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Step tunneling enhanced asymmetry in asymmetric electrode metal-insulator-insulator-metal tunnel diodes

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The impact of nanolaminate insulator tunnel barriers on asymmetric metal workfunction metal-insulator-metal-insulator (MIMIM) devices is investigated. We demonstrate experimentally that bilayer insulators introduce additional asymmetry and can be arranged to either enhance or oppose the asymmetry induced by the asymmetric workfunction electrodes. It is also shown that step tunneling can dominate the I-V asymmetry of M1IIM2 diodes. By combining bilayer tunnel barriers with the standard approach of asymmetric metal electrodes, we are able to achieve low voltage asymmetry and non-linearity exceeding both that of standard single layer asymmetric electrode metal-insulator-metal devices as well as symmetric electrode M1I1I2M1 devices. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4799964]

Thin film metal-insulator-metal (MIM) tunnel devices have seen renewed interest for high speed applications such as infrared (IR) detectors, optical rectennas for IR energy harvesting, and hot electron transistors, as well as for macroelectronic applications such as backplanes for liquid-crystal displays (LCDs). For many of these applications, highly asymmetric and non-linear 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 to use metal electrodes with different workfunctions to produce a built-in voltage, \( V_{bi} \), across the tunnel barrier. However, the amount of asymmetry achievable using this approach is limited by the \( \Delta \Phi_{M} \) that can be obtained using practical electrodes. An alternative approach to achieving asymmetric and non-linear operation 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/applied bias polarity. Formation of an asymmetric tunnel barrier can be accomplished using nanolaminate pairs of insulators, each having different band-gaps and band-offsets, to produce a built-in voltage, \( V_{bi} = (\Phi_{M1} - \Phi_{M2})/e \) (where \( e \) is the electronic charge) across the tunnel barrier. However, the amount of asymmetry achievable using this approach is limited by the \( \Delta \Phi_{M} \) that can be obtained using practical electrodes. An alternative approach to achieving asymmetric and non-linear operation 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/applied bias polarity.

Formation of an asymmetric tunnel barrier can be accomplished using nanolaminate pairs of insulators, each having different band-gaps and band-offsets, to produce metal-insulator-insulator-metal (MIM) devices. Very recent work has shown that insulator heterojunctions can be used to produce asymmetric I-V behavior in symmetric metal electrode M1IM2 diodes. It has not been shown whether a bilayer insulator tunnel barrier can be combined with asymmetric workfunction metal electrodes to produce M1I1I2M1 diodes with superior I-V asymmetry. In addition, whereas asymmetry due to resonant tunneling has been studied, asymmetry due to step tunneling, a step reduction in tunnel distance in a bilayer insulator tunnel barrier, has not yet been experimentally demonstrated. In this work, we investigate the combined effect of bilayer tunnel barriers and asymmetric electrodes in M1I1I2M2 tunnel diodes.

Much previous work on MIM diodes has focused on native oxides of rough polycrystalline metals. We recently showed that roughness at the bottom metal-insulator interface can dominate the I-V behavior of MIM diodes and that the use of atomically smooth bottom electrodes combined with high quality insulators deposited via atomic layer deposition (ALD) allowed for fabrication of high quality MIM diodes with well controlled quantum mechanical tunneling. Therefore, we fabricate M1IM2 diodes using smooth amorphous metal ZrCuAlNi (ZCAN) bottom electrodes and nanolaminate insulator bilayers of HfO2 and Al2O3 deposited via ALD. We demonstrate that bilayer insulator tunnel barriers enable tuning of the current vs. voltage (I-V) asymmetry and non-linearity via a step reduction in the minimum tunnel distance at the applied bias at which tunneling may begin to occur through only the wider band-gap insulator layer. We find that I-V asymmetry and non-linearity are sensitive to the arrangement of the individual insulator layers with respect to the larger and smaller workfunction electrodes (e.g., M1I1I2M2 vs. M1I2I1M2) and that bilayer tunnel insulators can be arranged to enhance or oppose the built in asymmetry of the asymmetric workfunction electrodes.

