Determination of hole effective mass in SiO_2 and SiC conduction band offset using Fowler–Nordheim tunneling characteristics across metal-oxide-semiconductor structures after applying oxide field corrections

Ravi Kumar Chanana[a)]
Department of Electrical and Electronics Engineering, Galgotias College of Engineering and Technology, affiliated with Uttar Pradesh Technical University, 1 Institutional Area, Knowledge Park II, Greater Noida 201306, U.P., India and Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA

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Fowler–Nordheim electron and hole tunneling characteristics across 4H-SiC MOS diodes are studied. Their slope constants are used to determine the hole effective mass in the thermal SiO_2 and the 4H-SiC conduction band offset. The hole effective mass in the SiO_2 is found to be 0.58 m, where m is the free electron mass. The 4H-SiC conduction band offset is found to be 2.78 eV. The average oxide fields used in the carrier tunneling characteristics are formulated. It is found that anode and cathode field corrections by the flatband voltage are critical in the evaluation of the above tunneling parameters. © *2011 American Institute of Physics*. [doi:10.1063/1.3587185]

I. INTRODUCTION

Fowler–Nordheim (FN) tunneling is a wave-mechanical tunneling of carriers through an exact or rounded barrier.[1,2] It models the current–voltage characteristics of a metal-oxide-semiconductor (MOS) structure at high fields,[3,4] and having a charged barrier.[5] One of the applications of the phenomenon is found in Flash memories, where the electrons are trapped and removed from a floating gate using FN electron tunneling.[2] Another application is the study of oxide reliability and breakdown mechanism. The holes have been found to tunnel from the anode into the oxide and cause defect formation in the oxide and at the anode/oxide interface.[6,7] The FN carrier tunneling equation is also used to determine the electron effective mass in the SiO_2.[3]

Figure 1 presents the energy-band diagram of a degenerate poly-Si/SiO_2/4H-SiC MOS structure biased in accumulation. It shows the occurrence of electron and hole tunneling. In particular, Fig. 1(a) shows the occurrence of FN electron tunneling from n-4H-SiC conduction band (CB) to oxide CB. At the same time, FN hole tunneling from n^+-poly-Si valence band (VB) to oxide VB is also competing. The electron tunneling dominates, since the energy barrier of 2.7 eV from the SiC CB to oxide CB is lower than the hole energy barrier of 4.55 eV from n^+-poly-Si VB to oxide VB. Figure 1(b) shows the occurrence of FN hole tunneling from p-4H-SiC VB to oxide VB. At the same time, FN electron tunneling from p^+-poly-Si CB to oxide CB is also competing. The hole tunneling dominates, since the hole energy barrier of 2.9 eV from p-4H-SiC VB to oxide VB is smaller than the electron energy barrier of 3.25 eV from p^+-poly-Si CB to oxide CB. Thus, in a particular MOS structure, electron and hole tunneling are two competing mechanisms and one dominates over the other.

The MOS diode is a two terminal device and therefore, at a time one dominating current can be measured when the device is biased in accumulation. The electron current can be measured in n-4H-SiC MOS diode and the hole current can be measured in the p-4H-SiC MOS diode. Carrier separation can be achieved by utilizing three terminal devices, such as MOSFETs,[8,9] or a p-n junction in conjunction with a MOS diode.[10] This facilitates study of the oxide degradation mechanism at high fields due to separate carriers. This forms one of the motivations for carrier separation. *N*-channel MOSFET fabricated on p-4H-SiC with n^+-poly-Si gate can be used to measure electron tunneling current from the inversion layer to the gate. It can be measured as gate-to-source/drain current. The hole current can be measured as the substrate current.[8] Similarly, p-channel MOSFET fabricated on n-4H-SiC with p^+-poly-Si gate can be used to measure hole tunneling current from the inversion layer to the gate. It can be measured as the gate-to-source/drain current. The electron current can be measured as the substrate current.[9] Metal/oxide/p^+-n SiC structure in accumulation can also be used for carrier separation. Here, the current measured at the n-type contact is due to tunneling electrons. The electrons tunnel from the gate cathode into the oxide conduction band and then diffuse through the p-type layer to the n-type substrate. The current measured at the p^+ contact is due to tunneling holes. The holes tunnel from the VB of SiC to the metal gate.[10]

FN tunneling of electrons or holes is expressed as[11]

$$J/E^2 = A\exp(-B/E). \tag{1}$$

In the equation, J is the current density in A/cm^2, E is the oxide field in V/cm, and the pre-exponent A and the slope B are given by

$$A = \frac{e^3 m}{16\pi^2 \hbar m_{ox}\varphi_0} = 1.54\times10^{-6}\frac{m}{m_{ox}}\frac{1}{\varphi_0}(A/V^2), \tag{2}$$

[a)]Electronic mail: ravikumarchanana@yahoo.co.in.

