Step tunneling enhanced asymmetry in metal-insulator-insulator-metal (MIIM) diodes for rectenna applications

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ABSTRACT

We combine nanolaminate bilayer insulator tunnel barriers ($\text{Al}_2\text{O}_3/\text{HfO}_2$, $\text{HfO}_2/\text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3/\text{ZrO}_2$) deposited via atomic layer deposition (ALD) with asymmetric work function metal electrodes to produce MIIM diodes with enhanced I-V asymmetry and non-linearity. We show that the improvements in MIIM devices are due to step tunneling rather than resonant tunneling. We also investigate conduction processes as a function of temperature in MIIM devices with Nb$_2$O$_5$ and Ta$_2$O$_5$ high electron affinity insulators. For both Nb$_2$O$_5$ and Ta$_2$O$_5$ insulators, the dominant conduction process is established as Schottky emission at small biases and Frenkel-Poole emission at large biases. The energy depth of the traps that dominate Frenkel-Poole emission in each material are estimated.

Keywords: tunnel diodes, metal-insulator-metal, MIM diodes, MIIM, step tunneling, conduction mechanisms, atomic layer deposition

1. INTRODUCTION

Thin film MIM based tunneling devices are seeing renewed attention for high speed applications [1-6]. Besides rectenna solar cells [7-9], these applications include hot electron transistors [10,11] and infrared (IR) detectors [12,13]. MIM diodes have also been proposed for macroelectronics applications [14] such as backplanes for liquid-crystal displays (LCDs) [15]. We have recently shown that combining ultrasmooth amorphous metal bottom electrodes with high quality insulators deposited via atomic layer deposition allows the formation of MIM devices with well controlled quantum-mechanical tunneling [1,2]. For rectenna based solar cells as well as other potential applications of MIM diodes, highly asymmetric and non-linear current vs. voltage (I-V) behavior at low applied voltages is desired [8]. The ultrahigh frequency terahertz operation regime desired for these devices requires that the electron transport time between terminals be as short as a few femtoseconds. The standard approach to achieving high speed rectification in an MIM device is based on Fowler-Nordheim tunneling (FNT) conduction in conjunction with the use of asymmetric work function metal electrodes (metals with different work functions, $\Phi_{\text{M1}} \neq \Phi_{\text{M2}}$) to produce asymmetric, polarity dependent electron transport [16,17]. However, the amount of asymmetry achievable using this approach is limited by the $V_{\text{bi}}$ ($\Delta\Phi_{\text{M}}$) that can be obtained using practical electrodes. Here we investigate an alternative approach in which an asymmetric bilayer tunnel barrier is formed by combining two insulators with different band-gaps ($E_g$) and electron affinities ($\chi$), to produce metal-insulator-insulator-metal (MIM) devices [6], as illustrated in Figure 1.

In this work, we combine nanolaminate bilayers of $\text{Al}_2\text{O}_3/\text{HfO}_2$, $\text{HfO}_2/\text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3/\text{ZrO}_2$ with asymmetric work function electrodes and demonstrate experimentally (i) that bilayer insulator tunnel barriers enable tuning of asymmetry ($\eta_{\text{sym}}$) and non-linearity ($f_{\text{NL}}$), (ii) that $\eta_{\text{sym}}$ and $f_{\text{NL}}$ values are sensitive to the arrangement of the individual insulator layers with respect to the larger and smaller $\Phi_{\text{M}}$ electrodes (e.g. $\text{M}_1\text{I}_1\text{M}_2$ vs. $\text{M}_1\text{I}_2\text{M}_2$), and (iii) that bilayer tunnel insulators can be arranged to either enhance or oppose (even reverse) the built-in asymmetry of the asymmetric work function electrodes. Although as illustrated in Figure 1, I-V asymmetry could in principle be enhanced through either resonant tunneling or step tunneling, we show that step tunneling – the step reduction in the minimum tunnel distance that occurs at the applied bias at which tunneling may begin to take place through only the wider band-gap insulator layer – dominates the influence of the bilayer tunnel barrier on the electrical behavior of the $\text{M}_1\text{I}_1\text{M}_2$ devices in this study.