MIM and MIIM diodes were fabricated on Si substrates capped with 100 nm of thermally grown SiO2. A 150 nm thick ZCAN bottom electrode was deposited directly on the SiO2 via DC magnetron sputtering using a Zr40Cu35Al15Ni10 metal target. ZCAN RMS and peak roughness were measured to be 0.3 nm and 3 nm, respectively. Next, thin oxide tunnel barriers were deposited via ALD using a Picosun SUNALE R-150B. Trimethylaluminum (TMA) and tetrakis (ethylmethylamino) hafnium (TDMAHf) were used as the metal precursors for Al2O3 and HfO2, respectively. All ALD films were deposited at a chamber temperature of 250°C using deionized water as the oxidant. Nanolaminate bilayer barriers were deposited in one continuous run without breaking vacuum. Finally, top electrodes were formed by evaporating Al dots (~0.8 mm2) through a shadow mask. Insulator thickness on Si was measured with a J.A. Woollam WVASE32 spectroscopic ellipsometer using a Cauchy model. Transmission electron microscopy (TEM) images were taken on a FEI Titan 80–200 using samples prepared with a Quanta 3D Dual Beam focused ion beam. Metal workfunctions (\( \Phi_{M} \)) were measured in air using a KP
The behavior of the individual insulators was first measured in single layer MIM diodes. Shown in Fig. 1 are plots of (a) log (J) vs. V and (b) log (η) vs. V for M1M2 diodes, where the bottom electrode M1 is ZCAN, the top electrode M2 is Al, and I is an approximately 3.5 nm or 10 nm thick single layer of either Al2O3 or HfO2. As expected, the total current flow in Fig. 1(a) is a rough function of the relative barrier heights (see band diagrams shown as inset in Fig. 1(b)). In Fig. 1(a), the dominance of FN tunneling is apparent from the presence of the “knees” in the log (J)–V data at positive and negative biases, which are followed by several orders of magnitude of exponentially increasing current. Not shown, FN plots of ln (I/(V + ΔΦ)) vs. 1/(V + ΔΦ) confirm that Al2O3 and HfO2 devices are dominated by FN tunneling in the post turn on regime.13 Due to the asymmetric workfunction electrodes, the devices are expected to show asymmetry. In Fig. 1(b), it is seen that the 10 nm Al2O3 diode shows a maximum η (ηmax) of approximately 1350 at 4.1 V. Although the Al2O3 devices show excellent η at higher biases, asymmetric operation at low voltage is desirable for many applications, including energy harvesting. As seen in Fig. 1(b), decreasing the tunnel barrier thickness to 3.5 nm resulted in decreased turn on voltages and increased current. However, ηmax was not improved, most likely due to the increased influence of direct tunneling. Since decreasing the dielectric thickness in a single layer MIM diode does not improve asymmetry, another strategy is required.

Two key figures of merit are defined to characterize the devices. First, I-V asymmetry, η, is defined as negative device current divided by positive current (|I−/I+|) so that η = 1 indicates symmetric operation. Second, non-linearity, fNL, is defined as (dI/dV)/(I/V). All band diagrams were simulated using the Boise State University Band Diagram program.23 Materials’ parameters used in simulations are consistent with reported values for similar ALD films: electron affinity (χ) = 1.3 eV, bandgap (Eg) = 6.4 eV, and relative dielectric constant (κ) = 7.6 for Al2O3; χ = 2.5 eV, Eg = 5.8 eV, and κ = 18 for HfO2; and ΦAl = 4.2 eV.