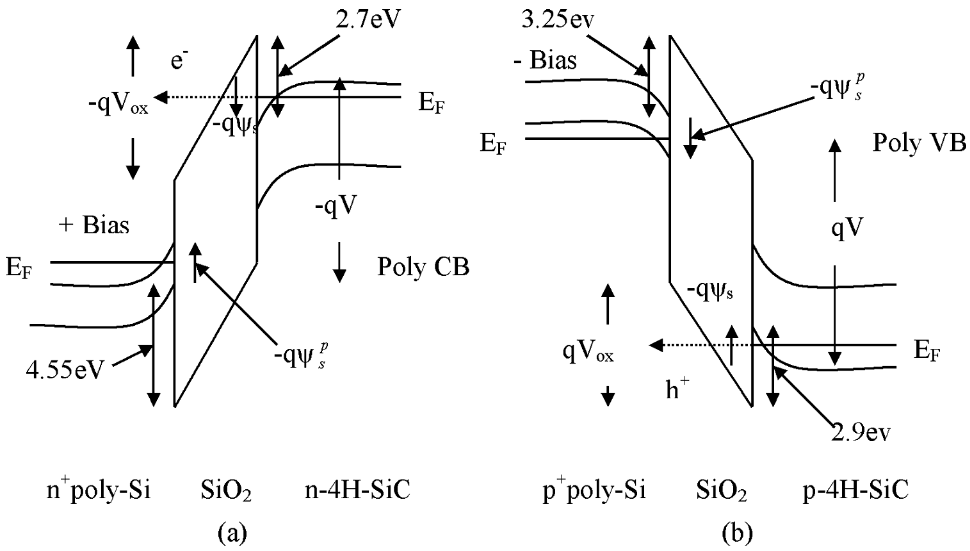

FIG. 1. Energy-band diagram of degenerate poly-Si/SiO_2/SiC MOS structures biased in accumulation. Dominant FN electron tunneling is shown in part (a) and the dominant hole tunneling is shown in part (b).

$$B = \frac{4}{3}\frac{(2m_{ox})^{1/2}}{e\hbar}\varphi_0^{3/2} = 6.83\times 10^7\left(\frac{m_{ox}}{m}\right)^{1/2}\varphi_0^{3/2}(\mathrm{V/cm}) \quad (3)$$

Here, e is the electronic charge, m is the free electron mass, m_{ox} is the electron or hole mass in the oxide, $2\pi\hbar$ is Planck's constant and φ_0 is the barrier height expressed in electron volts. A plot of $\ln(J/E^2)$ vs $1/E$ called a FN plot gives the value of the slope constant B, from which the $(m_{ox}/m)^{1/2}\varphi_0^{3/2}$ product can be obtained. Then, with a known effective mass φ_0 can be calculated, or with a known φ_0, the effective mass can be calculated. In the equation, the slope constant B is mainly sensitive to the oxide field. The $\ln(J/E^2)$ term is relatively insensitive to the changes in the oxide field. Therefore, an accurate determination of the oxide field is necessary for the accurate determination of the slope constant B. This will in turn give a correct value of effective mass or barrier height. This can be done by choosing a thick oxide, and correcting the oxide voltage by the flatband voltage. The error in the oxide thickness determination can be tolerated in the field due to large thickness.

FN tunneling of holes from the SiC anode into the oxide valence band has been observed in p-6H-SiC and p-4H-SiC MOS structures, when biased in accumulation.[10,12] Many reports on the value of hole effective mass in SiO_2 have been made.[4,9,10,12–14] The study by Waters and Van Zeghbroeck[10] have determined a range of hole effective masses from 0.23–0.37 m which are all lower than the electron effective mass of 0.42 m.[3] In another two recent studies,[12,13] the flatband voltage correction was not applied resulting in values of hole effective mass lower than the electron effective mass. Weinberg *et al.*[4] modeled the hole tunneling from the Si anode. They used the slope of the time evolution of flatband voltage to determine an approximate value of hole effective mass of 0.5 m for thermal hole. This value was considered low, thereby suggesting that the hole tunneling current is due to hot holes. Hou and Li[14] have determined a value of 0.40 m, which is again lower than that of the electron effective mass. Yang *et al.*[9] have assumed a value of 0.51 m to model the hole tunneling current in p-MOSFETs. The above research groups[4,9,10,14] have subtracted the flatband voltage from the applied voltage for oxide field determination. This is true for electron tunneling in the oxide with positive charges. In case of hole tunneling in the oxide with positive charges, the flatband voltage needs to be added to the applied voltage for oxide field determination. In the present study, a hole effective mass of 0.58 m has been determined using equations 1 and 3 on the current–voltage measurements in p-4H-SiC MOS structures in accumulation after applying the oxide field correction.