The selection of insulator is critical. Insulators with a large electron affinity ($\chi$) are attractive for MIM devices as they produce small energy barriers at the metal electrodes and ideally allow FNT to occur at small applied bias (low $V_{\text{ON}}$). It has been suggested that Nb$_2$O$_5$ and Ta$_2$O$_5$, insulators with large $\chi$, should be promising candidate insulators for rectenna applications [18,19]. In this work, we also investigate conduction processes in Nb$_2$O$_5$ and Ta$_2$O$_5$ and find that conduction...
in these materials is dominated by thermal processes - Schottky emission at low bias and Frenkel-Poole emission at higher biases. Because tunneling does not appear to play a strong role in the operation of these MIM devices, it is concluded that an Nb$_2$O$_5$ / Ta$_2$O$_5$ bilayer would not be a good candidates for improving asymmetry in an MIIM device.

![Figure 1.](http://proceedings.spiedigitallibrary.org/) Energy band diagrams of symmetric electrode MI$_1$I$_2$M tunnel diodes, illustrating resonant tunneling (left) and step tunneling (right). For all band diagrams, the left electrode is grounded and voltage is applied to the right electrode (adapted from [20]).

## 2. EXPERIMENTAL DETAILS

### 2.1 Fabrication

MIM and MIIM diodes were fabricated on Si substrates capped with 100 nm of thermally grown SiO$_2$. A 150 nm thick ZrCuAlNi (ZCAN) amorphous metal bottom electrode was then deposited via DC magnetron sputtering using a Zr$_{40}$Cu$_{35}$Al$_{15}$Ni$_{10}$ metal target [1,2]. Insulating tunnel barrier layers were deposited via ALD using a Picosun SUNALDE R-150B at a deposition temperature of 250 °C. Trimethylaluminum (TMA), tetrakis (ethylmethylamino) hafnium (TDMA-Hf) tetrakis (ethylmethylamino) zirconium (TEMA-Zr), Tantalum ethoxide (Ta$_2$(OC$_2$H$_5$)$_{10}$) and niobium ethoxide (Nb$_2$(OC$_2$H$_5$)$_{10}$) were used as the metal precursors for Al$_2$O$_3$, HfO$_2$, ZrO$_2$, Ta$_2$O$_5$, and Nb$_2$O$_5$, respectively. Deionized water was used as the oxidant in all depositions. Nanolaminate insulator bilayers (HfO$_2$/Al$_2$O$_3$, Al$_2$O$_3$/HfO$_2$, or ZrO$_2$/Al$_2$O$_3$) were deposited in one continuous run without breaking vacuum. Top electrodes were formed by evaporating Al dots (~0.25 mm$^2$) through a shadow mask. To avoid any possibility of crystallization of either the ALD insulators or the ZrCuAlNi bottom electrode, all devices were studied without post-deposition annealing.

### 2.2 Characterization

The thickness of the insulator films on Si was measured with a J.A. Woollam WVASE32 spectroscopic ellipsometer using a Cauchy model. Optical dielectric constants were also determined with spectroscopic ellipsometry using 10 nm thick films deposited on silicon substrates. Electrical measurements were conducted at room temperature using a probe station, a dark box, and an Agilent 4156C semiconductor parameter analyzer. The noise floor of this system is estimated to be on the order of 10$^{-2}$ pA. The ZCAN bottom electrode was always held at ground with bias applied to the Al top gate. To mitigate the impact of displacement current, all I-V curves were swept from zero-bias to either the maximum positive or negative bias. I-V asymmetry, $\eta_{asym}$, is defined as negative device current divided by positive current $|I_{-}| / I_{+}$, so that $\eta_{asym} = 1$ indicates symmetric operation. Non-linearity, $f_{NL}$, is defined as $(dI/dV) / (I/V)$. Band diagrams were simulated using the Boise State University Band Diagram program [21]. Materials parameters used in simulations are: electron affinity ($\chi$) = 1.3 eV, bandgap ($E_G$) = 6.4 eV and relative dielectric constant ($\kappa$) = 7.6 for Al$_2$O$_3$; $\chi$ = 2.5 eV, $E_G$ = 5.8 eV and $\kappa$ = 18 for HfO$_2$; $\chi$ = 4 eV, $E_G$ = 4.3 eV and $\kappa$ = 25 for Nb$_2$O$_5$ [18,22]; $\chi$ = 3.75 eV, $E_G$ = 4.4 eV and $\kappa$ = 26 for Ta$_2$O$_5$ [22,23]. The work function ($\Phi_M$) of the ZrCuAlNi and Al electrodes were determined to be 4.2 eV and 4.8 eV, respectively, as have reported in previous work [6].

