Impact of Metal Work-Function on Current Rectification by Metal-Insulator-Metal Diodes

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ORIGINAL RESEARCH

Abstract- This article presents the experimental investigation of the effect of metal work-function on current rectification by metal–insulator–metal (MIM) diodes. Diverse MIM diode topologies that utilized various types of metal configurations were fabricated and subjected to DC electrical (J-V) characterization, and it was found that the work-function of the various metals impacts the symmetry and linearity of the diodes’ current–voltage curves, the amount of current the diodes can rectify, and their typical zero-bias curvature coefficients. The diodes whose both metal layers have the same work-function exhibits more linear and symmetrical current–voltage curves, with the curves becoming more nonlinear and asymmetrical as the variation in work-function of the metals increase, impacting the applications where MIM diodes can be used.

Keywords- Metal-insulator-metal diodes, current–voltage curves, Zero-bias curvature coefficient, work-function, current rectification.

1 INTRODUCTION

Significant amount of work has been directed to the development of metal-insulator-metal (MIM) diodes due to their promise in a wide range of applications including wireless power transfer such as in radio-frequency identification (RFID) tags and intraocular pressure (IOP) measurement soft-contact lens, high frequency detectors and thermal-energy harvesting (Etor et al., 2021; Jinpeng et al., 2012; Pan et al., 2014; Periasamy et al., 2011). MIM diode is an ultrafast quantum device consisting of a thin dielectric layer deposited between two thin film metal layers which cause an electric current to flow through the dielectric from one metal layer to another metal layer and can operate at frequencies well into the infrared range, making it suitable for ultra-high frequency applications such as thermal energy harvesting and infrared imaging (Sakuma & Evenson, 1974; Evenson et al., 1970; Drullinger et al., 1983; Denisov et al., 2007; Evenson et al., 1984).

The high promise of the MIM diode have been, however, limited by manufacturing challenges including the deposition of a uniform and conformal dielectric layer, as a dielectric layer in a few atomic scales, not more than 4 nm, needs to be used. The deposition techniques mostly available include thermal annealing, exposure to ambient environment, sputtering, reactive ion etching (RIE) and exposure to a moist elevated temperature environment (Dodd et al., 2012). These techniques often result in defective thin dielectric layers with many pin holes, which causes reduced current rectification and/or undefined electron conduction mechanism and short-circuit to occur in diode terminals, greatly reducing yield. To overcome this challenge, attention has been directed on developing MIM diodes using single molecule (Elbing et al., 2005; Diez-Pérez et al., 2009; Lortsch et al., 2012; Batra et al., 2013; Siya et al., 2015), and recently, the use of an octadecyltrichlorosilane (OTS) self-assembled monolayer (SAM) (Etor et al., 2016), which consists of carbon chains strongly packed together with an overall thickness of approximately 2 nm. Due to the nature of the self-assembly, a second layer cannot grow on top of the first one, resulting in a uniform thickness over large areas determined by the SAM chemistry (Etor et al., 2016; Etor et al., 2019). The electrical results obtained upon characterization, such as current–voltage characteristics, zero-bias curvature coefficient, zero-bias resistance, and electron conduction (Etor et al., 2019), competes favourably with the state-of-the-art (Mitrovic et al., 2021; Hemmetter et al., 2021).

For MIM diode to be utilized in applications such as high frequency detection and energy harvesting, the diode needs to be able to produce an asymmetric current-voltage curve with respect to the polarity of the metals. It is also vital for the diode to operate at zero-bias, in which case, close attention needs to be paid on the topology of the diode. It has been speculated that the work-function of the metals utilized in the diode structure impacts the nature of the current they rectify (Dodd et al., 2015).

2 METHODOLOGY

To investigate the above hypothesis in Dodd et al. (2015), this project presents experimental results from utilizing diverse metals with a wide range of work-function differences in the diode structure. In this work, platinum (Pt), nickel (Ni), titanium (Ti), chromium (Cr), Aluminium (Al) and copper (Cu) metals were used to fabricate and electrically characterize Ti/OTS/Ti, Ti/OTS/Ni, Ti/OTS/Cr, Ti/OTS/Cu, Ti/OTS/Al, and Ti/OTS/Pt MIM structure topologies.

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Section B- ELECTRICAL/ COMPUTER ENGINEERING & RELATED SCIENCES

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2.1 ELECTRON WORK-FUNCTION

Work-function, $\phi$, is the minimum amount of external energy required to move an electron with the Fermi energy from the surface of an electrode or crystal to the field-free region external to the surface at absolute zero (Halas et al., 1998; Chrzanowski et al., 2018; Surma et al., 2018). The work-function is an important physicoelectronic characteristic of the interfaces between thin film metals and dielectric surfaces (Dodd et al., 2015; Chrzanowski et al., 2018). In theory, a MIM diode structure utilizing metals with similar work-function, $\phi$, will have symmetric energy barrier heights at each metal-dielectric interface, as shown in Fig. 1(a), and asymmetric barrier heights if the work-functions are dissimilar, as shown in Fig. 1(b).

The case in Fig. 1(a) will result in a diode producing linear and symmetric current-voltage curve and Fig. 1(b), non-linear and asymmetric current-voltage curve.

![Energy-barrier diagram of typical MIM diodes with metals of similar (a), and (b) dissimilar work-functions. $\phi_m$ and $\phi_m$ are work-functions for metals 1 and 2 respectively, and d, the thickness of the dielectric.](image)

Fig. 1: Energy-barrier diagram of typical MIM diodes with metals of similar (a), and (b) dissimilar work-functions. $\phi_m$ and $\phi_m$ are work-functions for metals 1 and 2 respectively, and d, the thickness of the dielectric.

The values of the work-function of metals that is obtained from measurements greatly depends on conditions such as the cleanliness of the metal surface, the atomic surface density of the metal, or the degree of surface packing (Surma, 2000). Therefore, for the same metal, the work-function value can differ for different measurements depending on the above conditions of the metal. Table 1 shows the work-function of the metals used in this experiment, with values obtained under diverse measurement conditions and from different sources (Surma, 2001; Liu et al., 2015; Brodie et al., 2014; Ji et al., 2016; Kawano, 2008; Hua et al., 2011; Lu et al., 2018; Michaelson, 1997). Analyses were performed using the average work-function of each metal (as in Table 1).

<table>
<thead>
<tr>
<th>Metals</th>
<th>Pt</th>
<th>Ni</th>
<th>Ti</th>
<th>Cr</th>
<th>Al</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi$(eV)</td>
<td>5.63</td>
<td>5.15</td>
<td>4.33</td>
<td>4.44</td>
<td>4.28</td>
<td>4.70</td>
</tr>
<tr>
<td>$\phi$(eV)</td>
<td>5.64</td>
<td>5.22</td>
<td>4.33</td>
<td>4.50</td>
<td>4.39</td>
<td>4.70</td>
</tr>
<tr>
<td>Average $\phi$</td>
<td>5.70</td>
<td>5.35</td>
<td>4.33</td>
<td>4.50</td>
<td>4.34</td>
<td>4.70</td>
</tr>
<tr>
<td>$\Delta \phi$</td>
<td>5.36</td>
<td>4.96</td>
<td>4.33</td>
<td>4.60</td>
<td>4.38</td>
<td>4.65</td>
</tr>
<tr>
<td>STD eV</td>
<td>0.36</td>
<td>0.25</td>
<td>0.08</td>
<td>0.04</td>
<td>0.02</td>
<td>0.18</td>
</tr>
<tr>
<td>STD error</td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>0.02</td>
<td>0.01</td>
</tr>
</tbody>
</table>

2.2 DIODE FABRICATION

Fig. 2 (not drawn to scale) shows the process of fabricating the diode as in (Etor et al. 2016). A two-layer film of approximately 25 nm of titanium metal (m1) coated with 100 nm of gold metal was deposited by electron beam evaporation and lift-off (a). In a subsequent photolithographic step, gold was removed by an iodine/potassium-iodide (4:1.8 KI:I$_2$) wet etch, leaving exposed small areas of m1 (b-c). After removing the photoresist (d) a 2 nm thick layer of OTS was deposited on the exposed m1 (e) using the technique described in Etor et al. (2016). After a further photolithographic step, a 40 nm thick layer of m2 (Ti, Ni, Cr, Cu, Al, and Pt) was coated on the sample and then patterned through lift-off in the covered regions, resulting in small m1/OTS/m2 junctions (g-h), concluding the MIM diodes fabrication.

![Fabrication process for the m1/OTS/m2 MIM diode.](image)

Fig. 2: Fabrication process for the m1/OTS/m2 MIM diode.

![A sketch of the mi/OTS/m2 device (a) and a SEM image of a fabricated structure (b). m1 and m2 acts as the anode and the cathode, respectively.](image)

Fig. 3: A sketch of the m1/OTS/m2 device (a) and a SEM image of a fabricated structure (b). m1 and m2 acts as the anode and the cathode, respectively.

2.3 DC CHARACTERIZATION OF THE M1/OTS/M2 DIODES

The fabricated diodes were electrically characterized using a source measurement unit (SMU) and a 4-point probe station. They (diodes) were tested over a bias voltage range of ±0.2 V, and MIMs’ figures of merit...
including bias voltage (V) sweep and their corresponding rectified current density (J), and zero-bias curvature coefficient (YZB), were extracted for analysis using a MATLAB program. Curvature coefficient, Y, expressed in Eq. 1, is an important figure of merit used to characterize the MIM structure. It is the ratio of the second derivative to the first derivative of the diode’s J-V curve, and is typically used in quantifying the non-linearity of the structure’s J-V curve at a given voltage, \( V_g \) (Etor et al. 2016).

\[
Y = \left( \frac{d^2I}{dV^2} \right) \left/ \frac{dI}{dV} \right|_{V=V_g}
\]

(1)

Although Y can be obtained at any desired voltage, it is more useful at zero-bias, especially for applications like detection or energy harvesting where biasing is absent during operation (Etor et al. 2021)). Zero-bias curvature coefficient, \( Y_{ZB} \), is, therefore.

\[
Y_{ZB} = \left( \frac{d^2I}{dV^2} \right) \left/ \frac{dI}{dV} \right|_{V=0}
\]

(2)

3 RESULTS AND DISCUSSION

Fig. 4 shows the J-V curves of the various diode topologies. The linearity and asymmetry of the J-V curves for the various diode topologies differ. Diode topologies who’s m1 and m2 have similar work-functions tend to have a more linear and symmetric J-V curves. This changes as the difference in metals work-functions begins to increase, as can be seen in Fig. 4(b) to 4(f).

Although in theory the diode J-V curve is linear and symmetric if the work-function of the two metals is the same as described in Fig. 1(a), the diode is, however, unlikely to have a perfectly linear and symmetrical J-V curve despite the work-function of the two metals being the same, due to the roughness of the surface of the crystalline metal film when deposited, which is often large enough to cause imperfection of the metal-dielectric interface across the diode junction area. This is evident in the J-V curve of Fig. 4(a) where m1 and m2 have the same work-function but then the J-V curve is not perfectly linear and symmetrical. Another observation from the J-V curves in Fig. 4 is that the more linear and symmetrical the diodes’ J-V curves are, the more current is being produced but with less rectification taking place, as rectification is typically proportional to the asymmetry of a diode’s J-V curve. Although MIM diodes utilizing metals with similar work-function tend to produce more current, they are not suitable for applications where more current rectification is required. Table 2 shows the \( Y_{ZB} \) for 23 diodes from each of the m1/OTS/m2 fabricated diode topology. It can be observed that the nature of the diodes’ J-V curves also impacts the \( Y_{ZB} \) of the diodes. The Ti/OTS/Pt structure, who’s metals have the highest work-function difference (\( \Delta \phi = 1.25 \ eV \) (see Table 1)) has the highest non-linear and asymmetric J-V curve (see Fig. 4(i)) and consequently has the highest average \( Y_{ZB} (Y_{ZB} = 4.98 \ V^{-1}) \) as can be seen in Table 2.

Table 2. \( Y_{ZB} \) values for 23 MIM diodes from each of the m1/OTS/m2 fabricated topology

<table>
<thead>
<tr>
<th>Topology</th>
<th>Ti/OTS</th>
<th>Ti/OTS</th>
<th>Ti/OTS</th>
<th>Ti/O</th>
<th>Ti/OTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti/PT</td>
<td>4.70</td>
<td>2.91</td>
<td>0.26</td>
<td>0.53</td>
<td>0.25</td>
</tr>
<tr>
<td>Ti/Ni</td>
<td>5.40</td>
<td>2.52</td>
<td>0.19</td>
<td>0.52</td>
<td>0.29</td>
</tr>
<tr>
<td>Ti/Ti</td>
<td>6.45</td>
<td>1.04</td>
<td>0.21</td>
<td>0.48</td>
<td>0.28</td>
</tr>
<tr>
<td>Ti/Cr</td>
<td>5.95</td>
<td>2.62</td>
<td>0.25</td>
<td>0.56</td>
<td>0.23</td>
</tr>
<tr>
<td>Ti/Al</td>
<td>5.08</td>
<td>2.24</td>
<td>0.24</td>
<td>0.50</td>
<td>0.55</td>
</tr>
<tr>
<td>Ti/Cu</td>
<td>4.26</td>
<td>1.62</td>
<td>0.25</td>
<td>0.63</td>
<td>0.23</td>
</tr>
<tr>
<td>Ti/TS</td>
<td>5.19</td>
<td>2.80</td>
<td>0.31</td>
<td>0.35</td>
<td>0.16</td>
</tr>
<tr>
<td>Ti/TS</td>
<td>5.13</td>
<td>1.90</td>
<td>0.28</td>
<td>0.49</td>
<td>0.17</td>
</tr>
<tr>
<td>Ti/TS</td>
<td>4.59</td>
<td>1.11</td>
<td>0.15</td>
<td>0.47</td>
<td>0.31</td>
</tr>
<tr>
<td>Ti/TS</td>
<td>4.98</td>
<td>2.76</td>
<td>0.28</td>
<td>0.48</td>
<td>0.20</td>
</tr>
<tr>
<td>Ti/TS</td>
<td>5.12</td>
<td>2.65</td>
<td>0.33</td>
<td>0.40</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Diode \( Y_{ZB} \)

| Ti/OTS | 5.17 | 3.17 | 0.25 | 0.51 | 0.32 | 1.30 |
| Ti/OTS | 5.05 | 2.52 | 0.16 | 0.37 | 0.28 | 0.73 |
| Ti/OTS | 5.18 | 3.05 | 0.28 | 0.55 | 0.23 | 1.33 |
| Ti/OTS | 6.08 | 3.16 | 0.37 | 0.60 | 0.47 | 0.56 |
| Ti/OTS | 5.41 | 2.76 | 0.55 | 0.37 | 0.28 | 1.20 |
| Ti/OTS | 5.31 | 2.50 | 0.22 | 0.42 | 0.43 | 1.50 |
| Ti/OTS | 4.40 | 1.91 | 0.22 | 0.37 | 0.25 | 1.12 |
| Ti/OTS | 2.16 | 2.12 | 0.32 | 0.42 | 0.46 | 1.28 |
| Ti/OTS | 3.88 | 2.99 | 0.20 | 0.72 | 0.28 | 1.15 |
| Ti/OTS | 4.98 | 2.42 | 0.27 | 0.49 | 0.30 | 1.10 |
| Ti/OTS | 0.89 | 0.63 | 0.09 | 0.10 | 0.11 | 0.42 |
| Ti/OTS | 0.20 | 0.14 | 0.02 | 0.02 | 0.02 | 0.09 |

| Average \( Y_{ZB} \) | 4.98 | 2.42 | 0.27 | 0.49 | 0.30 | 1.10 |
| STD eV | 0.89 | 0.63 | 0.09 | 0.10 | 0.11 | 0.42 |
| STD error | 0.20 | 0.14 | 0.02 | 0.02 | 0.02 | 0.09 |
Fig. 5 shows a plot of the average zero-bias curvature coefficient, $Y_{ZB}$, of the diodes as a function of the work-function difference, $\Delta \phi$, of their metals. The error bars in the graph show the standard deviation (see Table 1) from the different work-function of the various metals obtained from the literature. Despite the error margins, the trend in the graph is clear, which is, $\Delta \phi$ significantly changes $Y_{ZB}$.

Therefore, MIM diodes may have a symmetric or asymmetric $J$-$V$ curve depending on the shape of the electron tunnelling barrier as in Fig. I, which is to a large extent determined by the work-function difference between the two metal films utilized. Dissimilar metals create different energy barrier heights at each metal-dielectric interface due to the work-function difference. As a result, a non-linear and asymmetric current is generated.

The choice of topology will depend on application. In energy harvesting and detection applications, the diode zero-bias parameters such as the $Y_{ZB}$ is of paramount importance (the more the $Y_{ZB}$, the more rectification can occur without the need for an externally applied bias). In which case, the $\Delta \phi$ between metals should be maximized.

5 CONCLUSION

The fabrication of MIM diodes using diverse metal combinations have been presented. Electrical tests show that the diode structure which utilizes metals of similar work-function exhibits a more linear and a symmetric current-voltage characteristic, resulting in the production of more current but lower zero-bias curvature coefficient. Conversely, diodes that utilizes metals with dissimilar work-function tend to produce non-linear and an asymmetric current-voltage characteristic, with these increasing as the work-function difference between metal increases, and results in the production of higher zero-bias curvature coefficient, a parameter that allows the MIM diode to rectify current without the need for an externally applied bias and making it an excellent candidate for energy harvesting and sensing applications. The results obtained shows that the work-function of metals utilized in the MIM structure significantly impacts the symmetry and linearity of the diodes’ current–voltage curves, the amount of current the diodes can rectify, their typical zero-bias curvature coefficients, and ultimately the applications where they can be utilized.

REFERENCES