A. Oxide field formulations

Klein has studied the electronic breakdown in insulating films.[15] He proposed the field distortion model due to the presence of trapped charges in the insulator. His model demonstrated that cathode field is enhanced due to the presence of charges in the insulator. The cathode field enhancement is relevant for the electron tunneling current from the cathode of the MOS device. Miranda *et al.*[5] has curve fitted the distorted potential in the insulator with a second order polynomial. They have shown that the FN electron tunneling characteristics can be modeled with an effective-field approach having an effective injection energy.[16] As the injection energy is varied from 0 to qV_g,[16] the effective field can be calculated at any point in the oxide from anode to cathode. In the present study, Klein's field distortion model is revisited to formulate both the cathode and anode fields. Subsequently, average oxide fields for electron and hole tunneling currents are formulated. The anode field has now become important for the case of hole tunneling.

Consider a MOS capacitor with grown thermal oxide as dielectric. It has oxide charges that are located as a sheet of charge with its centroid approximately equal to the oxide thickness.[17] Figure 2 represents this MOS capacitor. The semiconductor in accumulation acts as the anode, the metal acts as the cathode, and the oxide is the dielectric between them, having thickness d. Consider a voltage V is applied across this capacitor. The capacitance of this parallel plate capacitor equals $\varepsilon_{ox}A/d$, where ε_{ox} is the oxide dielectric constant and A is the plate area. The stored charge Q equals

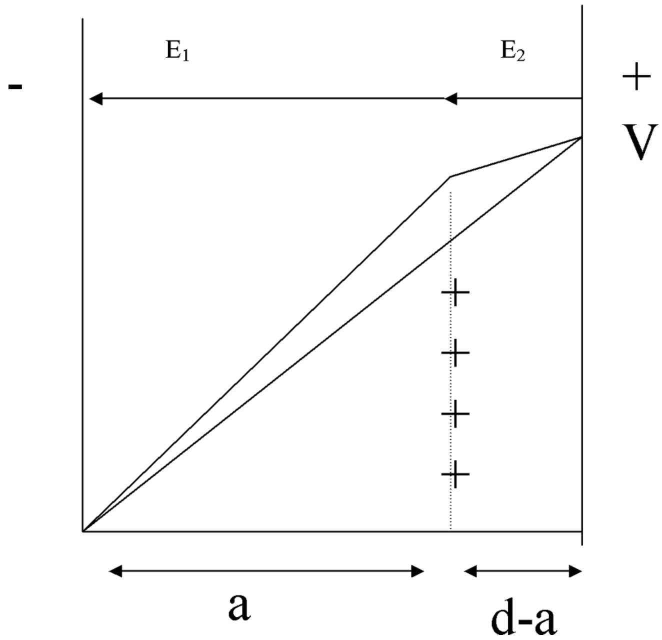

FIG. 2. The oxide dielectric between cathode and anode separated by distance *d* and with *V* volts applied across it. A uniform sheet of positive charges are shown trapped at a distance a from the cathode, enhancing the field at the cathode and reducing the field at the anode.

ε_{ox}AV/d. This can be expressed as ε_{ox}F per unit area, where *F* is the applied field. Let a small fraction $\sigma\varepsilon_{ox}F$ represent positive charges trapped in the oxide as a uniform sheet of charge. The centroid of this charge sheet is located at a distance a from the cathode and $0 < \sigma < 1$. Then the field in the oxide is distorted with the field termination from positive charges in the oxide to the cathode of E_1, and field termination from the anode to the positive charges in the oxide of E_2 as shown in the figure. Using the Gauss's law around this uniform positive charge sheet gives

$$\int \tilde{E}.ds = \frac{\sigma Q}{\varepsilon_{ox}} = E_1 A - E_2 A. \tag{4}$$

