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Enhanced tunneling in stacked gate dielectrics with ultra-thin HfO_2 (ZrO_2) layers sandwiched between thicker SiO_2 layers

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Abstract

There has been a search for alternative dielectrics with significantly increased dielectric constants, K, which increases in physical thickness proportional to K, and therefore would significantly reduce direct tunneling. However, *increases* in k to values of 15–25 in transition metal and rare earth oxides are generally accompanied by *decreases* in the conduction band offset energy with respect to Si, E_B, and the effective electron tunneling mass, m_{eff}, which mitigate gains from increased thickness. A novel technique, based on stacked dielectrics, is used to obtain the tunneling mass-conduction band offset energy product. When combined with optical measurements of tunneling barriers, this yields direct estimates of the tunneling mass.

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1. Introduction

In order to reduce direct tunneling in metal oxide semiconductor, MOS, devices with equivalent oxide thickness, EOT, less than 1.5 nm, and extending below 1 nm, there has been a search for alternative dielectrics with significantly increased dielectric constants, K, allowing increases in physical thickness proportional to K, and thereby have the potential to significantly reduce direct tunneling. However, large *increases* in K to values of 15–25 in transition metal and rare earth oxides are generally accompanied by *decreases* in the conduction band offset energy with respect to Si, E_B, and the effective electron tunneling mass, m_{eff}. Since direct tunneling scales as an exponential function of the square root of the $(E_{Bi})(m_{eff})$ product, it is important do determine this product relative to K in order to calculate the extent to which decreases in this product can mitigate decreases in tunneling anticipated from increased physical thickness along. This paper presents a novel method for obtaining the $(E_{Bi})(m_{eff})$ product for high-K gate dielectrics. It is based on a quantum mechanical *WKB-approximation* applied to large bias dependent *increases* in tunneling with respect to reference SiO_2 devices, in *symmetric stacked devices* with ultra-thin HfO_2 layers (~0.5 nm) sandwiched between thicker SiO_2 layers

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(~1.0–1.5 nm). The extension to other high-K alternative dielectrics is obvious.

In addition to providing a method for obtaining the $(E_{Bi})(m^{*}_{\mathrm{eff}})$ product, the results presented below are of importance for advanced dielectrics with stacked high-K components with different dielectric constants, K, tunneling barriers, E_B, and effective tunneling masses, m_{eff}, as for example the HfO_2–Al_2O_3 laminates of Refs. [1,2].

2. Experimental results

Stacked structures were comprised of remote plasma processed Si–SiO_2 substrates 1.5 nm thick, remote plasma deposited HfO_2 layers 0.5–1.5 nm thick, and SiO_2 layers 1.5 nm thick [3]. N^+ Si substrates and Al metal gates were used to set the flat band voltage, V_{fb}, of the stacked structures close to zero. Analyses of capacitance–voltage, C–V, traces were based on the profile in Fig. 1. The increased thickness of ~1.2 nm for initially-deposited and *encapsulated* 0.5 nm HfO_2 film is due to interfacial Hf *silicate formation* during deposition and annealing as has been identified by on-line X-ray photoelectron spectroscopy, XPS. There is also an accompanying reduction of the SiO_2 layer thickness from 1.5 to 1.2 nm. Values of EOT were determined from C–V measurements using the procedures developed by Hauser and co-workers [4]. EOT decreased from ~2.97 nm for the SiO_2 reference device with 3 nm of SiO_2, to ~2.75 nm for the HfO_2 device with the initially-deposited 0.5 nm HfO_2 layer. The analysis of the C–V data based on Fig. 1 gives a value of K of ~20 for the middle layer consistent with a silicate terminated HfO_2 layer. Current density versus voltage, J–V. traces were obtained in a substrate injection mode. Fig. 2 compares room temperature J–V traces for a MOS capacitor, MOSCAP, with a 3.0 nm SiO_2 dielectric, with traces for MOSCAP stacks including *initially-deposited* 0.5 and 1.0 nm HfO_2 films. The J–V characteristic for the SiO_2 reference device is in agreement with a J–V simulation of Ref. [5]. All J–V curves display a similar weak temperature dependence confirming that tunneling is the dominant transport mechanism. J–V curves for the stacked devices are qualitatively different than the SiO_2 device, displaying bias voltage dependent increases in current at 3 V of ~1000 for the 0.5 nm HfO_2 device and ~3000 for 1.0 nm HfO_2 device.