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Shown in Fig. 2 are cross sectional TEM images of ZCAN/Al2O3/HfO2/Al M1I1I2M2 devices in (a) and (c), and ZCAN/HfO2/Al2O3/Al M1I1I2M2 devices in (b). For each insulator 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 TEM images in (a) and (b) reveal that while the top insulator layer is indeed approximately 5 nm thick, in each case, the insulator layer deposited directly on the ZCAN bottom electrode is only approximately 3.5 nm thick. The reduced thickness is due to an inhibition of the ALD nucleation rate on ZCAN 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 (IL) between the ZCAN and the insulator. This layer was previously determined to be composed of ZrOx.22 Fig. 2(c) is a lower magnification image of the device from (a), revealing the smooth nature of the ZCAN/Al2O3 border over an extended range. We previously found that a smooth interface is critical to achieving high yield, high quality MIM tunnel devices.20,21
shown in Fig. 3(b). Note that since \( \varphi_{\text{Al-Al2O3}} > \varphi_{\text{ZCAN-HfO2}} \), at higher magnitude applied biases, the current density will pass through both insulator layers. Thus, a smaller current is expected at positive bias than at an equivalent magnitude negative bias so that \( \eta > 1 \) is expected, again confirmed in Fig. 3(b). In this case, the asymmetry of the bilayer insulator barrier \textit{enhances} the built-in asymmetry of the \( \Delta \Phi \) and \( \eta \) is increased over that of the single Al2O3 layer M1IM2 diode. Note that since \( \varphi_{\text{Al-Al2O3}} > \varphi_{\text{ZCAN-HfO2}} \), at higher magnitude applied biases, the current density will begin to increase more quickly under positive bias than negative bias and the slope of the \( \eta \)-V plot will be expected to decrease. This behavior is confirmed in Fig. 3(b).

In Fig. 3(c), it is seen that all devices exhibit excellent \( f_{\text{NL}} \) with the bilayer ZCAN/HfO2/Al2O3/Al1M13M2 device showing the highest maximum non-linearity \( (f_{\text{NL-max}} \sim 27) \). This device also shows enhanced \( f_{\text{NL}} \) at low negative bias exceeding that of single layer Al2O3 and HfO2 devices, consistent with its enhanced \( \eta \). The reverse insulator stack orientation ZCAN/Al2O3/HfO2/Al M1IM2 device shows improved \( f_{\text{NL}} \) over the single layer Al2O3 M1IM2 diode at low positive bias and reduced \( f_{\text{NL}} \) at negative bias, consistent with the polarity of its \( \eta \). Below \( \sim 2 \text{ V} \), the single layer HfO2 device shows the best \( f_{\text{NL}} \) consistent with its lower turn-on voltage.

Shown in Fig. 4 are (a) \( \log (J) \) vs. \( V \), (b) \( \log (\eta) \) vs. \( V \), and (c) \( f_{\text{NL}} \) vs. \( V \) plots for thinner insulator bilayer ZCAN/Al2O3/HfO2/Al1M13M2 and ZCAN/HfO2/Al2O3/Al M1IM2 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 insulator layers are \( \sim 1 \text{ nm} \) and \( \sim 2.5 \text{ nm} \), respectively. For
reference, also plotted are the approximately 3.5 nm thick single insulator layer Al2O3 and HfO2 M1IM2 diodes from Fig. 1, which were deposited using 56 and 65 ALD cycles, respectively. The behavior of these thinner bilayer devices is qualitatively the same as for the thicker devices. However, in all cases \( I_{\text{max}} \) is reduced, behavior that was also seen for the single layer MIM devices. Once again for the ZCAN/Al2O3/HfO2/Al M1I1I2M2 device, the insulator bilayer opposes the \( \Delta \Phi_M \) induced asymmetry. At voltages greater than about 2.5 V, \( \eta < 1 \) for the M1I1I2M2 device opposite to the \( \eta > 1 \) of the neat Al2O3 MIM device. For the reverse insulator orientation ZCAN/HfO2/Al2O3/Al M1I1I2M2 device, the asymmetry induced by \( \Delta \Phi_M \) is once again enhanced by the bilayer insulator tunnel barrier, resulting in an \( \eta \) of higher magnitude than that of the neat Al2O3 MIM device.