## 3. EXPERIMENTAL RESULTS & DISCUSSION

### 3.1 Step tunneling in metal-insulator-insulator-metal (MIIM) diodes

Figure 2 shows (a) log (J) vs. V, (b) log ($\eta_{asym}$) vs. V, and (c) $f_{NL}$ vs. V plots for ZrCuAlNi/Al$_2$O$_3$/HfO$_2$/Al/M$_1$I$_2$M$_2$ and ZrCuAlNi/HfO$_2$/Al$_2$O$_3$/Al M$_1$I$_2$M$_2$ diodes. The HfO$_2$ and Al$_2$O$_3$ layers in these devices were deposited using 32 and 28...
ALD cycles, respectively. The estimated thicknesses of the bottom and top insulator layers are ~1 nm and ~2.5 nm, respectively. Included for reference are approximately 5 nm thick single insulator Al₂O₃ and HfO₂ M₁M₂M₃ diodes, deposited using 56 and 65 ALD cycles, respectively.

The inherent asymmetry of these dual insulator barriers is seen in the equilibrium band diagrams shown in Figure 3. The difference in the electrical behavior of these devices is qualitatively explained by the non-equilibrium band diagrams, which illustrate the approximate onset of step tunneling (a) at positive bias (right side) for the ZrCuAlNi/Al₂O₃/HfO₂/Al device and (b) at negative bias (left side) for the ZrCuAlNi/HfO₂/Al₂O₃/Al device. The "onset of step tunneling" refers to the applied bias at which the E_f in the electron emitting metal rises just above the E_C of the lower barrier HfO₂ so that tunneling may occur through only the larger barrier Al₂O₃ layer. It should be noted that only step tunneling is of concern to this work. As shown in Figure 2(a), the electric field required to reach resonant tunneling exceeds the breakdown strength of the constituent HfO₂ and Al₂O₃ insulators. Thus, for the insulators used in this study, resonant tunneling is not relevant.

The "knee" in the log (J-V) curves of all Al₂O₃ containing devices is an indication of the onset of FNT. In FNT, J is related to V as

\[ J_{FNT} = C_1 \left( \frac{V + \Delta \phi}{S} \right)^2 \exp \left( C_2 \sqrt{m^* q_b} \left( \frac{S}{V + \Delta \phi} \right) \right) \]

where q is the electron charge, V is the applied bias, \( \phi_b \) is the barrier height of the electrode-insulator interface from which electrons are tunneling, \( \Delta \phi \) is the difference in barrier heights between the top and bottom electrode / insulator interfaces (for single insulator layer MIM devices \( \Delta \phi = \Delta \Phi \)), \( m^* \) is the effective electron mass, S is the tunnel barrier thickness, and \( C_1 \) and \( C_2 \) are constants.

Figure 3. Energy band diagrams illustrating (a) ZCAN/Al₂O₃/HfO₂/Al M₁M₂M₃ and (b) ZCAN/HfO₂/Al₂O₃/Al M₁M₂M₃ diodes under negative bias (left), equilibrium (center), and positive bias (right) (adapted from [6]).

