Chapter 6
Impact of Electrode Roughness on Metal-Insulator-Metal (MIM) Diodes and Step Tunneling in Nanolaminate Tunnel Barrier Metal-Insulator-Insulator-Metal (MIIM) Diodes

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Abstract In this chapter, the impact of electrode roughness and bilayer insulator tunnel barriers on the performance of metal-insulator-metal (MIM) diodes are discussed. The effect of bottom electrode roughness on the current versus voltage (I-V) characteristics of asymmetric electrode $M_1IM_2$ tunnel diodes is discussed first. Atomic layer deposition (ALD) is used to deposit high quality insulators independent of bottom metal electrode. It is shown that bottom electrode roughness can strongly influence the $I-V$ characteristics of $M_1IM_2$ diodes, overwhelming even the metal work function difference induced asymmetry. Devices with smoother bottom electrodes are shown to produce $I-V$ behavior with better agreement with Fowler–Nordheim tunneling theory as well as yield a higher percentage of well-functioning devices. By combining high quality uniform tunnel barriers deposited by ALD with atomically smooth (~0.3 nm RMS roughness) bottom electrodes, highly nonlinear and asymmetric MIIM tunnel diodes with good reproducibility and stable $I-V$ behavior are produced. Next, the impact of nanolaminate bilayer insulator tunnel barriers on asymmetric metal work function metal-insulator-insulator-metal (MIIM, $M_1I_1I_2M_2$ & $M_1I_2I_1M_2$) devices is discussed. It is demonstrated that bilayer tunnel barriers can be arranged to enhance, oppose, or even reverse the asymmetry induced by the asymmetric work function electrodes. These results represent experimental demonstration that step tunneling (a step change in the tunneling distance through a bilayer tunnel barrier) can dominate the $I-V$ asymmetry of MIIM diodes with asymmetric work function electrodes. By combining bilayer tunnel barriers with asymmetric metal electrodes, devices are made with voltage asymmetry and nonlinearity that exceed that of standard single layer asymmetric electrode $M_1IM_2$ devices as well as that of symmetric electrode $M_1I_1I_2M_1$ devices.

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6.1 Introduction/Background

Thin film MIM-based tunneling devices are seeing renewed interest for high speed applications [1-11]. Besides rectenna solar cells [12-15], as discussed in Chap. 5, these applications include hot electron transistors [16-18], and infrared (IR) detectors [19-24]. MIM diodes have also been proposed for macroelectronics applications [25] such as backplanes for liquid-crystal displays (LCDs) [26]. Before any of these applications can be realized, a manufacturable process will be required that can produce uniform, high quality MIM tunnel devices with high asymmetry and nonlinearity. Despite investigation by many groups over many decades [27-34], progress toward commercialization of MIM-based electronics has been hindered by a lack of a manufacturable process. In particular, inattention to electrode roughness along with the lack of a high quality deposited oxide appears to have slowed development of this technology—most experimental work to date on thin film MIM diodes has focused on the use of thin native dielectrics produced by oxidation or nitridation of an underlying rough polycrystalline metal electrode [3, 4, 7-9, 19-24, 27-34]. The operation of MIM diodes is based on quantum mechanical tunneling through a thin insulating film positioned between two metal electrodes [35, 36]. The impact of roughness can be appreciated if it is remembered that the tunneling probability depends exponentially on the electric field in the thin dielectric film [37, 38]. The tunneling current in a MIM tunnel diode should therefore depend strongly on the atomic scale roughness and the uniformity of the electrode-insulator interfaces [39]. Basic studies on electrode and interface roughness and their correlation with the tunneling current will therefore be very important for the advancement of MIM technology. In Sect. 6.3, the performance of MIM tunnel diodes formed on bottom electrode materials with various levels of RMS roughness is compared. Whereas previous MIM diode work has focused primarily on native oxides, the use of atomic layer deposition (ALD) in this work allows for deposition of the same high quality insulator, independent of the bottom metal electrode. It is shown here that bottom electrode roughness can have a dominant impact on the electrical characteristics of MIM diodes, overwhelming the trends expected based on metal electrode work function differences. It is also shown that as electrode roughness decreases, the percentage yield of well-functioning devices trends higher.

As discussed in Chap. 1, for rectenna-based solar cells as well as other potential applications of MIM diodes, highly asymmetric and nonlinear current vs. voltage (I-V) behavior at low applied voltages is desired. The standard approach to achieving asymmetric I-V characteristics in tunnel devices is the M_{1}I_{2}M_{3} diode—the use of metal electrodes with different work functions (\( \Phi_{M1} \neq \Phi_{M2} \)) to produce a built-in voltage, \( V_{bi} = (\Phi_{M1} - \Phi_{M2})/e \) (where \( e \) is the electronic charge) across the tunnel barrier [38, 40]. However, even with low roughness electrodes, the amount of asymmetry achievable using this approach is limited by the \( V_{bi} (\Delta \Phi_{M}) \) that can be obtained using practical electrodes. An alternative approach to achieving asymmetric and nonlinear operation is therefore needed. The approach investigated in Sect. 6.4 involves engineering of the tunnel barrier so that electrons tunneling from one metal electrode to the other are presented with a different barrier shape depending on the direction of tunneling. Theoretically, formation of an asymmetric tunnel barrier can be accomplished using stacking of insulators [41], with each insulator having different band-gaps (\( E_{g} \)) and electron affinities (\( \chi \)), to produce metal-insulator-insulator-metal (M_{1}I_{2}M_{3}) devices [42, 43].