$E_1, E_2 > 0$ and *A* is the area of cross section of the Gaussian surface

$$E_1 = E_2 + \sigma F. \tag{5}$$

Equation of the potential V across the oxide with positive charges is given by

$$V = E_1(a) + E_2(d - a). \tag{6}$$

Using the two equations of potential and field, E_1 and E_2 can be calculated

$$E_1 = F\left[1 + \sigma\frac{d - a}{d}\right], \tag{7}$$

$$E_2 = F\left[1 - \sigma\frac{a}{d}\right]. \tag{8}$$

Here, E_1 is the field at the cathode and E_2 is the field at the anode. It can be observed from these formulae that as the number of positive charges increases, i.e., σ tends to 1, the field at the cathode increases and the field at the anode reduces. If negative charges were trapped in the oxide, the field at the cathode will decrease and the field at the anode will increase. When the current carriers across the oxide are predominantly electrons with the MOS sample biased in accumulation, the field at the cathode is considered. The presence of positive charges in the oxide enhances the field at the cathode given by Eq. (7). Therefore, the applied voltage results in larger current due to electrons through the oxide. To obtain the true field across the oxide (without positive charges), $|V_{fb}|$ is subtracted from $|V|$, as V_{fb} is the measure of the amount of positive charges. It equals $(\sigma|V|)/2$, if the centroid of the charges is assumed to be at $a = d/2$. The relationship between trapped charge density within the oxide and the flatband voltage is also arrived at by Miranda *et al.*[16] It can be shown to be the same as above. The corrected cathode field E_1 now becomes the same as the cathode field *F* in the oxide without charges. The corrected average field across the oxide becomes equal to $(|V| - |V_{fb}|)/d$. The formulation presented above can be used to arrive at this average field. When the current carriers across the oxide are predominantly holes with the MOS sample biased in accumulation, the field at the anode is considered. The presence of positive charges in the oxide reduces the field at the anode given by Eq. (8). Therefore, the applied voltage results in smaller current due to holes through the oxide. To obtain the true field across the oxide (without positive charges), $|V_{fb}|$ must be added to $|V|$, as again V_{fb} is the measure of the positive charges in the oxide. The corrected anode field E_2 now becomes the same as the anode field *F* in the oxide without charges. The corrected average field across the oxide becomes $(|V| + |V_{fb}|)/d$. Once again, the formulation given above can be used to arrive at this average field.

The expression for the oxide voltage for degenerate n^+ poly-Si/SiO_2/n-Si MOS structure undergoing FN electron tunneling when biased in accumulation and having positive charges in the oxide has been obtained recently,[18] and can also be determined from Fig. 1(a) as:

$$V_{ox} = |V| - |V_{fb}| - \psi_s + \psi_s^p, \tag{9}$$

where ψ_s^p is the amount of band bending in poly-Si gate due to depletion of electrons at the n^+-poly-Si surface. It is shown in the figure with a negative sign, since the electron depletion results in lowering of the Fermi level E_F rather than the CB moving up. It can be eliminated from the equation if metal gate is used. The band bending in SiC due to electron accumulation at the SiC surface, ψ_s, can also be ignored, as it is negligible compared to $(|V| - |V_{fb}|)$ for thick oxides. Therefore, the oxide field needs to be corrected only by the flatband voltage in case of use of metal gates and thick oxides, as in the present study. For electrons as carriers across the oxide, the field at the cathode is considered. It increases due to the presence of positive charges in the oxide. Therefore, the true voltage across the oxide without charges is given by

$$V_{ox} = |V| - |V_{fb}|. \tag{10}$$

This is the case in the Si technology where charges in the oxide after gate oxidation are usually positive. For oxide with net negative charges, the field at the cathode decreases. Therefore, the true voltage across the oxide without charges will be

$$V_{ox} = |V| + |V_{fb}|. \tag{11}$$

Figure 1(b) shows the dominating hole tunneling current in p-4H-SiC MOS biased in accumulation. For holes as carriers across the oxide, the field at the anode is considered. It reduces due to the presence of positive charges. Therefore, the true voltage across the oxide without the charges is given by

$$V_{ox} = |V| + |V_{fb}|. \tag{12}$$

For oxide with net negative charges, the field at the anode increases. Therefore, the true voltage across the oxide without charges is given by