Figure 2. Plots of (a) log (J) vs. V, (b) log \( \left( \frac{\eta_{asym}}{\eta_{asym}} \right) \) vs. V, and (c) fNL vs. V for ZCAN/Al₂O₃/HfO₂/Al M₁M₂M₃ and ZCAN/HfO₂/Al₂O₃/Al M₁M₂M₃ diodes. Single layer Al₂O₃ and HfO₂ devices are included for comparison (adapted from [6]).
Consider first the ZrCuAlNi/Al2O3/HfO2/Al M1I1I2M2 device, in which the smaller \( \chi \) Al2O3 layer (I1) is adjacent to the larger \( \Phi_{M1} \) ZrCuAlNi electrode. Application of approximately +3.1 V (Figure 3(a), right) brings \( E_F-\text{ZrCuAlNi} \) to just above the \( E_{C-HfO2} \) so that direct tunneling may occur from left to right through only the Al2O3 layer - a step reduction in the minimum required tunnel distance. For application of an opposite polarity -3.1 V bias (Figure 3(a), left) electrons tunneling from right to left at \( E_F-\text{ZrCuAlNi} \) must pass through both insulating layers. Therefore, a larger current is expected for positive bias than for an equivalent magnitude negative applied bias and \( \eta_{\text{asym}} < 1 \) is expected. This expectation of \( \eta_{\text{asym}} < 1 \) is confirmed in Figure 2(b). Note that the asymmetry (\( \eta_{\text{asym}} < 1 \)) for the ZrCuAlNi/Al2O3/HfO2/Al device is reverse that of the single Al2O3 layer device (\( \eta_{\text{asym}} > 1 \)), indicating that the asymmetry of the bilayer insulator barrier not only opposes that of the built-in voltage induced by \( \Delta \Phi_{M1} \) but overwhelms its impact on device operation. As indicated in Eqn. 1, the tunnel current is exponentially dependent upon \( \Phi_{M1}^{3/2} \). Since the barrier height \( \Phi_{Al-HfO2} < \Phi_{ZrCuAlNi-Al2O3} \), at higher magnitude applied biases the negative bias current (tunneling from Al) will begin to increase more rapidly than the positive bias current (tunneling from ZrCuAlNi) and it is expected that the slope of the log (\( \eta_{\text{asym}} \))-V plot will decrease [16]. In Figure 2(b) it is seen that for application of +4 V, the slope of the log (\( \eta_{\text{asym}} \))-V plot has decreased.

Next consider the reverse insulator stack orientation ZrCuAlNi/HfO2/Al2O3/Al M1I2I1M2 device, in which the smaller \( \chi \) Al2O3 layer (I1) is now adjacent to the smaller \( \Phi_{M2} \) Al electrode. With -2.8 V applied to the Al gate (Figure 3(b), left), \( E_F-Al \) lies just above \( E_{C-HfO2} \) and electrons injected from the Al (M2) may tunnel directly through only the Al2O3 layer (a step reduction in tunnel distance). On the other hand, for +2.8 V applied to the Al gate (Figure 3(b), right) electrons injected from the ZrCuAlNi (M1) must pass through both insulator layers. Therefore, a smaller current is expected at positive bias than at an equivalent magnitude negative bias so that \( \eta_{\text{asym}} > 1 \) is expected. This expectation is also confirmed in Figure 2(b). In this case bilayer insulator barrier enhances the electrode \( \Delta \Phi_{M1} \) asymmetry and \( \eta \) is increased over that of the single Al2O3 layer M1IM2 diode. Since \( \Phi_{Al-Al2O3} > \Phi_{ZrCuAlNi-HfO2} \) as the magnitude of the applied bias increases, the current density will begin to increase more quickly under positive bias (injection from ZrCuAlNi) than negative bias (injection from Al) and the slope of the \( \eta_{\text{asym}} \)-V plot will be expected to decrease. This expectation is also confirmed in Figure 2(b).

Considering non-linearity, bilayer devices have their highest \( f_{\text{NL}} \) for the bias polarity at which the step reduction in tunneling distance occurs, as seen in Figure 2(c). Consistent with the \( \eta \) data, \( f_{\text{NL}} \) is highest at positive bias for the ZrCuAlNi/Al2O3/HfO2/Al M1I1I2M2 devices, while \( f_{\text{NL}} \) is highest at negative bias for the ZrCuAlNi/HfO2/Al2O3/Al M1I1I2M2 devices.

Overall the bilayer ZrCuAlNi/HfO2/Al2O3/Al device, despite reduced \( \eta_{\text{asym}} \) and \( f_{\text{NL}-\text{max}} \) as compared to the single layer Al2O3 device, shows excellent low voltage characteristics with \( \eta_{\text{asym}} > 10 \) and \( f_{\text{NL}} > 5 \) at voltages as low as 0.8 V, an improvement over recent work, which has shown that insulator heterojunctions can be used to produce asymmetric I-V behavior in symmetric metal electrode M1I2M devices in which the same metal is used for the top and bottom electrodes [5,18,24]. Maragechi et al. [24], reported \( \eta_{\text{asym}} \sim 10 \) at 3 V and \( f_{\text{NL}} < 5 \) at 0.8 V for a symmetric electrode Cr/2nm HfO2/2nm Al2O3/Cr diode.