In Sect. 6.4 the combined effect of bilayer tunnel barriers and asymmetric (\( \Phi_{M1} \neq \Phi_{M2} \)) electrodes are investigated [11]. M_{1}I_{2}M_{3} diodes are fabricated using nanolaminate dielectric bilayers deposited via ALD on smooth bottom electrodes [1, 2]. As illustrated in Fig. 6.1, for a pair of insulators, asymmetry may be enhanced through either resonant tunneling or step tunneling. Whereas most work in the literature has been concerned with resonant tunneling [9, 42, 43], here it is experimentally demonstrated that bilayer insulator tunnel barriers enable tuning of asymmetry (\( \eta_{asym} \)) and nonlinearity (\( f_{NL} \)) via 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. Experimentally obtained \( \eta_{asym} \) and \( f_{NL} \) values are shown to be sensitive to the arrangement of the individual dielectric layers with respect to the larger and smaller \( \Phi_{M} \) electrodes (e.g., M_{1}I_{2}M_{3} vs. M_{1}I_{2}M_{3}) and it is experimentally demonstrated that bilayer tunnel dielectrics can be arranged to either enhance or oppose (even reverse) the built-in asymmetry of the asymmetric work function electrodes. Finally, it is shown that M_{1}I_{2}M_{3} diodes with superior I-V asymmetry can be produced by combining bilayer dielectric tunnel barriers with asymmetric work function metal electrodes.

6.2 Experimental

MIM and MIIIM diodes were fabricated on Si substrates capped with 100 nm of thermally grown SiO_{2}. A typical schematic device cross section is shown in Fig. 6.2. To serve as bottom electrodes, blanket films of either Al, Pt, Ir, or ZnCuAlNi were deposited directly on SiO_{2}. A thin Ti adhesion layer was used for Pt and Ir. Al was deposited via thermal evaporation, Ir was deposited via
6.3 The Impact of Bottom Electrode Roughness on MIM Devices

In this section, the performance of MIM tunnel diodes formed using ALD deposited Al₂O₃ on low work function (ZrCuAlNi and Al) and high work function (Ir and two types of Pt) bottom electrodes with various levels of RMS roughness is compared.

AFM images of the as-deposited ZrCuAlNi, Pt-1, Pt-2, and Ir bottom electrodes are shown in Fig. 6.3. In order to assess potential roughening as a result of the ALD thermal cycle or interaction of the TMA precursor with the electrodes, additional AFM images were also taken after deposition of a 10 nm Al₂O₃ layer (post-ALD). AFM images of the Al electrode, as-deposited and post-ALD, are shown in Fig. 6.4. (Post-ALD AFM images of the other electrodes are not shown as they show similar properties to the as-deposited films.) As summarized in Table 6.1, the AFM images revealed a wide variation in both RMS average roughness and peak roughness, with roughness values being averaged from a minimum of three images each. With the exception of Pt-2, the RMS and peak roughness tend to scale together. ZrCuAlNi is seen to show the lowest roughness by a factor of 10X. ZrCuAlNi is a well-known...

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Fig. 6.3 Atomic force microscopy (AFM) images of as-deposited (a) Ir, (b) electron-beam deposited Pt-2, (c) sputtered Pt-1, (d) ZrCuAlNi blanket bottom electrodes. Adapted from [1]
Fig. 6.5 (a) Plots of simulated current density vs. voltage ($J$-$V$) for $M_1$-$M_2$ diodes with either ZrCuAlNi, Ir, or Pt bottom ($M_1$) electrodes, a 10 nm thick $Al_2O_3$ tunnel barrier, and an Al top electrode ($M_2$). (b) Measured $J$-$V$ for actual devices fabricated using ZrCuAlNi, Ir, sputtered Pt-1, and electron-beam deposited Pt-2 bottom electrodes ($M_1$). Adapted from [1]

- Growth during the ALD thermal cycle, rather than due to the ALD $Al_2O_3$ deposition itself.

- Shown in Fig. 6.5a, b, are simulated and representative measured $J$-$V$ curves, respectively, for $M_1$-$M_2$ devices with either Ir, Pt, or ZrCuAlNi as the bottom electrodes ($M_1$), an approximately 10 nm thick $Al_2O_3$ tunnel barrier, and an Al top electrode ($M_2$). Simulations are conducted in Matlab using the Fowler–Nordheim (FN) tunneling equation of Simmons [37, 38],

$$J = \frac{q^3}{16\pi \hbar} \left( \frac{m_0}{m_{ee}} \right) \frac{1}{\varphi_b} \left( \frac{V + \Delta \varphi}{S} \right)^2 \exp \left( -\frac{4\sqrt{2m_{ee}}}{3\hbar V + \Delta \varphi} \frac{S}{\varphi_b} \right)$$

(6.1)

- where $q$ is the electron charge, $\hbar$ is the reduced Plank’s constant, $V$ is the applied bias, $\varphi_b$ is the barrier height of the electrode-insulator interface from which electrons are tunneling, $\Delta \varphi$ is the difference in barrier heights between the top and bottom electrode/insulator interfaces (for single insulator layer MIM devices $\Delta \varphi = \Delta \Phi$), $m_{ee}$ is the electron effective tunneling mass in the dielectric, and $S$ is the tunnel barrier thickness. It was assumed that the thickness of the $Al_2O_3$ layer was 10 nm and that the electron effective mass was 0.79 $m_0$ where $m_0$ is the mass of the free electron [2, 9]. The only difference between the three simulated curves is the value used for work function of the bottom electrode ($\varphi_{M1}$) as given in Table 6.1 [49], and thus the barrier height of the bottom electrode, $\varphi_{b1} (= \varphi_{M1} - \chi_{Al_2O_3})$. 

- AFM images of the Al electrode (a) as-deposited and (b, c) post atomic layer deposition. The post-ALD image is shown on a lower magnification z-scale in (c).

- Table 6.1: Work function, as-deposited and post-ALD RMS and peak roughness, and percentage functioning devices of metal bottom electrode/10 nm $Al_2O_3$/Al top electrode $M_1$-$M_2$ nodes.

<table>
<thead>
<tr>
<th>$\phi_M$ (eV)</th>
<th>As-deposited</th>
<th>Post-ALD</th>
<th>Functioning devices (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RMS</td>
<td>Peak</td>
<td>RMS</td>
</tr>
<tr>
<td>Beam</td>
<td>4.2</td>
<td>4</td>
<td>43</td>
</tr>
<tr>
<td>Sputtered</td>
<td>5.3</td>
<td>6</td>
<td>220</td>
</tr>
<tr>
<td>Electrode</td>
<td>5.1</td>
<td>11</td>
<td>120</td>
</tr>
<tr>
<td>Source</td>
<td>5.3</td>
<td>2</td>
<td>22</td>
</tr>
<tr>
<td>4.8</td>
<td>0.3</td>
<td>0.3</td>
<td>0.1</td>
</tr>
</tbody>
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From [1]
Fig. 6.6 Equilibrium band diagrams of (a) symmetric M₁M₂ and (b) asymmetric M₁M₂ tunnel diodes. \( \varphi_{b1} \) and \( \varphi_{b2} \) indicate the barrier height of the bottom (high work function M₁) and top (low work function M₂) metal electrodes, respectively. Also shown are energy band diagrams of the asymmetric tunnel diode under (c) positive, (d) negative, and (e) equal magnitude applied bias showing the onset of FN tunneling and direct tunneling. In all band diagrams, M₁ is grounded and voltage is applied to M₂.

