now, using the assured value of $0.42m$ as the electron effective mass from the above paragraph and 254 MV/cm as the slope constant for the FN characteristics for Si, gives the Si- SiO_2 barrier height as 3.205 eV instead of 3.25 eV reported by Lenzlinger and Snow. Four different IPE (internal photoemission)

experiments to obtain the Si- SiO_2 barrier height have been reviewed by the author. The Si VB to SiO_2 CB reported by Yan et al. [12] is 4.3 eV using a graphene/ SiO_2 /Si device. Subtracting the Si bandgap of 1.12 eV gives the Si- SiO_2 barrier height as 3.18 eV. This is close to the obtained barrier height of 3.205 eV above. The photoemission experiment by Richard Williams [13] with the Au/ SiO_2 /n-Si device gave a Si VB to SiO_2 CB barrier height of 4.25 ± 0.06 eV. This data supports the Si- SiO_2 barrier height of 3.19 eV if $+0.06$ eV variation is taken, and after subtracting the Si bandgap of 1.12 eV [13]. Gobeli and Allen [14] showed electron emission into vacuum from p-Si giving energy from Si VB to vacuum of 5.2 eV. After subtracting 0.9 eV as the electron affinity of the SiO_2 , the Si VB to SiO_2 CB barrier height becomes 4.3 eV same as what Yan et al. [12] had obtained. This again gives the Si- SiO_2 barrier height as 3.18 eV after subtracting the Si bandgap of 1.12 eV. This is close to 3.205 eV. The Polish experimenters by Piskorski and Przewlocki [15], have found the Si VB- SiO_2 CB barrier height to be 4.4 eV. After subtracting the Si bandgap of 1.12 eV, the Si- SiO_2 barrier height is higher at 3.28 eV. It is to be noted that Al is hydrophilic whereas graphene and Au are hydrophobic. This may cause the Al-based MOS device to give a higher Si- SiO_2 barrier height due to water adsorption which is known to reduce the work function by as much as 1 eV [16]. Reduction in Al work function results in increase in metal-semiconductor work function difference ϕ_{ms} which being negative reduces the gate voltage and consequently the photoelectron current. This means that a higher photon energy is required to compensate the reduction in the photocurrent. Higher photon energy implies a higher Si- SiO_2 barrier height of 3.28 eV. It needs to be noted that the difference in barrier height is only of 0.1 eV from 3.18 to 3.28 eV. The results of the three experiments of Yan et al. [12], Richard Williams [13], and Gobeli and Allen [14] are consistent to a Si- SiO_2 CB barrier height of 3.20 eV. Thus, the author vouches for a Si- SiO_2 barrier height at the oxide/Si interface of

a Si MOS device of 3.20 eV instead of 3.25 eV as reported by Lenzlinger and Snow [9]. Moreover, a variation of ± 0.05 eV in the photoemission experiments is known to be present as shown by Richard Williams [13]. IPE of holes is not efficient. Both, Yan et al. [12] and Goodman [17] reported a SiO₂ bandgap of about 8 eV instead of 8.93 eV based on the incorrect IPE of holes.

Observing the FN onset electric field across a MOS device can also lead to determining the Si-SiO₂ barrier height. The minimum field for electron heating in the thermal SiO₂ is 2 MV/cm-eV, where 1 eV is the minimum energy needed for vacuum emission of hot electrons. This has been shown by DiMaria et al. and confirmed by the author in his earlier study on ionization in the thermal SiO₂ [18, 19]. The FN onset field in a MOS device divided by this minimum field for electron heating of 2 MV/cm-eV gives the CBO (conduction band offset) in the MOS device. Lenzlinger and Snow [9] reported an FN onset electric field of 6.41 MV/cm as shown in the graph for electron emission from Si cathode in Fig. 5 of their study [9]. This divided by the electron heating threshold in SiO₂ of 2 MV/cm-eV gives the CBO of 3.205 eV in the Si MOS device. This method further assures the Si-SiO₂ barrier height of 3.205 eV. It is to be noted that the thermal oxide is a grown oxide on semiconductors such as Si and 4H-SiC, whereas plasma or atomic layer deposited oxides of Si and Al are utilized on hetero-surfaces of GaN, GaAs or Ga₂O₃ semiconductors. They show lower bandgaps and electrical breakdown strengths and higher density of interface traps, compared to the thermally grown oxide.

The Si-SiO₂ barrier height of 3.20 eV is substantiated by the photoemission experiments as described above. The intrinsic Fermi energy level E_i in Si below its conduction band (CB) is calculated by using the universal mass-energy equivalence relation $dE/E = dm/m$, where dm/m is the relative longitudinal electron effective mass in Si in the [100] direction for one conduction valley, E is the Si semiconductor

bandgap and dE is the differential electron potential energy from E_i to the CB in Si [4]. At 300 K temperature, the longitudinal electron effective mass in Si (100) is $0.98m$ for two conduction valleys. So, $dm/m = 0.49$ for one conduction valley and the bandgap of Si is 1.12 eV. This gives dE at 300 K as $0.49 \times 1.12 = 0.5488$ eV. At low temperature near 0 K temperature, the longitudinal electron effective mass in Si (100) is $0.9163m$ for two conduction valleys [20]. So, $dm/m = 0.458$ for one conduction valley and the bandgap of Si is 1.17 eV near 0 K. This gives dE near 0 K temperature as 0.5359 eV. It shows that the position of E_i changes by only 0.0129 eV in Si between 0 K and 300 K, which is a very small change. Rounding the dE at 300 K as 0.55 eV and adding it to 3.20 eV gives the dE in SiO₂ as 3.75 eV when this CBO is aligned to E_i in Si due to charge neutrality [4]. Applying the theoretical universal mass-energy equivalence relation of $dE/E = dm/m$, where dE of 3.75 eV is divided by 8.93 eV as the SiO₂ bandgap gives the electron effective mass dm in thermal SiO₂ as $0.42m$ [4]. From the universal mass-energy relation the hole effective mass has to be $0.58m$ as dE for holes will be E minus dE for electrons or $8.93 - 3.75 = 5.18$ eV. This gives $dE/E = dm/m$ for holes to be $5.18/8.93 = 0.58$.

4. Conclusion

The electron and hole effective masses in thermal silicon dioxide is convincingly $0.42m$ and $0.58m$. The CBO at the oxide/semiconductor interface of a Si-MOS device is 3.20 eV. The universal mass-energy equivalence relation applied to SiO₂ shows that only one of the masses needs to be determined correctly. The hole mass in materials is always larger than the electron effective mass. The character of a MOS device on any parabolic semiconductor can be known theoretically given the electron and hole effective masses in materials and their bandgaps. The characterization includes the total intrinsic defects density in semiconducting materials.

Conflict of Interest

The single corresponding author declares that there is no conflict of interest.

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