$$V_{ox} = |V| - |V_{fb}|. \tag{13}$$

II. EXPERIMENTAL

The samples utilized in the present study have 40 nm thick SiO_2 grown on n- and p-type 4H-SiC, and annealed in NO at 1150°C for 2 h. The procedure for the oxide growth is described in an earlier study.[19] Three MOS samples were used. One n-4H-SiC MOS with Mo gate was used in accumulation to reveal electron tunneling current, and two p-4H-SiC MOS with Au and Mo gates were used in accumulation to identify hole tunneling current. Keithley's CV-82 system has been used for measurement of capacitance–voltage (C–V) and current–voltage (I–V) characteristics on the MOS samples. The C–V/I–V combination system employs Metrics ICS software. It uses the model 590 C–V analyzer, model 595 Quasistatic C–V meter and model 230 programmable voltage source. The samples were prepared at Auburn University, AL, and the measurements were performed at the Vanderbilt University, Nashville, TN. It needs to be mentioned here that, the applied voltage V on p-type MOS device in accumulation is negative in value. In the n-type device, it is positive in value. Also, the flatband voltages are negative for positive charges in the oxide, and positive for negative charges in the oxide. Keeping the above in view, the absolute values of voltages are used in the oxide field formulations.

III. RESULTS AND DISCUSSION

Figure 3 presents typical I–V measurements for MOS capacitors in accumulation. It shows increased current at the onset of FN electron tunneling and beyond in n-4H-SiC MOS with Mo gate and FN hole tunneling in p-4H-SiC MOS with Au and Mo gates. The dominating hole current in p-4H-SiC MOS with Au and Mo gates are same as the hole barrier from SiC VB to oxide VB of 2.9 eV is lower than the electron barrier of 4.2 eV for Au and 3.8 eV for Mo gate to oxide CB.

Figure 4 presents the FN plots for the three MOS samples at large oxide fields. Using Eqs. (1) and (3), the slope constants for electron and hole tunneling currents have been calculated. The slope constant B for electron tunneling equals 206 MV/cm. Here the oxide voltage correction is given by Eq. (11), but is ignored as the measured flatband voltage is less than 1 V. Given the electron effective mass of 0.42 m, the barrier height for electrons from SiC CB to oxide CB is calculated to be 2.78 eV. The slope constant B for hole tunneling in p-4H-SiC equals 258 MV/cm after applying the oxide voltage correction. Here, the measured flatband voltage from the capacitance–voltage plot equals -6 V. This value indicates the existence of positive charges in the oxide, and therefore the oxide voltage correction is given by Eq. (12). The corrected average field across the oxide becomes $(|V| + |V_{fb}|)/d$. Using the hole barrier height from SiC VB to oxide VB of 2.9 eV, the hole effective mass in the SiO_2 is calculated to be 0.58 m. The above results are presented in Table I.

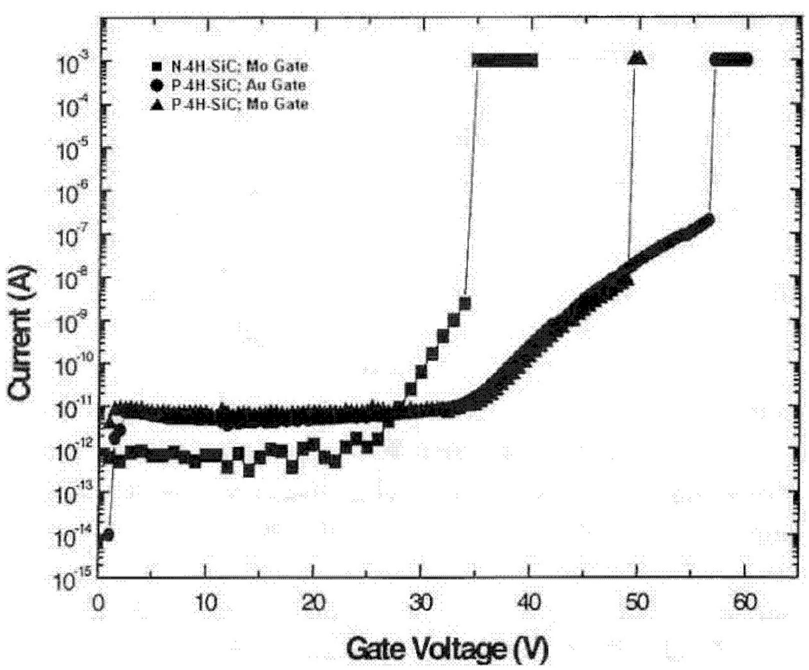

FIG. 3. Current vs voltage curves on n-4H-SiC MOS and p-4H-SiC MOS biased in accumulation. The magnitudes of voltages and currents are plotted. The MOS capacitors have 40 nm thick wet oxide annealed in NO at 1150 °C for 2 h. The device gate area is 10^{-3} cm^2.