In order to explain the trends in the \( J-V \) curves in Fig. 6.5, it is helpful to consider MIM energy band diagrams. An equilibrium band diagram of a symmetric M₁M₂M₁ tunnel device is shown in Fig. 6.6a. The \( J-V \) characteristic of a symmetric M₁M₂ device is expected to be symmetric because the barrier to electron tunneling is equivalent in either direction. However, the diodes investigated in this chapter have asymmetric electrodes. An equilibrium band diagram of an asymmetric M₁M₂ tunnel diode is shown in Fig. 6.6b. \( \varphi_{b1} \) and \( \varphi_{b2} \) indicate the barrier height of the bottom electrode metal M₁ (Ir, Pt, or ZrCuAlN). The smaller work function top gate electrode metal M₂ (Al), respectively. Additional band diagrams of the asymmetric diode (c) the onset of FN tunneling for a positive bias applied to M₂ and (d) direct tunneling for the same absolute magnitude negative bias applied to M₂. The last two band diagrams illustrate the origin of the expected symmetry in M₁M₂ devices.

Consider first the application of a sufficiently large positive bias to electrode M₂ (Al), so that FN tunnel emission occurs from M₁ (Ir, Pt, or ZrCuAlN). This situation is illustrated in energy band diagrams shown in Fig. 6.7a-c which depict the applied bias at which tunnel emission from electrode M₁ transitions from direct tunneling (through the entire insulator thickness) to FN tunneling (through a triangular shape barrier in which the tunnel distance increases further with decreasing bias). Since the insulator thickness (~10 nm) is sufficient to suppress direct tunneling, current conduction is dominated by FN tunneling. As indicated in (a, c), the magnitude of the FN tunneling current depends on the inverse exponential of \( S \) and the square root of cube of the barrier height presented to the tunneling electron \( J \propto \exp(-S\varphi_{b2}^{3/2}) \). Thus, while the onset of FN tunneling at positive bias would be roughly the same for all bottom electrodes (as it involves overcoming the same barrier height, \( \varphi_{b2} \), of the Al top electrode as shown in Fig. 6.7a-c), the magnitude of the FN tunneling current at larger positive fields (\( V_{app} \gg \varphi_{b2} \)) should be in reverse order of increasing \( \varphi_{b1} \) (increasing \( \Phi_{M1} \)). Based on relative \( \varphi_{b1} \), it is expected that a diode with the ZrCuAlN electrode (\( \Phi_{ZrCuAlN} = 4.8 \text{ eV} \)) should show the highest current density, the Ir electrode (\( \Phi_{Ir} = 5.1 \text{ eV} \)) should show the next highest current density, and that the devices with the Pt electrodes (\( \Phi_{Pt} = 5.3 \text{ eV} \)) should show the lowest current density. This trend is observed in the simulations (Fig. 6.5a). Although the ZrCuAlN bottom metal electrode device is well predicted by simulation, decreased current density with increased \( \Phi_{M1} \) is clearly not the trend exhibited by the experimental data (Fig. 6.5b) [2].

Assuming that the Al₂O₃ thickness is the same for all devices and that conduction is dominated by FN tunneling, a likely explanation for the unexpected trend shown by the data in Fig. 6.5b is associated with the relative roughness of the bottom electrode. A rough bottom electrode could lead to electric field nonuniformity across the insulator due to field enhancement at nm scale sharp features [50, 51]. This field enhancement would result in locally increased conduction [3]. As listed in Table 6.1 and illustrated in Fig. 6.3, Ir showed the largest as-deposited RMS roughness (11 nm) followed by e-beam deposited Pt-2 (6 nm), sputtered Pt-1 (2 nm), and finally ZrCuAlN (0.3 nm). Looking again at Fig. 6.5b, it is apparent that increasing positive polarity current density correlates with increasing bottom electrode roughness, rather than with decreasing \( \Phi_{M1} \). As the RMS roughness for both Ir and Pt-2 is comparable to the overall dielectric
thickness, it is not surprising that bottom electrode roughness overwhelms the expected influence of $\Phi_M$. A clear indication of the impact of roughness can be seen by directly comparing MIM tunnel diodes made using the same bottom electrode metal (Pt) with two different levels of roughness. As seen in Fig. 6.5b, despite what should be nominally the same $\Phi_M$, the rougher (RMS = 6 nm) e-beam evaporated Pt-2 device shows a higher positive bias current density than the smoother (RMS = 2 nm) DC sputtered Pt-1 device.

Considering now the application of a sufficiently large negative bias to electrode $M_2$ so that FN emission occurs from $M_2$ (Al). As indicated in the energy band diagrams in Fig. 6.7d-f, for larger $q_{\phi_1}$, the onset of FN tunneling should require application of larger negative voltages. The simulations in Fig. 6.5a are consistent with this expectation. After the onset of FN tunneling at negative bias, since the barrier height of the emission electrode is nominally the same for all devices as shown in Fig. 6.7d-f, the $I$–$V$ curves of all devices should exhibit roughly the same slope. Once again, the devices made with ZrCuAINi as a bottom electrode match fairly well with simulation (Fig. 6.5). As compared with the simulation, the voltage required to achieve a given current density is reduced only slightly for both the Pt and Ir electrode devices. Ir shows the greatest deviation from simulation while the rougher Pt-2 once again deviates more than Pt-1.