For rectenna applications, high \( \eta_{\text{asym}} \) and high \( f_{\text{NL}} \) at low voltage are desired. Reducing the tunnel barrier thickness can help. For example, reducing the total tunnel barrier thickness from approximately 10 nm to approximately 5 nm resulted in improved \( f_{\text{NL}} \) at small biases as well as bilayer devices [6], due primarily to the lower turn on voltages and higher conductivity for the thinner devices. However, the improvement for the bilayer devices was found to be even greater than for single layer devices. Shown in Figure 4 are J-V plots of various devices in which the total thickness of the tunnel barrier is 10 nm and consists of either (i) a single layer of Al2O3, (ii) a single layer of ZrO2, or (iii) various Al2O3/ZrO2 I1/I2 bilayers with different relative layer thicknesses. In all cases, ZrCuAlNi bottom electrode devices and Al top electrodes are used. It is seen that relative thickness of the individual insulator layers in the bilayer stack allows further tuning of electrical behavior.

In this section, it was shown that bilayer tunnel barriers can be used to effectively tune asymmetry, non-linearity, and \( V_{\text{ON}} \) in MIIM devices. In next section, the use of high \( \chi \) insulators for reduced tunnel barrier height as a potential route to further improvements will be assessed.
Figure 4. J-V plots for M1I1I2M2 diodes made with ZrCuAlNi bottom and Al top electrodes. The tunnel barrier consists of either a single layer of Al2O3, a single layer of ZrO2, or various Al2O3/ZrO2 I1/I2 bilayers. In all cases, the total thickness of the tunnel barrier is 10 nm (adapted from [20]).

3.2 Investigation of conduction mechanisms in Nb2O5 and Ta2O5 MIM diodes

Besides high asymmetry and nonlinearity, an additional requirement for rectenna applications is low VON. Assuming that operation is based on tunneling, insulators with a large electron affinity (χ) are desired to produce small energy barriers at the metal electrodes and potentially allow FNT to occur at small applied bias (low VON). It has thus been suggested that Nb2O5 and Ta2O5, insulators with large χ, should be promising candidate insulators for rectenna applications [3,18]. It has also been predicted that Nb2O5/Ta2O5 bilayers should be promising candidate insulators for MIIM devices for rectenna applications [18,19]. Shown in Figure 5 are simulated band diagrams for a symmetric electrode Al/Nb2O5/Ta2O5/Al device. It is seen that the minimum voltages required for resonant tunneling and step tunneling are predicted to be much smaller than for the Al2O3/HfO2 stacks shown in Figure 3. However, as we have shown in the last section, conduction should be dominated by tunneling. In this section, the dominant conduction processes for MIM diodes made with Nb2O5 or Ta2O5 are determined.

Figure 5. Simulated energy band diagrams of Al/Nb2O5/Ta2O5/Al symmetric electrode tunnel diodes, showing step tunneling (right) and resonant tunneling (left). In all diagrams, the left electrode is grounded and voltage is applied to right electrode (adapted from [20]).

Shown in Figure 6 are log J-V plots for (a) ZCAN / 5 nm Nb2O5 / Al and (b) ZCAN / 5 nm Ta2O5 / Al M1IM2 devices at temperatures ranging from 300°K to 375°K. As expected based on the electron affinities and expected relative barrier heights (χNb2O5 > χTa2O5), devices made using Nb2O5 show a larger current density than devices made using Ta2O5. The strong temperature dependence exhibited by both the Nb2O5 and Ta2O5 devices suggest the dominance of a thermal emission conduction mechanism rather than FNT.

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Figure 6. Log (J)-V plots as a function of temperature for (a) 5 nm thick Nb$_2$O$_5$ and (b) 5 nm Ta$_2$O$_5$ diodes.