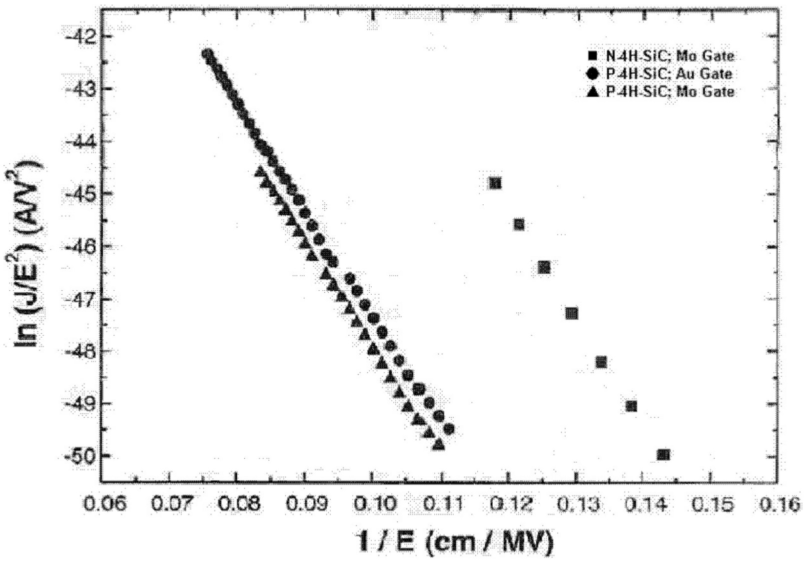

FIG. 4. FN-plots on *n*- and p-4H-SiC MOS capacitors obtained from the I–V measurements in accumulation. The MOS capacitors have 40 nm thick wet oxide annealed in NO at 1150 °C for 2 h. The device gate area is 10^{-3} cm^2.

A discussion on the flatband voltage is also made here. The flatband voltage V_{fb} is given by

$$V_{fb} = W_{ms} - (Q_f/C_{ox}), \quad (14)$$

where W_{ms} is the metal-semiconductor work function difference, Q_f is the density of fixed oxide charges, and C_{ox} is the oxide capacitance per unit area. It can be observed that if (Q_f/C_{ox}) is made negligible, as in the Si technology, then $V_{fb} = W_{ms}$. That is, the correction for W_{ms} will still have to be made in the oxide field. This may be the case for tunnel oxides of Vexler *et al.*,[13] who have not applied the anode field correction for hole tunneling. This correction is all the more important for thin tunnel oxides in order to determine precise values of oxide fields and thereby the hole effective mass. The measurement of V_{fb} from the C–V plot includes the effect of W_{ms} along with the oxide charges. It has been used directly to obtain the corrected average oxide fields. However, in the formulation of the cathode and anode fields, only the effect of charges in the oxide has been considered.

IV. CONCLUSION

The oxide field correction by the flatband voltage is critical in the determination of effective mass of electrons or holes, or the determination of barrier heights. For electron tunneling, cathode field correction is applied and for hole tunneling anode field correction needs to be applied. With the above in view, a value of hole effective mass in the SiO_2 of 0.58 m is determined and it assures a 4H-SiC VB offset of 2.9 eV. The 4H-SiC CB offset of 2.78 eV is determined by using the electron effective mass of 0.42 m, and it confirms the band offset of 6 eV from top of the 4H-SiC VB to oxide CB determined earlier.[20] The results also negates the conclusion that there is a barrier lowering due to large density of interface states near the SiC CB.[21] Further, the above method can be used to find electron or hole effective masses or band offsets in insulating materials utilizing the metal-insulator-semiconductor test structures.

TABLE I. Parameters of FN tunneling characteristics on *n*- and *p*- 4H-SiC MOS.

Serial no.	Sample	Flatband voltage (V)	Slope constant B (MV/cm)	m_{ox}/m	φ_o (eV)
1.	*n*-4H-SiC-MOS	<1	206	0.42 (used)	2.78 (determined)
2.	*p*-4H-SiC-MOS	−6	258	0.58 (determined)	2.9 (used)

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