The deviation between measured and simulated current density is much less on the negative bias side than on the positive bias side (Fig. 6.5). Additional FN tunneling simulations show that in an asymmetric $M_1 M_2$ device, tunnel emission from the higher work function $M_1$ (the situation at positive bias) is more sensitive to changes in the tunnel barrier (such as in thickness, electron effective mass, or electron affinity) than tunneling from the lower work function side $M_2$ (the situation at negative bias). The data in Fig. 6.5 suggests that tunneling from the higher work function $M_1$ side (again, positive bias in these experiments) is also more sensitive to roughness than tunneling from the smaller work function side (negative bias in these experiments).

Desired $J$–$\xi$ characteristics for diodes include high $f_{NL}$ and high $\eta_{asym}$. As illustrated by the simulations in Fig. 6.8a, assuming that FN tunneling dominates conduction, a larger $\Delta \Phi_M$ between electrodes should lead to higher maximum $\eta_{asym}$ ($\eta_{max}$) so that the Pt (largest $\Phi_M$) device should show the highest $\eta_{max}$ and the ZrCuAINi device (lowest $\Phi_M$) the lowest $\eta_{max}$. Because of the smaller energy barrier heights, the ZrCuAINi bottom electrode device would be expected to show asymmetric response at the lowest bias.

As shown in Fig. 6.8b, this trend was not observed. The largest $\eta_{max}$ for the actual devices is associated with the ZrCuAINi electrode device, the device with the smoothest $M_1$. Clearly opposite to expectations, the devices with rough Pt and Ir bottom electrodes show asymmetry of reverse polarity to what was predicted. The qualitative $J$–$V$ response of the Pt and Ir devices, higher current for positive bias than for negative bias, means that a larger tunneling current is flowing from the larger tunnel barrier electrode. This cannot be explained by the FN tunneling equation in (6.1). However, this situation may be explained by electrode roughness. Choi et al. [3] have shown that the tunneling probability may be enhanced by electrode geometry. They report geometric electric field enhancement, in which one of the electrodes is deliberately fabricated with a sharp geometry, produced an asymmetric $J$–$V$ response in an otherwise electrically symmetric MIM device with Ni top and bottom electrodes. In our experiments, it appears that geometry enhanced asymmetry is seen for devices with the rough Pt and Ir electrodes. In fact, as shown in Fig. 6.8b, the asymmetric response of diodes made with rough bottom electrodes is correlated with the roughness. Diodes made with largest RMS roughness bottom electrode (Ir) show the largest reversed asymmetry values followed by the Pt-2 (e-beam) and the Pt-1 (sputtered) devices. It appears that the full extent of $\Delta \Phi_M$ induced asymmetry can be realized only if the roughness of the larger work function electrode is minimized.

A bottom electrode $M_1$ roughness was also found to be inversely correlated with the percentage of functioning MIM diodes. Diodes were considered nonfunctioning due to either electrical shorts or early breakdown under a low applied electric field. It is seen in Table 6.1 that smoother bottom electrodes were found to yield a greater percentage of functioning devices. Devices fabricated using ZrCuAINi, the smoothest bottom electrode investigated, have the highest fraction of functioning devices. At the opposite end of the roughness spectrum, the Al films were the roughest metal films investigated, with a post-ALD RMS roughness of 21 nm (greater than the tunnel barrier thickness) and a peak roughness of more than 450 nm. It is not surprising that no functioning diodes could be obtained using Al bottom electrodes. Comparing the two types of Pt, use of the smoother Pt-1 resulted in a higher percentage of functioning devices than the rougher Pt-2 devices. Finally, despite lower as-deposited and roughly equivalent post-ALD RMS roughness, Pt-2 bottom electrodes are found to yield a lower percentage of working devices than Ir bottom electrodes. This appears to be due to the larger peak roughness of the Pt-2 electrode devices.

Using the ultra-smooth ZrCuAINi as $M_1$, uniform and repeatable device characteristics were produced with high yield that are well predicted by FN tunneling theory and the Simmons equations. Shown in Fig. 6.9a are $J$–$\xi$ curves for seven Al top electrode ($M_2$)/10 nm thick Al2O3 tunnel barrier/ZrCuAINi ($M_1$)

![Fig. 6.8: (a) Simulated and (b) experimental plots of $\log (\eta_{asym})$ vs. $V$, for MIM diodes with either ZrCuAINi, Ir, or Pt bottom electrodes, 10 nm Al2O3, and Al top electrodes where asymmetry $\eta_{asym} = |J_+/J_-|$](image-url)
Fig. 6.9 (a) J-ξ sweeps for even different MIM tunnel diodes taken from five different substrates fabricated in four different critical process runs. Different shades indicate different devices. The fact that the devices overlap and are barely distinguishable from one another is an indication of the run-to-run device-to-device uniformity. (b) Hundred sequential J-ξ sweeps on a single device. In all cases, the stack structure of the devices consists of ZrCuAlNi/1 nm Al$_2$O$_3$/Al. Adapted from [6].

...des from five different substrates produced in four different process runs. Note that despite the inverse dependence of yield on bottom electrode roughness and agreement with FN theory for the rough bottom electrode devices, when ionized devices are obtained, even the devices with rough bottom electrode Pt-1, and Pt-2) exhibit little variation in J-ξ characteristics. Shown in Fig. 6.9b are 100 sequential J-ξ sweeps (−4.5 V to +6 V to −4.5 V) on CuAlNi M$_1$/10 nm thick Al$_2$O$_3$ tunnel barrier/Al M$_2$ device showing stable response. Further reliability investigations described in [6] have shown that devices with rougher bottom electrodes are more susceptible to failure due to biasing. Finally, we have also observed that increased bottom electrode roughness is correlated with increased I-V hysteresis in these devices, suggesting that increased roughness may lead to increased charge trap density, which in turn would lead to energy barrier height variations.

**Step Tunneling Enhanced Asymmetry in MIIM Diodes**

In this section, the combined effect of bilayer tunnel barriers and asymmetric (≠ Φ$_{M2}$) electrodes are investigated on M$_1$M$_2$M$_3$ diodes fabricated atomically smooth ZrCuAlNi amorphous metal bottom electrodes and nanolaminate dielectric bilayers of HfO$_2$/Al$_2$O$_3$ and ZrO$_2$/Al$_2$O$_3$ deposited via ALD [11].