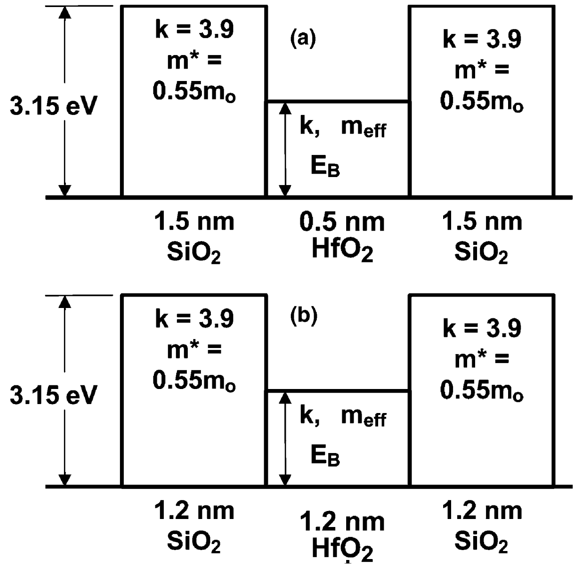

Fig. 1. Barrier layer model for the stacked dielectrics in Fig. 2 with 0.5 nm as-deposited HfO_2. (a) As-deposited, (b) after device processing.

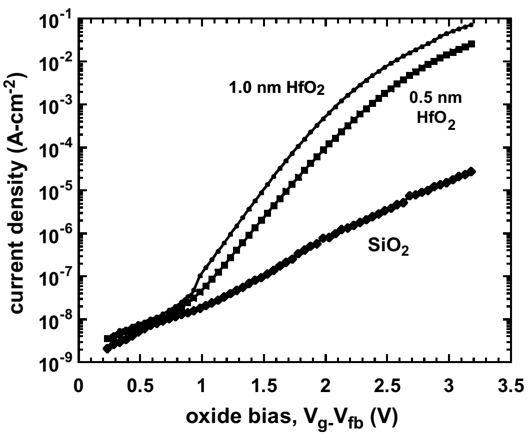

Fig. 2. Room temperature J–V characteristics for 3 nm SiO_2 and two stacked devices with 0.5 and 1.0 nm HfO_2.

3. Analysis of tunneling data in devices with stacked dielectrics

The objective of this section is to provide an explanation for the significant increases in tunnel-

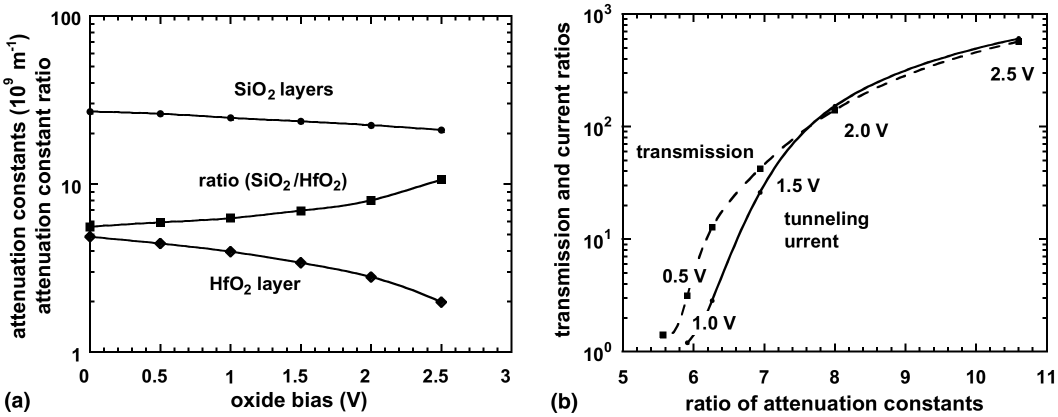

Fig. 3. (a) Transmission attenuation constants, and their ratio versus oxide bias. (b) Current ratio, and normalized transmission ratio versus ratio of SiO$_2$/HfO$_2$ attenuation constants of (a). Bias voltages are indicated as well.