As seen in Fig. 4(c), reducing the tunnel barrier thickness results in improved \( f_{\text{NL}} \) at small biases for all devices. This is due primarily to the lower turn on voltages and higher conductivity of these devices (see Fig. 4(a)). The relative improvement for the bilayer devices is even greater than for the single layer devices—as compared to single layer Al2O3, both of the thin MIM devices show enhanced low bias \( f_{\text{NL}} \) for both polarities. Both MIM devices have their highest \( f_{\text{NL}} \) for the bias polarity at which the step reduction in tunneling distance occurs. For the ZCAN/Al2O3/HfO2/Al M1I1I2M2 devices, \( f_{\text{NL}} \) is highest at positive bias, while for ZCAN/ HfO2/Al2O3/Al M1I1I2M2 devices, \( f_{\text{NL}} \) is highest at negative bias, consistent with \( \eta \) data.

Overall, the thin bilayer ZCAN/HfO2/Al2O3/Al device, despite reduced \( I_{\text{max}} \) and \( f_{\text{NL, max}} \) as compared to the single layer Al2O3 device, shows excellent low voltage characteristics with \( \eta > 10 \) and \( f_{\text{NL}} > 5 \) at voltages as low as 0.8 V. For comparison, Maraghechi et al. recently reported \( \eta \sim 10 \) at 3 V and \( f_{\text{NL}} < 5 \) at 0.8 V for a symmetric electrode Cr/2 nm HfO2/2 nm Al2O3/Cr diode.

It is clear that bilayer insulators can have a significant impact on M1IM2 device operation. Examining more closely the ZCAN/Al2O3/Al band diagram inset in Fig. 1(b) and considering asymmetry due only to tunneling based conduction, the onset of FN tunneling should be roughly at the same voltage, independent of insulator thickness. However, in Fig. 1(b), it is seen that while significant asymmetry occurs above about 3 V in the 10 nm Al2O3 device, significant asymmetry occurs above about 1 V in the 3.5 nm Al2O3 device. While part of the reason for this may be the increased thickness of the Al2O3 reducing conduction below the noise floor of our measurement system, another possible explanation for this discrepancy could be the thin ZrOx IL between the ZCAN electrode and the overlying insulator (see Fig. 2 as well as Ref. 22). Because of this IL, even the nominally single layer devices might be, in fact, bilayer devices. To model the potential impact of the ZrOx IL, band diagrams similar to those in Fig. 3(e) may be used, if HfO2 is replaced with 2 nm of ZrOx and an Al2O3 thickness of approximately either 3.5 nm or 10 nm is used. For ZCAN/2 nm ZrOx IL/ Al2O3/Al bilayer devices, the minimum voltage 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 Al2O3 layer, while in the thinner device, the electrons tunnel through only an approximately 3.5 nm thick Al2O3 layer. Tunneling current is exponentially dependent upon the inverse of the barrier thickness \((1 \propto \exp(1/d_{\text{ox}}))\).

In conclusion, we have experimentally demonstrated that ALD nanolaminate bilayer tunnel barriers add additional asymmetry and can be used to tune I-V asymmetry and non-linearity in asymmetric metal electrode M1IM2 devices via step tunneling. I-V asymmetry and non-linearity were found to be sensitive to the arrangement of the individual insulator layers with respect to the asymmetric workfunction metal electrodes (M1I1I2M2 vs. M1I2I1M2). The bilayer insulators can be arranged to either enhance or oppose the built in asymmetric electrode workfunction induced asymmetry, depending on whether the smaller \( \chi \) insulator is adjacent to the smaller or larger \( \Phi_M \) electrode, respectively. By combining two methods of producing asymmetry, asymmetric metal electrodes and a bilayer insulator tunnel barrier, we were able to achieve excellent low voltage asymmetry and non-linearity in a ZCAN/HfO2/Al2O3/Al diode exceeding both of that standard single insulator layer asymmetric electrode M1I2M2 devices as well as symmetric electrode M1I1I2M1...
It is very likely that the relative thickness of the layers in the bilayer may be used to further enhance asymmetry. These results represent clear experimental demonstration that the asymmetry and non-linearity of MIIM diodes with asymmetric workfunction electrodes can be tuned by controlling step tunneling in the bilayer insulator, thus representing an advancement in the understanding necessary to engineer thin film MIIM tunnel devices for microelectronics applications.

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