...in Fig. 6.10 are plots of (a) log (J) vs V and (b) log (η$_{asym}$) vs V for the single layer M$_1$M$_2$ diodes with ZrCuAlNi bottom electrodes (M$_1$) and Al top gates (M$_2$) where the I is a single 3.5 nm or 10 nm layer of either Al$_2$O$_3$, HfO$_2$, or ZrO$_2$. As expected, current density is a rough function of the relative barrier heights, as shown in the band diagrams in Fig. 6.11. In Fig. 6.10 the dominance of FN tunneling is apparent from the presence of the "knees" in the log (J)-V data at positive and negative bias that are followed by several orders of magnitude of exponentially increasing current. Not shown, FN plots of ln (I/(V + ΔΦ)) vs. 1/(V + ΔΦ) indicate that Al$_2$O$_3$ and HfO$_2$ devices are dominated by FN tunneling in the post-turn-on regime. The ZrO$_2$ devices, on the other hand, appear to be dominated by thermionic emission. Due to the ΔΦ$_M$
High magnification cross-sectional transmission electron microscopy (TEM) images of (a) ZrCuAlNi/Al₂O₃/HfO₂/Al \text{M}_1\text{I}_1\text{M}_2\text{I}_2\text{M}_2 and (b) ZrCuAlNi/HfO₂/Al₂O₃/Al \text{M}_1\text{I}_1\text{M}_2\text{I}_2\text{M}_2 devices. A lower magnification TEM image of the ZrCuAlNi/Al₂O₃/HfO₂/Al \text{M}_1\text{I}_1\text{M}_2\text{I}_2\text{M}_2 device is shown in (c).

Fig. 6.12. The effect of electrode roughness on the leakage current and breakdown strength of 10 nm thick dielectric Al₂O₃ and HfO₂ with \text{M}_1\text{I}_1\text{M}_2\text{I}_2\text{M}_2 diodes. The leakage current decreases as the roughness of the electrode increases.

In Fig. 6.10b, it is seen that the 10 nm Al₂O₃ diode shows a \( \eta_{\text{max}} \) of approximately 1.350 at 4.1 V. Although the Al₂O₃ devices show excellent \( \eta_{\text{sym}} \) at higher biases, for many applications, including energy harvesting, asymmetric operation at low voltage is desirable. As seen in Fig. 6.10b, decreasing the tunnel barrier thickness to 3.5 nm resulted in decreased turn-on voltages and increased current for all devices. However, \( \eta_{\text{max}} \) was not improved, most likely due to the increased influence of direct tunneling. Decreasing the thickness of the single insulator layer in an \text{M}_1\text{I}_1\text{M}_2\text{I}_2\text{M}_2 diode does not lead to improved asymmetry.

In order to create an asymmetric tunnel barrier, Al₂O₃ and HfO₂ were stacked to form bilayer insulator MIM devices. Cross-sectional TEM images of ZrCuAlNi/Al₂O₃/HfO₂/Al \text{M}_1\text{I}_1\text{M}_2\text{I}_2\text{M}_2 devices and ZrCuAlNi/Al₂O₃/HfO₂/Al \text{M}_1\text{I}_1\text{M}_2\text{I}_2\text{M}_2 devices are shown in Fig. 6.12. For each dielectric bilayer, 56 ALD cycles were used to deposit Al₂O₃ and 65 cycles were used to deposit HfO₂, targeting a thickness of 5 nm for each layer. The high magnification TEM images in (a) and (b) show that the thickness of the top dielectric layer is indeed approximately equal to the 5 nm target. However, in each case, the thickness of the bottom dielectric layer deposited directly on the ZrCuAlNi bottom electrode is only approximately 5 nm. This reduced thickness is likely due to an inhibition of the ALD nucleation rate on ZrCuAlNi as compared to that on oxide. Also visible in the high resolution TEM images is the presence of an approximately 2 nm thick interfacial layer between the ZrCuAlNi and the bottom dielectric. This interfacial layer was previously determined to be composed of ZrO₂ [2]. In Fig. 6.12c, a lower magnification image of the device from (a), reveals the smooth nature of the ZrCuAlNi/Al₂O₃ interface over an extended range. As discussed above in Sect. 6.3, a smooth bottom interface is critical to achieving high yield, high quality MIM tunnel devices [1, 6].

Figure 6.13 shows (a) \( \log(J) \) vs. \( V \), (b) \( \log(\eta_{\text{sym}}) \) vs. \( V \), and (c) \( f_{\text{NL}} \) vs. \( V \) plots for “thick” bilayer ZrCuAlNi/3.5 nm Al₂O₃/5 nm HfO₂/10 nm Al₂O₃/10 nm Al₂O₃/Al \text{M}_1\text{I}_1\text{M}_2\text{I}_2\text{M}_2 diodes. Included for reference are the 10 nm thick single dielectric Al₂O₃ and HfO₂/Al \text{M}_1\text{I}_1\text{M}_2\text{I}_2\text{M}_2 diodes from Fig. 6.10. Also shown are (d) \( \log(J) \) vs. \( V \), (e) \( \log(\eta_{\text{sym}}) \) vs. \( V \), and (f) \( f_{\text{NL}} \) vs. \( V \) plots for “thin” bilayer ZrCuAlNi/Al₂O₃/HfO₂/Al \text{M}_1\text{I}_1\text{M}_2\text{I}_2\text{M}_2 and ZrCuAlNi/HfO₂/Al₂O₃/Al \text{M}_1\text{I}_1\text{M}_2\text{I}_2\text{M}_2 diodes. Al₂O₃ and HfO₂ layers were deposited using 28 and 32 ALD cycles, respectively. \text{M}_1\text{I}_1\text{M}_2\text{I}_2\text{M}_2 diodes with 3.5 nm layers of either Al₂O₃ or HfO₂ are included for comparison.
The inherent asymmetry of these dual dielectric barriers is evident in the equilibrium band diagrams shown in Fig. 6.14. Differences in the electrical behavior are qualitatively explained by the nonequilibrium band diagrams, which illustrate the approximate onset of step tunneling at positive bias for the ZrCuAlNi/Al2O3/HfO2/Al device and at negative bias for the ZrCuAlNi/HfO2/Al2O3/Al device, respectively. 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.