ing current in the stacked-dielectric MOSCAPs of Fig. 2. These increases reflect changes in the energy of the tunneling electron relative to the dielectric conduction band as it *traverses* the homogeneous SiO$_2$ dielectric and the stacked dielectric of Fig. 1. The departure from a near exponential dependence in the reference SiO$_2$ device is correlated with differences between the tunneling attenuation constants, $\alpha_i t_i$, in the three regions of the stacked dielectric of Fig. 3. If $E_{\mathrm{B}i}$ is the tunneling barrier with respect to the substrate/gate metal Fermi level, and $m_{\mathrm{eff}i}$ is tunneling mass, then the tunneling attenuation factor for the ith layer) $\alpha_i t_i$, is given by $4\pi t_i(2m_{\mathrm{eff}i}E_{\mathrm{B}i})^{0.5}/h$ with $i = 1$, 2, and 3 for stack, and 1 for the homogeneous SiO$_2$ device. Neglecting reflections at potential steps in Fig. 1 for the device with the composite or staked dielectric, the relative tunneling current is proportional to the product of tunneling transmission terms, $\Pi_i \exp(-\alpha_i t_i)$ [5].

This *WKB* approach is supported by plots in Fig. 3(a) and (b). The data in Fig. 4 have been fit by setting $(E_{\mathrm{B}i})(m_{\mathrm{eff}}) = 0.23 \pm 0.01m_0$ for HfO$_2$. This value was obtained by iterating between the plots in Fig. 3(a) and (b) until an acceptable fit between the calculation and experiment was obtained. Using a value of $E_{\mathrm{B}} \sim 1.5$ eV for the Si–HfO$_2$ conduction band offset energy, this corresponds to a value of $m_{\mathrm{eff}} = 0.15 \pm 0.02m_0$, in good agreement with other analyses of tunneling through HfO$_2$ films [7].

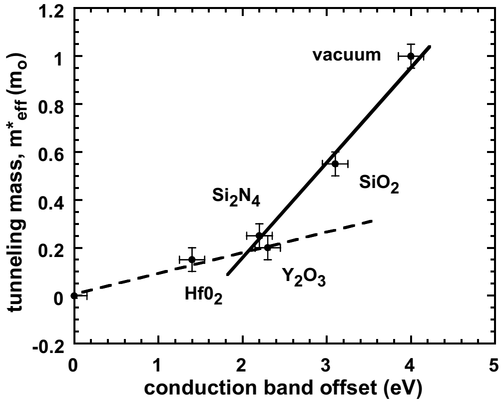

Fig. 4. Plot of the tunnel mass versus the conduction band offset energy with respect to silicon. The solid line is what is expected on the basis of the Franz two-band model for conduction band states that are extended in character. The dotted line represents the changes that occur when the conduction band states are localized as in the transition metal and rare dielectrics.

The values of $\alpha_i t_i^*$ as a function of bias in Fig. 3(a) are obtained by assuming the applied potential drops in the three regions of Fig. 1 are proportional to the relative values of K, i.e., the continuity of $k_i\varepsilon_0 E_i$, where E_i is the electric field in the ith region. The sum of $E_i t_i$'s is set equal to the bias voltage across the oxide, $V_{\mathrm{g}} - V_{\mathrm{fb}}$. After the iterations, the product of the $\alpha_i t_i^*$'s is eventually used for the fit in Fig. 3(b), so that values of $E_{\mathrm{B}i}$

can be obtained and inserted in the $\alpha_i t_i^*$ for HfO_2. $E_{Bi}(V)$ values are approximated by $E_{Bi}(0)$ minus the average potential drop in that region, with t_i^* normalized to 1.2 nm. The relatively small decreases in $\alpha(SiO_2)$ compared to larger decreases in $\alpha(HfO_2)$ are due the differences in the $E_{Bi}(0)$, 3.15 eV for SiO_2 and 1.5 eV for HfO_2, are reflected in the marked increase in their ratio with increasing bias. This means that as the bias across the composite in these films is increased, the current is increasingly determined by the SiO_2 layers. The increased ratio of current at 3 V is ~1000 is due to *minimal wave function attenuation* in the HfO_2 layer. The magnitude of the increase is consistent with a decrease of the SiO_2 thickness from 3.0 in the reference device to *an effective thickness* of 2.4 nm in the stacked device; i.e., a 10× increase in current for each 0.2 nm thickness decrease. This explanation is supported in Fig. 3(b), which displays ratios of measured currents, and normalized transmission for the SiO_2 stack component, both as functions of the ratio of the normalized attenuation constants. Differences between these plots for $V < 1.5$ V indicate HfO_2 layers are contributing to attenuation at low voltages, but not at biases >1.5 V where the traces overlap.

If the thickness of the HfO_2 layer is *increased* by >5, instead of current increasing with increasing bias, it is reduced relative to SiO_2 devices. Identifying the HfO_2 *thickness* at which this change occurs yields a direct measure for an approximate high-K $(m_{\rm eff})(E_{Bi})$ product.

4. Discussion and conclusions

This paper has demonstrated a new approach for obtaining the $(m_{\rm eff})(E_{Bi})$ product for high-K dielectrics. In addition, the results presented above identify a significant limitation for stacked dielectrics in which the band offset energy and dielectric constant of one component are significantly less than in the second, as for example in HfO_2–Al_2O_3 laminates, where $m_{\rm eff} \sim 0.15m_0$ and $E_B = 1.5$ eV, and Al_2O_3, where $m_{\rm eff} \sim 0.4m_0$ and $E_B = 2.7$ eV, and where the respective K-values are ~20–25 for HfO_2 and ~9 for Al_2O_3. The J–V tunneling curve will display a significant rise in current for bias voltages greater than 1 eV, which may be detrimental in mobile device applications.

Next, it is important to comment on the magnitude of the low effective value for tunneling mass for HfO_2, and its impact on direct tunneling in silicate alloys. It is significantly smaller than the mass of $\sim 0.55m_0$ for SiO_2 and it is important to understand the microscopic origin for this difference. Fig. 5 contains a plot of tunneling mass versus band offset energy that is consistent with the Franz two band model of Ref. [6]. The masses for vacuum, SiO_2, Al_2O_3 and Si_3N_4 dielectrics fall on a straight line, along with the extrapolated mass for Y_2O_3; however the mass for HfO_2 does not. The Franz two-band model is an effective mass approximation that works best when the conduction and valence band states are extended and free electron like. This is the case for SiO_2 and Al_2O_3, where the lowest conduction band states are 3s* anti-bonding states, and it is a good approximation for Si_3 N_4 where Si 3s* state dominate. The lowest conduction band states in transition metal oxides are anti-bond transition metal d* states; however the overlap of these states with transition metal s* states is differs and is proportional to the difference between the atomic nd and $n+1$s states of the transition metal; n is the principal quantum num-

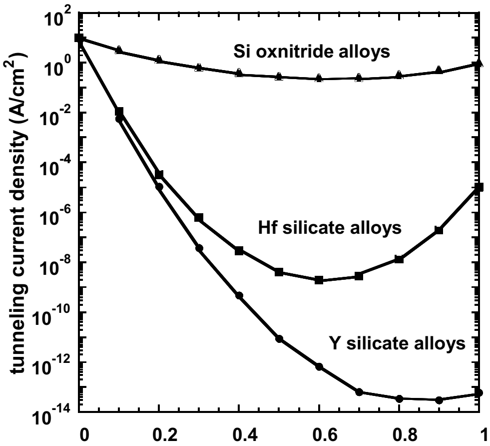

Fig. 5. Calculated direct tunneling currents for an oxide bias of 1 V, and for an equivalent oxide thickness of 1.2 nm for Si oxynitride alloys, Hf silicate alloys and Y silicate alloys as function of alloy composition as based on a WKB model calculation.

ber equal to 5 for Hf and 4 for Y. The point for Y_2O_3 falls on the plot for the oxides with extended free electron like conduction band states, and the point for HfO_2 is well removed from this fit to the data. Finally, the low value of $m_{\mathrm{eff}} = 0.15m_0$ coupled with an $E_{\mathrm{B}} \sim 1.5$ eV gives tunneling current for a given EOT in the middle of the silicate alloy regime, whereas for Y silicates, the higher values of both $m_{\mathrm{eff}} \sim 0.25m_0$ and $E_{\mathrm{B}} \sim 2.3$ gives a minimum tunneling current at the Y_2O_3 composition [7,8].

Acknowledgements

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