Besides FNT and direct tunneling, possible conduction mechanisms include Schottky emission (SE), Frenkel-Poole emission (FPE), and space-charge-limited (SCL) conduction. SCL is ruled out because $J$ does not exhibit a $V^2$ dependence [25]. In SE, conduction is limited by emission over a barrier and the current density, $J_{SE}$, has the following relationship with electric field, $E$ [15].

$$J_{SE} = A^* T^2 \exp \left[ -q \left( \Phi_B - \sqrt{qE / 4\pi e_0} \right) / kT \right],$$

where $A^*$ is the effective Richardson constant, $T$ is temperature, $q$ is the elementary charge, $\Phi_B$ is the barrier height between the $E_F$ of the injecting metal and the conduction band minimum of the insulator, $\kappa$ is the optical insulator constant, $\varepsilon_0$ is the permittivity in vacuum, and $k$ is Boltzmann’s constant. For FPE, where conduction is limited by capture and emission from traps, the relationship between $J_{FPE}$ and $E$ is [15],

$$J_{FPE} = E \exp \left[ -q \left( \phi_T - \sqrt{qE / \pi \kappa e_0} \right) / kT \right],$$

where $\phi_T$ is the trap energy depth referenced to the conduction band minimum of the insulator.

To examine whether the dominant conduction process is related to SE or FPE, the room temperature $J$-V data from Figure 6 were replotted as $\ln (I/T^2)$ vs. $V^{1/2}$ and $\ln (I/V)$ vs. $V^{1/2}$ in Figure 7 and Figure 8, respectively. Shown in Figure 7, it was found that both the Ta$_2$O$_5$ and Nb$_2$O$_5$ devices produced linear $\ln (I/T^2)$ vs. $V^{1/2}$ curves ($R^2 > 0.999$) at low biases (0.1 to 0.3 V) at both polarities, suggesting that SE dominates in the low bias regime. At higher biases (0.75 to 1 V), both the Ta$_2$O$_5$ and Nb$_2$O$_5$ devices produced linear $\ln (I/V)$ vs. $V^{1/2}$ plots (see Figure 8), suggesting that FPE dominates at higher biases.
Figure 8. FPE conduction plots of both (a) Nb$_2$O$_5$ and (b) Ta$_2$O$_5$ devices show linearity in the high voltage regime.

To assess the validity of these conduction mechanism assignments, the relative dielectric constants, $\kappa$, of Nb$_2$O$_5$ and Ta$_2$O$_5$ were extracted from the slopes of the plots in Figure 7 and Figure 8. For Nb$_2$O$_5$, $\kappa = 4.7 \pm 0.3$ was extracted from the SE plot in Figure 7, and $\kappa = 5.5 \pm 0.1$ from FPE plot in Figure 8. For Ta$_2$O$_5$, $\kappa = 4.0 \pm 0.3$ was extracted from the SE plot in Figure 7 and $\kappa = 4.6 \pm 0.1$ from the FPE plot in Figure 8. Note that for both Nb$_2$O$_5$ and Ta$_2$O$_5$, the values of $\kappa$ are essentially the same for both polarities. Although it is clear that all of these extracted dielectric constants are much smaller than the static dielectric constant $\kappa$ of greater than 20 expected for both insulators, it is the high frequency optical dielectric constant to which they should be compared [26]. Using spectroscopic ellipsometry, the optical dielectric constant in the wavelength range of 400 – 1200 nm was measured to range from 5.5 to 6.2 for Nb$_2$O$_5$ and from 4.6 to 4.95 for Ta$_2$O$_5$. The $\kappa$ values extracted from the FPE plots (5.5 ± 0.1 for Nb$_2$O$_5$ and 4.6 ± 0.1 for Ta$_2$O$_5$), both match well with the range of values measured optically, supporting the assignment of FPE as the dominant mechanism at higher biases. For the SE plots, the extracted $\kappa$ values (4.7 ± 0.3 for Nb$_2$O$_5$ and 4.0 ± 0.3 for Ta$_2$O$_5$) match reasonably well but are somewhat below the range of the values measured optically, so that the designation of SE at low voltages is more tentative.

FPE may be thought of as being limited by transport through a dominant trap. The activation energy, $E_a$, required to escape from this trap at a given applied voltage may be extracted from Arrhenius plots of ln (I/V) vs. $1/kT$ as shown in Figure 9 for the 5 nm thick Nb$_2$O$_5$ devices and Figure 10 for 5 nm thick Ta$_2$O$_5$ devices. Using these field dependent $E_a$ values, we may estimate the energy depth of the dominant trap referenced to the conduction band minimum of the insulator, $\phi_T$. To account for the Schottky barrier lowering of the trap depth when a field is applied across the insulator, the obtained values of $E_a$ are plotted vs. the square root of the voltage across the insulator, as shown in Figure 11. $\phi_T$ is then estimated by extrapolating to $V = 0$. For Ta$_2$O$_5$, $\phi_T$ was estimated to be 0.58±/−0.01 eV below the conduction band minimum. For Nb$_2$O$_5$, the $\phi_T$ was found to be 0.60 ±/−0.04 eV below the conduction band minimum. Similar values were obtained for 10 nm thick insulators. For both Nb$_2$O$_5$ and Ta$_2$O$_5$, the extracted trap depths were the same for both positive and negative bias, further evidence that FPE is indeed dominant in this bias region.
Figure 9. FPE Arrhenius plots of 5 nm thick Nb$_2$O$_5$ device at (a) negative and (b) positive bias.

Figure 10. FPE Arrhenius plots of 5 nm thick Ta$_2$O$_5$ device at (a) negative and (b) positive bias.

Figure 11. Plot of $E_a$ vs. $\sqrt{V}$ for Nb$_2$O$_5$ and Ta$_2$O$_5$ diodes. The trap depth, $\phi_{T0}$, is estimated by extrapolation to zero bias.

4. SUMMARY / CONCLUSION

Nanolaminate bilayer of insulators (each with different $E_G$ and $\chi$) were deposited via ALD and used to create asymmetric tunnel barrier MI$_1$I$_2$M devices in which electrons tunneling from one metal electrode to the other are presented with polarity dependent barrier shape. It was found that these bilayer tunnel barriers dominate the electrical characteristics of asymmetric metal electrode M$_1$I$_2$M$_2$ devices. I-V asymmetry and non-linearity were shown to be sensitive to the...
arrangement of the individual insulator layers with respect to the different metal electrodes (M₁I₁I₂M₂ vs. M₁I₂I₁M₂). Depending on whether the smaller χ insulator was adjacent to the smaller or larger ΦM electrode, the bilayer insulators were arranged to either enhance or oppose (even reverse), respectively, the ΔΦM induced asymmetry. In addition to placement with respect to the electrodes, the relative thickness of the insulator layers was shown to further tune electrical behavior. It was shown that these results can be qualitatively well explained by step tunneling. For the insulators used in this study, resonant tunneling is not relevant as the field required to reach resonant tunneling exceeds the breakdown strength of the constituent oxides. By combining bilayer insulator tunnel barriers with the standard method of producing asymmetry, asymmetric metal electrodes, we were able to produce excellent low voltage asymmetry and non-linearity in a ZrCuAlNi/HfO₂/Al₂O₃/Al diode exceeding both that of standard single insulator layer asymmetric electrode M₁I₁M₂ devices as well as symmetric electrode M₁I₂M₁ devices.

Next, the dominant conduction mechanisms in Nb₂O₅ and Ta₂O₅ insulators deposited via ALD were investigated. Conduction in both insulators was found to be dominated by thermal emission, rather than tunneling based mechanisms. For both insulators, it was found that Schottky Emission dominates at low biases whereas Frenkel-Poole Emission dominates at larger biases. Using FPE analysis, the dominant "bulk" trap depths were estimated to be 0.58±/−0.01 eV below the conduction band minimum for Ta₂O₅ and 0.60 ± 0.04 eV for Nb₂O₅. The fact that FNT conduction does not play a role in either Nb₂O₅ or Ta₂O₅ suggests that this insulator combination will not be able to support the step tunneling mechanism we found to improve asymmetry and reduce V_ON in MIM diodes [6]. Thermal emission at high electric fields can in principle be fast (possibly of order 10s of THz as assessed from spectroscopic ellipsometry). However, FPE dominated conduction cannot provide asymmetry as the traps behave in the same manner under positive and negative bias. Although interface-dominated SE can provide low voltage asymmetry if asymmetric work function electrodes are used to produce different barrier heights, the exponential temperature dependence of SE may make it unsuitable for applications where careful temperature control is not viable. Thus, because conduction is dominated by thermal emission, ultrahigh frequency applications of Nb₂O₅ or Ta₂O₅ based MIM devices may be limited.

In conclusion, these results represent an advancement in the understanding necessary to engineer thin film MIM tunnel devices for microelectronics and rectenna applications.

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REFERENCES