Considering first the ZrCuAlNi/Al2O3/HfO2/Al M1I2M3 device, in which the larger $E_g$ Al2O3 layer (I2) is adjacent to the larger $\Phi_{M1}$ ZrCuAlNi electrode, application of approximately +3.1 V (Fig. 6.14 top, right) brings the Fermi level of the ZrCuAlNi to just above the conduction band of the HfO2 so that direct tunneling may occur from left to right through only the 3.5 nm thick Al2O3 layer—a step reduction in the minimum required tunnel distance. For application of an opposite polarity −3.1 V bias (Fig. 6.14 top, left) electrons tunneling from right to left at the Fermi level must pass through both insulating layers. Therefore, a larger current is expected for positive bias than for an equivalent magnitude negative applied bias and $\eta_{asym} < 1$ is expected. This expectation of $\eta_{asym} < 1$ is confirmed in Fig. 6.13b. Note that the direction of the asymmetry ($\eta_{asym} < 1$) for the ZrCuAlNi/Al2O3/HfO2/Al device is reverse that of the single Al2O3 layer device ($\eta_{asym} > 1$), indicating that the asymmetry of the bilayer dielectric barrier not only opposes that of the built-in voltage induced by $\Delta \Phi_M$, but overwhelms its impact on device operation. As seen in equation (6.1), the tunnel current is exponentially dependent upon $\varphi_b^{-3/2}$. Since $\varphi_{Al-HfO2} < \varphi_{ZrCuAlNi-Al2O3}$, 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 ($\eta_{asym}$)−V plot will decrease [38]. In Fig. 6.13b it is seen that for application of +4 V, the slope of the log ($\eta_{asym}$)−V plot has decreased.

Also shown are (d) log (J) vs. V, (e) log (\eta_{asym}) vs. V, and (f) \(f_{NL}v_s\) vs. \(V\) plots for “thinner” bilayer ZrCuAlNi/Al2O3/HfO2/Al M1I1M2 and ZrCuAlNi/HfO2/Al2O3/Al M1I1M2 diodes. Al2O3 and HfO2 layers were deposited using 28 and 32 ALD cycles, respectively. M1IM2 diodes with 3.5 nm layers of either Al2O3 or HfO2 are included for comparison.

Considering next the reverse insulator stack orientation ZrCuAlNi/HfO2/Al2O3/Al M1I2M1 device, in which the larger band-gap Al2O3 layer (I1) is now adjacent to the smaller $\Phi_{M2}$ Al electrode. With −2.8 V applied to the Al gate (Fig. 6.14 bottom, left), the Fermi level in the Al gate lies just above the conduction band of the 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 (Fig. 6.14 bottom, right) electrons injected from the ZrCuAlNi (M1) must pass through both dielectric layers. Therefore, a smaller current is expected at positive bias than at an equivalent magnitude negative bias so that $\eta_{asym} > 1$ is expected. This expectation is also confirmed in Fig. 6.13b. In this case bilayer dielectric barrier enhances the electrode $\Delta \Phi_M$ asymmetry and $\eta_{asym}$ is increased over that of the single Al2O3 layer M1IM2 diode. Since $\varphi_{Al-Al2O3} > \varphi_{ZrCuAlNi-HfO2}$, 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 $\eta_{asym}$−V plot will be expected to decrease. This expectation is confirmed in Fig. 6.13b.

Shown in Fig. 6.13c, it is seen that all devices exhibit excellent $f_{NL}$ with the bilayer ZrCuAlNi/HfO2/Al2O3/Al M1I2M1 diode showing the highest maximum nonlinearity ($f_{NL_{max}}$ ≈ 27). Consistent with its enhanced $\eta_{asym}$, this device also shows enhanced $f_{NL}$ at low negative bias exceeding that of the single layer Al2O3 and HfO2 devices. The reverse orientation ZrCuAlNi/HfO2/Al2O3/Al device shows improved $f_{NL}$ over the single layer Al2O3 diode at low positive bias and reduced $f_{NL}$ at negative bias, consistent with the direction of its $\eta_{asym}$. The single layer HfO2 device shows the best $f_{NL}$ below ~2V, due to its lower turn-on voltage. The appearance of the sharp increase in $f_{NL}$ for both bilayer devices is at the bias and polarity expected for step tunneling (based on the band diagram simulations in Fig. 6.14).

Also shown in Fig. 6.13 are (d) log (J) vs. V, (e) log (\eta_{asym}) vs. V, and (f) \(f_{NL}v_s\) vs. \(V\) plots for thinner dielectric bilayer ZrCuAlNi/Al2O3/HfO2/Al M1I2M2 and ZrCuAlNi/HfO2/Al2O3/Al M1I2M2 diodes. The HfO2 and Al2O3 layers in these devices were deposited using 32 and 28 ALD cycles, respectively. The estimated thicknesses of the bottom and top dielectric layers are ~1 and ~2.5 nm, respectively. For reference, also plotted are the thinner single dielectric layer Al2O3 and HfO2, M1IM2 diodes from Fig. 6.10, which were deposited using 56 and 65 ALD cycles, respectively. Qualitatively, the behavior of the thinner bilayer devices is similar to...
the thicker devices, but in all cases $\eta_{\text{max}}$ is reduced—behavior that was also seen for the single layer MIM devices. Once again for the ZrCuAlNi/Al$_2$O$_3$/HfO$_2$/Al M$_1$I$_2$M$_2$ device, the dual dielectric bilayer opposes the work function induced asymmetry. At voltages greater than about 2.5 V, $\eta_{\text{asym}} \approx 1$, opposite to the $\eta_{\text{asym}} > 1$ of the single layer Al$_2$O$_3$ device. For the reverse orientation ZrCuAlNi/HfO$_2$/Al M$_1$I$_2$M$_2$ device, the asymmetry induced by the different electrode work functions is once again enhanced by the bilayer dielectric tunnel barrier, resulting in a $\eta_{\text{asym}}$ of higher magnitude than that of the single layer Al$_2$O$_3$ device.

The reduced tunnel barrier thickness, as seen in Fig. 6.13f, resulted in improved $\eta_{\text{asym}}$ at small biases for all devices. This is due primarily to the lower turn-on voltages and higher conductivity (compare Fig. 6.13a, b). Note however that the improvement for the bilayer devices is even greater than for the single layer devices. As compared to single layer Al$_2$O$_3$, both of the thin MIM devices now have enhanced low bias $\eta_{\text{asym}}$ for both polarities. Again, both bilayer devices have their highest $f_{\text{NL}}$ for the bias polarity at which the step reduction in tunneling distance occurs. Consistent with the $\eta_{\text{asym}}$ data, for the ZrCuAlNi/Al$_2$O$_3$/HfO$_2$/Al M$_1$I$_2$M$_2$ devices $f_{\text{NL}}$ is highest at positive bias, while for ZrCuAlNi/HfO$_2$/Al M$_1$I$_2$M$_2$ devices $f_{\text{NL}}$ is highest at negative bias.

Note that for rectenna applications, MIM rectifying diodes must match the impedance of the antenna. As small device areas are required to minimize capacitance for high speed operation, ultrathin diodes will be needed in order to provide a sufficiently low resistance to match the impedance of antennas ($\sim$100 $\Omega$). The fact that the MIM devices appear to scale better than single layer MIM diodes suggests they are an excellent candidate for rectenna applications.

Overall, the thin bilayer ZrCuAlNi/HfO$_2$/Al$_2$O$_3$/Al device, despite reduced $\eta_{\text{max}}$ and $f_{\text{NL-max}}$ as compared to the single layer Al$_2$O$_3$ device, shows excellent low voltage characteristics with $\eta_{\text{asym}} \approx 10$ and $f_{\text{NL}} > 5$ at voltages as low as 0.8 V. These recent work has shown that insulator heterojunctions can be used to produce symmetric $I$-$V$ behavior in symmetric metal electrode M$_1$I$_2$M$_1$ diodes, devices in which the same metal is used for the top and bottom electrodes [5, 9, 10]. As a point of reference, Maraghechi et al. [5], recently reported $\eta_{\text{asym}} \approx 10$ at 3 V and $f_{\text{NL}} > 5$ at 0.8 V for a symmetric electrode Cr/2 nm HfO$_2$/2 nm Al$_2$O$_3$/Cr diode. It is clear that dielectric bilayers can have a significant impact on MIM device characteristics. Examining more closely the ZrCuAlNi/Al$_2$O$_3$/Al band diagram in Fig. 6.11 and only considering asymmetry due to tunneling-based conduction, the effect of the tunneling-based asymmetry should begin at roughly the same voltage, independent of insulator thickness. However, in Fig. 6.10b it is seen that while significant asymmetry appears above about 3 V in the 10 nm Al$_2$O$_3$ device, significant asymmetry occurs above about 2 V in the 3.5 nm Al$_2$O$_3$ device. One possible explanation for this discrepancy is the thin ZrCuAlNi electrode and the overlying dielectric (see Fig. 6.12) and the effect of this IL, even the nominally single layer devices might be, in fact, multi-layer devices. To model the potential impact of the ZrO$_x$ IL, band diagrams for those in Fig. 6.14 (bottom row) may be used, replacing HfO$_2$ with 2 nm of PZT and an Al$_2$O$_3$ thickness of either 3.5 or 10 nm. For both ZrCuAlNi/2 nm

ZrO$_x$/IL/Al$_2$O$_3$/Al bilayer devices, the minimum voltage required for the step reduction in tunneling distance is simulated to be approximately 2.25 V. However, in the thicker device, the electrons must tunnel through a 10 nm thick Al$_2$O$_3$ layer while in the thinner device, the electrons have to tunnel through only an approximately 3.5 nm thick Al$_2$O$_3$ layer. As seen in (6.1), tunneling current is exponentially dependent upon the inverse of the barrier thickness ($I \propto e^{-t}$) [38]. Thus in the presence of the ZrO$_x$ IL, the onset voltage for tunneling-based asymmetry is expected to be reduced as the thickness of the Al$_2$O$_3$ layer is reduced. Looking again at the single layer Al$_2$O$_3$ devices in Fig. 6.10, it seems evident that $I$-$V$ characteristics and $\eta_{\text{asym}}$ were impacted by the presence of the ZrO$_x$ IL, although it is also possible that an emission-based conduction mechanism [8] or barrier lowering in the ultrathin device structure, not considered here, may play a role. The IL layer likely plays a role in the nominally single layer HfO$_2$ device as well, but since the $E_G$ and $\chi$ of HfO$_2$ are likely similar to the $E_G$ and $\chi$ of the ZrO$_x$ IL, its impact is more difficult to predict. For the single layer ZrO$_2$ device, the ZrO$_x$ IL layer appears to have little impact.

It should be noted that only step tunneling is of concern to this work. For the same materials used in this study, resonant tunneling is not relevant. Simulations were performed for a variety of dielectric bilayer stacks with wide and narrow band-gaps. Shown in Fig. 6.15 are representative simulated band diagrams for various stacks showing the minimum voltage required for resonant tunneling and for step
Fig. 6.16 J-V plots for M1I3M2 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 1/1 bilayers. In all cases, the total thickness of the tunnel barrier is 10 nm.

tunneling. To present a simplified picture, symmetric work function electrodes were assumed. It was found that for almost all bilayer stacks of SiO2, Al2O3, HfO2, ZrO2, TiO2, Nb2O5, and TiO2, step tunneling occurs at a smaller absolute bias than resonant tunneling. The only exception was the Nb2O5/Ta2O5 bilayer stack shown in Fig. 6.15c, in which resonant tunneling is predicted to occur at a lower bias than step tunneling, consistent with recent simulation work on tunneling probability [9].

As shown in Figs. 6.14 and 6.15, for the bilayer stacks used in this study, the electric field required to reach resonant tunneling exceeds the breakdown strength of the constituent HfO2, Al2O3, and ZrO2 dielectrics.

Finally, shown in Fig. 6.16 is a J-V plot of ZrCuAlNi bottom electrode devices with Al top electrodes. In all cases, the total thickness of the tunnel barrier is 10 nm and consists of either a single layer of Al2O3, a single layer of ZrO2, or various Al2O3/ZrO2 1/1 bilayers. From this preliminary data, it is seen that relative thickness of the individual insulator layers in the bilayer stack may be used to further fine-tune electrical behavior.

Summary

Whereas most previous experimental work on MIM diodes has been conducted on oxide insulators produced by either oxidation or nitridation of the bottom metal electrode, the use of ALD in this work allowed deposition of high quality single layer and multilayer bilayer insulators independent of the bottom metal electrode material. Using these high quality ALD insulators, the impact of bottom electrode roughness on M1I3M2 diode performance and the impact of nanolamine bilayer insulators on M1I3M2 diode performance were explored.

In the first half of the chapter, the performance of MIM tunnel diodes with ALD 3 insulator tunnel barriers on low work function (ZrCuAlNi and Al) and high work function (Ir and two types of Pt) bottom electrode materials with RMS roughness ranging from ~3 Å to greater than 100 Å of the insulator thickness was investigated. It was demonstrated that the roughness at the bottom metal interface can overwhelm the influence of metal work function on the electrical characteristics of M1I3M2 diodes, even reversing the trends expected based on ΔΦM. It was also shown that the percentage yield of functioning devices tracks higher with decreasing roughness and that even for nominally the same metal (Pt), the level of roughness dominates electrical properties and yield. These results indicate that bottom electrode roughness levels of much less than 20 Å of the insulator thickness are necessary to achieve non-roughness dominated electrical behavior, suggesting that many previous MIM tunnel diode studies may have been compromised by uncontrolled bottom electrode roughness [19-24, 27-34]. By combining uniform insulator methods with ultra-smooth (~0.3 nm RMS) ZrCuAlNi amorphous metal bottom electrode, highly nonlinear and asymmetric MIM diode devices with good device uniformity and stable J-V behavior have been demonstrated.

For rectenna-based solar cells as well as other potential applications of MIM diodes, highly asymmetric and highly nonlinear I-V behavior at low applied voltages is required. The standard approach to achieving asymmetric I-V characteristics in tunnel devices is to make M1I3M2 diodes using metals with different work functions (ΦM1 ≠ ΦM2) so as to produce a built-in field across the tunnel barrier [6, 40]. Unfortunately, the amount of asymmetry achievable using the metal work function approach is limited by the ΔΦM that can be obtained using practical electrodes. Note that ultra-smooth amorphous metals such as ZrCuAlNi, despite multiple metal components, typically do not allow a broad tuning of their electrical properties such as work function [53, 54]. Therefore, in the second half of this chapter, an additional approach to achieving asymmetric and nonlinear operation is investigated in which a nanolamine pair of insulators (each with different EQ and χ) are used to create asymmetric tunnel barrier MIM devices. In MIM devices, electrons tunneling from one metal electrode to the other are presented with a different barrier shape depending on the direction of tunneling. It was demonstrated that high quality nanolamine bilayer tunnel barriers deposited via ALD dominate the electrical characteristics of asymmetric metal electrode M1I3M2 devices. I-V asymmetry and nonlinearity were found to be sensitive to the arrangement of the individual insulator layers with respect to the different metal electrodes (M1I3M2 vs. M1I3M2). Depending on whether the smaller χ insulator is adjacent to the smaller or larger ΦM electrode, respectively, the bilayer dielectrics were arranged to either enhance or oppose (even reverse) the ΔΦM induced asymmetry. Using band diagrams and assuming that conduction is dominated by tunneling mechanisms, these results are qualitatively well explained by step tunneling (Figs. 6.14 and 6.15). By combining two methods of producing asymmetry, asymmetric metal electrodes and a bilayer dielectric tunnel barrier, we were able to achieve excellent low voltage asymmetry and nonlinearity in a ZrCuAlNi/HfO2/Al2O3/Al diode exceeding both that of standard single dielectric layer asymmetric electrode M1I3M2 devices as well as recently reported symmetric electrode M1I3M1I3M1 devices. Finally, it was also demonstrated that the relative thickness of the insulator layers may be used to further fine-tune electrical behavior.
Overall, it was shown that combining uniform tunnel barriers deposited via ALD in ultra-smooth metal bottom electrodes, allows for the fabrication of Yler–Nordheim tunneling dominated MIM devices. It was also clearly experimentally demonstrated that nanolamine insulator tunnel barriers are a very way to enhance or tune the asymmetry and nonlinearity of asymmetricall metal electrode MIM devices. The good reproducibility, stable J–V behavior, and tolerance of working devices along with the enhanced properties achieved thinning insulator bilayers with asymmetric work function electrodes represent an advancement toward the understanding necessary to engineer thin film MIM cell devices for commercial microelectronics applications.

**Acknowledgments**

This work was supported in part by grants from the National Science Foundation (through DMR-0805372 and an REU supplement), the U.S. Army Research Office (through W911NF-07-2-0083), and the Oregon Nanoscience and Microtechnologies Initiative. The authors thank Matt Chin, Madan Dubey, and Steve Kilpatrick of the U.S. Army Research Lab for the annotated Pt films and support, Prof. John Wagner, Bill Cowell, and John Conley of the Oregon State University School of Electrical and Computer Engineering for the ZrO2AlN films used in this work, Prof. Douglas Keszler of the Oregon State University Dept. of Chemistry, Wei Wang for assistance with AFM, Chris Tasker for equipment support, Dr. P. Eschbach for assistance with TEM imaging, Cheng Tan and Ben Lambert for assistance with data collection, and Dr. David Evans of Sharp Labs of America for evaporated Pt films.

**References**


Chapter 7
Nanoscale Rectennas with Sharp Tips for Absorption and Rectification of Optical Radiation

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Abstract: We present a method for optical rectification that has been demonstrated both theoretically and experimentally and can be used for the development of a practical optical rectifier. The technique is based on the use of a combination of a metallic material and a metal-semiconductor junction. This technique is based on the observation that the rectification efficiency of a metal-semiconductor junction is improved when the metal is made of a high-conductivity material and the semiconductor is a high-bandgap material. The technique is particularly useful for the development of optoelectronic devices, such as photodetectors and photovoltaic cells.

References: