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Cite as: J. Appl. Phys. 125, 055301 (2019); https://doi.org/10.1063/1.5066569
Submitted: 15 October 2018 . Accepted: 09 January 2019 . Published Online: 01 February 2019

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Internal photoemission spectroscopy determination of barrier heights between Ta-based amorphous metals and atomic layer deposited insulators


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ABSTRACT
The energy barrier heights between two recently reported Ta-based amorphous metals (TaWSi and TaNiSi), TaN, and atomic layer deposited Al2O3 and HfO2 insulators are measured in metal/insulator/metal (MIM) structures with Au top electrodes using internal photoemission (IPE) spectroscopy. For Al2O3, the Ta-based metal barrier heights, wBn, increase with increasing metal work function, ΦM, for TaN, TaWSi, and TaNiSi, respectively. For HfO2, however, the barrier heights are relatively constant for all three metals wBn,TaNiSi ≈ wBn,TaWSi ≈ wBn,TaN. The difference between HfO2 and Al2O3 is attributed to enhanced Fermi-level pinning due to a larger dielectric constant. The slope parameter, S, was found to be roughly 0.89 and 0.44–0.69 for Al2O3 and HfO2, respectively. For devices with a TaWSi bottom electrode, a comparison was also made between Al and Au top electrodes. Significantly, smaller barrier heights were obtained with an Au top electrode than with an Al top electrode, 0.6 eV and 0.8 eV lower for HfO2 and Al2O3, respectively. IPE energy barriers are found consistent with current-voltage asymmetry of MIM diodes, whereas Schottky model predictions of barrier heights were inconsistent.
as if it has an effective work function, \( \Phi_{\text{M,eff}} \), different from \( \Phi_{\text{M,vac}} \), where

\[
\Phi_{\text{M,eff}} = E_{\text{CNL}} + S(\Phi_{\text{M,vac}} - E_{\text{CNL}}),
\]

where \( S \) is the slope of a plot of \( \varphi_{\text{In}} \) versus \( \Phi_{\text{M,vac}} \) for a given insulator\(^{21}\)

\[
S = \frac{\partial \varphi_{\text{In}}}{\partial \Phi_{\text{M,vac}}},
\]

\( S \) describes how much \( \Phi_{\text{M,eff}} \) actually changes in response to a change in \( \Phi_{\text{M,vac}} \), where \( S = 0 \) indicates complete “pinning” of \( E_{\text{F,In}} \) at \( E_{\text{CNL}} \) and \( S = 1 \) indicates an absence of pinning.

Despite good success of this theory, it is difficult to calculate or determine the \( E_{\text{CNL}} \) for a given material and it is often observed that \( \varphi_{\text{In}} \) can deviate substantially from predictions due to extrinsic defects that can arise from processing details such as the deposition method, interface traps and near interfacial trapped charge due to point defects, dipoles due to interfacial chemical reactions, and remote scavenging of oxygen. It is therefore necessary to directly measure \( \varphi_{\text{In}} \) for each metal/insulator combination.

An electro-optical technique that allows for the direct measurement of specific interfacial energy barriers within a device structure is internal photoemission (IPE) spectroscopy.\(^{17}\) Although IPE has been widely used to characterize the interfaces between various polycrystalline elemental metals and oxides within MOS structures,\(^{18,22,23}\) there have been only a few reports of IPE within MIM structures,\(^{17,24-27}\) and only one previous report of IPE on an amorphous electrode.\(^{24}\)

In this work, we use IPE spectroscopy to directly measure barrier heights in MIM device structures between two new Ta-based amorphous metals (TaNiSi and TaWSi), TaN, and insulators (Al\(_2\)O\(_3\) and HfO\(_2\)) deposited via atomic layer deposition (ALD).

II. EXPERIMENTAL

MIM devices were fabricated on Si substrates with 100 nm of thermally grown SiO\(_2\) to provide electrical isolation from the underlying Si. TaWSi and TaNiSi bottom electrodes were deposited using DC magnetron sputtering from single alloy targets targeting a thickness of 100 nm, verified via profilometry.\(^{10,30}\) TaN bottom electrode substrates (obtained from ON Semiconductor, Gresham, OR) consisted of a Si/SiO\(_2\)/Ta/TaN stack that was planarized via chemical mechanical polishing. Insulators were deposited on the bottom electrodes using atomic layer deposition (ALD), targeting a thickness of roughly 15 nm, such that the insulator was thick enough to prevent direct tunneling from dominating charge transport. Al\(_2\)O\(_3\) and HfO\(_2\) were deposited using thermal ALD in a Picossan SUNALE R-150 reactor at 250 °C. The precursors used for Al\(_2\)O\(_3\) and HfO\(_2\) were trimethylaluminum (TMA) and tetrakis(ethylmethylamo)fnium (TEMA-Hf), respectively, with H\(_2\)O as the oxidizing agent. Insulator thickness was monitored by including a Si witness wafer (with a ∼1.2 nm layer of native SiO\(_2\)) in the ALD chamber for each deposition. For the semi-transparent top contact needed for IPE measurements, approximately 10 nm of either Al or Au was deposited via thermal evaporation, monitored with a quartz crystal microbalance. Au top electrodes were patterned with a shadow mask to yield circular devices with a diameter of 250 μm. Al top electrodes were patterned with photolithography into 200 by 200 μm squares. No anneals were performed.

IPE measurements were conducted using a 150 W Xe arc lamp source that was passed through a monochromator and then a long-pass filter (to remove second-order diffraction). The light was then shined onto the device of interest using a parabolic mirror focused to a spot size of 1 mm\(^2\). Electrical bias was applied to the MIM bottom electrode and the top electrode was held at ground. At each applied bias, \( V \), the electrical current was measured as the photon energy (\( h\nu \)) was swept from 2 to 5 eV (620–248 nm). A large increase in current is detected as \( h\nu \) approaches the height of the electron energy barrier between the metal and the insulator. The current was normalized by subtracting the dark current for each applied bias, such that only photo-induced current was analyzed. The quantum yield, \( \gamma \), was calculated from normalized current, and spectral thresholds, \( \varphi_{\text{thresh}} \), the photon energy at which photo-induced current exceeds the dark current for a given applied bias, were determined from plots of \( \mu_{\text{phot}} \) versus \( h\nu \).\(^{16,28}\) To determine \( \varphi_{\text{thresh}} \) for each applied bias, an algorithm was implemented to find the largest region of the \( \mu_{\text{phot}} \) curve with the highest linearity, as determined from the \( R^2 \) value of a linear regression. A linear regression of this region intercepted with the baseline gives \( \varphi_{\text{thresh}} \) for that specific bias. The zero-field barrier height, \( \varphi_{\text{In}} \), for each interface was then found as the \( y \)-intercept of a Schottky plot of \( \varphi_{\text{thresh}} \) vs. the square root of the bias.\(^{29}\) Reported \( \varphi_{\text{In}} \) values have an estimated accuracy of ±0.1 eV. This is in line with commonly reported error values ranging from 0.05 to 0.1 eV.\(^{29}\)

III. RESULTS AND DISCUSSION

Shown in Fig. 1 are representative yield plots of \( \mu_{\text{phot}} \) vs. \( h\nu \) taken at various applied biases ranging between 0.4 and 1.2 MV/cm for (a) Al\(_2\)O\(_3\) and (b) HfO\(_2\) insulators in Au top electrode MIM devices with TaN, TaNiSi, or TaWSi bottom electrodes. The dashed lines indicate the linear regressions that were used to determine the \( \varphi_{\text{thresh}} \).

Next, to determine whether image force barrier lowering is present, Schottky plots of the \( \varphi_{\text{thresh}} \) values vs. \( \varphi_{\text{In}} \) for the MIM devices from (a) and (b) are shown in (c) and (d) for Al\(_2\)O\(_3\) and HfO\(_2\) insulators, respectively, under both positive and negative \( \varphi_{\text{In}} \). The zero-field barrier heights for the Au interfaces (\( \varphi_{\text{In}} \) Au) and the Ta-based metal interfaces (\( \varphi_{\text{In}} \) Ta\(_x\)N\(_{1-x}\)) are shown in (c) and (d). The zero-field barrier heights for the Au interfaces (\( \varphi_{\text{In}} \) Au) and the Ta-based metal interfaces (\( \varphi_{\text{In}} \) Ta\(_x\)N\(_{1-x}\)) were determined from the \( y \)-axis intersection of extrapolated linear fits of the \( \varphi_{\text{thresh}} \) vs. \( \varphi_{\text{In}} \) for each insulator are listed in Table I. Although the
Values are field dependent, the slopes of the Schottky plots do not correlate with the insulator dielectric constant for any of the devices tested. An absence of image-force barrier lowering for IPE measurements is not unusual and has previously been reported in IPE of metal–insulator interfaces, where it was attributed to interfacial charge or to the presence of an interfacial layer.24,30 A plane of charge located near the injecting interface can effectively “pin” the top of the barrier reducing the influence of electric field on the barrier height.18 Likewise, a higher \( \kappa \) interfacial oxide at the injecting interface can also reduce expected electric field lowering.29

Note that there are two non-idealities that can be seen in the yield curves in (a) and (b). First, the yield curves for the barrier between HfO\(_2\) and the top electrode show “tailing” at photon energies below the spectral threshold. This has been reported previously and may be attributed to conduction band tailing or charge in the HfO\(_2\).14,30 Second, the low positive bias yield curves (emission from the bottom electrode) for HfO\(_2\) shows a rollover at high photon energies that appears most prominently with TaN bottom electrodes. This was also seen in our previous report of SiO\(_2\) devices with the same electrodes.33 The rollover becomes less prominent with increasing applied positive bias. It is likely that this rollover at high photon energy is due to photoelectron emission from the top Au electrode overwhelming emission from the bottom TaN electrode when there is a low positive bias/weak field across the insulator. At higher positive biases, the insulator field will repel photoelectrons back into the Au electrode. The reasons for stronger emission from the Au electrode at large photon energy are (i) photon absorption and thus photoelectron generation in the top electrode is much stronger than in the bottom electrode and (ii) the Au barrier heights are larger than the TaN barrier heights so that photoemission over the Au/insulator barrier does not start until higher photon energies.

### Table I

Barrier heights extracted from devices with Au top electrodes, compared to literature values for the respective Au barrier height. Measured barrier heights are given with an expected error of ±0.1 eV. Electron affinities from the literature are provided.

<table>
<thead>
<tr>
<th>Insulator (( \chi_i ))</th>
<th>Measured ( \varphi_{\text{Bn}} ) (±0.1 eV)</th>
<th>Literature ( \varphi_{\text{Bn,Au}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}_2\text{O}_3 ) (1.4 eV)</td>
<td>4.0, 4.1, 3.9</td>
<td>4.1</td>
</tr>
<tr>
<td>( \text{HfO}_2 ) (2.25 eV)</td>
<td>3.5, 3.5, 3.4</td>
<td>3.7</td>
</tr>
</tbody>
</table>
Energy band diagrams based on the experimentally determined $\varphi_{\text{bn}}$ values listed in Table I are shown in Fig. 2. There are several interesting aspects of these results. At the top electrode, the Au/insulator barrier heights are consistent for each insulator (within the $\pm0.1$ eV error), regardless of the bottom electrode used. Additionally, the $\varphi_{\text{bn,Au}}$ value of \(~4.0\) eV for Al$_2$O$_3$ is roughly consistent with the ideal Schottky model prediction ($\varphi_{\text{bn,Au-ideal}} = \Phi_M - \chi$) given $\Phi_{\text{Au}} \sim 5.2$ eV and $\chi_{\text{Al$_2$O$_3$}} \sim 1.4$. The $\varphi_{\text{bn,Au}}$ of \(~3.5\) eV for HfO$_2$ however, is higher than expected from the ideal theory prediction by about $1.1$ eV. Previous IPE reports.

Considering next the Ta-based metal bottom electrodes, previous Kelvin probe work with TaWSi has determined $\Phi_{\text{TaWSi}} = 5.06$ eV. Based on the average vacuum work functions of the constituent metals, it is expected that TaNiSi should have larger barrier heights than TaWSi which in turn should have larger barrier heights than TaN. This expected relative trend of $\varphi_{\text{bn,TaNiSi}} > \varphi_{\text{bn,TaWSi}} > \varphi_{\text{bn,TaN}}$ is indeed observed for Al$_2$O$_3$. For HfO$_2$, however, the barrier heights are essentially the same for all three metals ($\varphi_{\text{bn,TaNiSi}} \approx \varphi_{\text{bn,TaWSi}} \approx \varphi_{\text{bn,TaN}}$). Prior IPE work also appears to show a lack of a trend between various $\Phi_M$ metals and $\varphi_{\text{bn,M}} = \text{HfO}_2$. The insensitivity of the HfO$_2$ barrier heights to the various metals suggests that a strong degree of $E_{\text{fn}}$ pinning at $E_{\text{CNL}}$ is likely occurring at the HfO$_2$ interfaces. To quantify the degree of pinning, the slope parameter, $S$, from Eq. (2) is determined from the plots of $\varphi_{\text{bn}}$ versus $\Phi_M$ (Au, Al, and TaWSi) shown in Figs. 3(a) for HfO$_2$ and 3(b) for Al$_2$O$_3$. For HfO$_2$, considering the experimental error, an $S_{\text{HfO}_2}$ range roughly between 0.44 and 0.69 is found with $S_{\text{HfO}_2} = 0.56$ giving the best fit and shown by the dashed line in 3(a). This value is consistent with the 0.53 calculated by Robertson as well as reported experimental values of around 0.5. However, while the $S_{\text{Al$_2$O$_3$}} = 0.89$ determined from 3(b) is considerably higher than the calculated value of 0.63 it is in reasonably good agreement with the 0.83 value reported based on more recently measured IPE barrier heights from the literature.

According to Mönch, $S$ may also be correlated with the high-frequency dielectric constant ($\varepsilon_\infty$) of an insulator as

$$ S = \frac{1}{1 + 0.4(\varepsilon_\infty - 1)^2}. $$

This empirical relation reveals that as $\varepsilon_\infty$ increases, $S$ decreases indicating that $E_{\text{fn}}$ is more effectively pinned at

![FIG. 2. IPE based energy band diagrams for Al$_2$O$_3$ and HfO$_2$ MIM devices with Au top electrodes and TaWSi, TaNiSi, or TaN bottom electrodes as indicated.](image)

![FIG. 3. Plots of $\varphi_{\text{bn}}$ vs. $\Phi_M$ (Al, Au, and TaWSi) for (a) HfO$_2$ and (b) Al$_2$O$_3$.](image)
The fact that $\varepsilon_{\infty, HfO_2} > \varepsilon_{\infty, Al_2O_3}$ explains in part why $S_{HfO_2} < S_{Al_2O_3}$ and why barrier heights on HfO$_2$ are relatively independent of $\phi_{vac, HfO_2}$. As $\varepsilon_{\infty}$ is also influenced by film morphology and crystallographic direction, it is likely that much of the difference between the theoretical calculation of the S parameter for Al$_2$O$_3$ and the value found in this work is because the calculations were performed for crystalline Al$_2$O$_3$, which has a higher dielectric constant than the thin film amorphous Al$_2$O$_3$ deposited in this work. Using S values determined in this work and Eq. (3) yields $\varepsilon_{\infty, HfO_2} = 3.8$ and $\varepsilon_{\infty, Al_2O_3} = 2.1$. These values are both slightly lower than the range of 4.2–4.5 for HfO$_2$ and 2.5–3.0 for Al$_2$O$_3$ that were estimated from the square of the ellipsometric refractive index (RI) for similarly deposited materials, and may point to the presence of low x interfacial layer at the Ta-based metal interface.

Since we are directly measuring $\phi_{in}$, rather than $\phi_{in, eff}$, Eq. (1) can be rewritten as:

$$\phi_{in} = S\phi_{M, vac} - (X_i - E_{C_{\infty}}(I - S)), \quad (4)$$

assuming that the $E_{C_{\infty}}$ is referenced to the vacuum level, $E_{vac}$, rather than the insulator valence band edge, $E_v$. By finding the y-intercept of a linear regression of the data in Fig. 3 and assuming $X_{HfO_2} = 2.25$ eV and $X_{Al_2O_3} = 1.4$ eV, we roughly estimate $E_{C_{\infty,vac,HfO_2}} = 6.3 - 7.6$ eV and $E_{C_{\infty,vac,Al_2O_3}} = 6.2$ eV, both referenced to $E_{vac}$. Assuming $E_{G,HfO_2} = 5.6$ eV and $E_{G,Al_2O_3} = 6.4$ eV, typical values for ALD films, this translates to a rough estimate of $E_{C_{\infty,vac,HfO_2}} = 0.25 - 1.6$ eV and $E_{C_{\infty,vac,Al_2O_3}} = 1.6$ eV, referenced to $E_v$. Robertson calculated $E_{C_{\infty,vac}}$ values of 3.7 and 5.5 eV for HfO$_2$ and Al$_2$O$_3$, respectively.

Using $\phi_{M, eff}$ values extracted from flatband voltage shifts of capacitance-voltage measurements on arrays of MOS structures, Yeo et al. reported experimental $E_{C_{\infty}}$ values of 3.64 and 6.62 eV for HfO$_2$ and Al$_2$O$_3$, respectively, while Samavedam et al. reported values of 4.5 and 5.2 eV for HfO$_2$ and Al$_2$O$_3$, respectively, all referenced to $E_v$. Clearly the $E_{C_{\infty}}$ values determined here are significantly lower than the previous reports. It is important to note that the calculations were performed for crystalline systems, where the ALD thin films in this work are amorphous. In addition, all of the previous reports assume the crystalline $E_{G,Al_2O_3} = 8.8$ eV, which is much larger than the 6.4 eV measured by reflection electron energy loss spectroscopy (REELS) for similarly deposited unannealed ALD Al$_2$O$_3$ used in this work and the 6.4–6.9 eV values typically reported for unannealed ALD Al$_2$O$_3$. For example, the $E_{C_{\infty,Al_2O_3}} = 6.62$ eV reported by Yeo et al. would be above the conduction band of ALD Al$_2$O$_3$. The discrepancy between the $E_{C_{\infty}}$ values in this work and previously reported values is likely attributable to intrinsic effects. Whereas the MIGS model described by Eq. (1) is based entirely on ideal intrinsic induced interface states, barrier heights in real devices may be heavily influenced by extrinsic effects due to processing, etc., such as interface trap point defects, additional dipoles due to interfacial chemical reactions, interface layer formation, trapped charge in the dielectric near the interface, and remote oxygen scavenging from the opposing metal electrode. In this work, no post-deposition anneal is performed. In addition, MIM rather than MOS structures were used.

The absolute magnitudes of the extracted barrier heights for the Ta-based metals are much lower than predicted by the ideal model ($\phi_{in, ideal} = \phi_{M} - \chi$) based on their vacuum metal work functions. Two possible explanations to consider for the reduced barriers are hole emission and charge in the dielectric.

Although there are no reports of experimental IPE of holes from a metal into an insulator with a barrier above 2 eV, it is worth considering whether the lower than expected barrier measurements might be explained instead by hole emission from the Au electrode rather than electron emission from the bottom electrode. If this were the case, the measured barrier height would correspond to the Au/insulator barrier height ($\phi_{in, Au/HfO_2}$) rather than the TaWSi insulator electron barrier height. Considering first HfO$_2$, the bandgap of HfO$_2$ should be equal to the sum of the electron and hole barriers: $E_{G,HfO_2} = \phi_{in, Au/HfO_2} + \phi_{in, Ta/HfO_2}$. The $\phi_{in, Au/HfO_2}$ measured is 3.5 eV (close to the 3.7 eV reported in Ref. 30). The $E_G$ for these films was measured to be 5.6 eV via REELS, consistent with other reports for ALD HfO$_2$. Thus, the expected $\phi_{in, Au/HfO_2} = E_{G,HfO_2} - \phi_{in, Ta/HfO_2} = 5.6 - 3.5 = 2.1$ eV. This is well below the $\phi_{in, Ta WSi/HfO_2} = 3.0$ eV barrier measured in Fig. 1, evidence that the measured HfO$_2$ barrier is indeed due to electrons rather than holes. For Al$_2$O$_3$, $E_{G,Al_2O_3} = \phi_{in, Au/Al_2O_3} + \phi_{in, Ta/Al_2O_3}$. The measured $\phi_{in, Al_2O_3}$ is 4.1 eV ± 0.1 eV. The $E_G$ for these films was measured via REELS to be 6.4 eV, consistent with other reports for ALD Al$_2$O$_3$. Thus, the expected $\phi_{in, Al_2O_3} = E_{G,Al_2O_3} - \phi_{in, Ta/Al_2O_3} = 6.4 - 4.1 = 2.3$ eV. This is well below the $\phi_{in, Ta WSi/Al_2O_3} = 3.1$ eV barrier measured in Fig. 1, evidence that the measured Al$_2$O$_3$ barrier is also due to electrons rather than holes.

Considering the oxide charge, previous work with Ta-based metals postulated that negative Ta ion migration into the oxide following a post-deposition anneal could lead to an increase in the barrier height. While Ta diffusion could be playing a role, barrier heights here are reduced, rather than increased. Previous work has also shown that hole trapping ($\sim 10^{13}/\text{cm}^2$) can result in a local reduction of the barrier height by 0.3 eV, and Li$^+$ ions ($\sim 10^{13}/\text{cm}^2$) can reduce barrier heights by up to 1 eV. Positively charged Au ions are known to migrate rapidly through oxides and have even been shown to form conductive bridges that enable switching behavior in conductive bridging random access memory (CBRAM). Determination of the bottom electrode barrier heights in this work is performed with a positive bias applied to the Au top electrodes over a relatively long period of time (hours compared to less than a second for CBRAM devices), giving ample time for Au$^+$ ions to drift to the bottom electrode where they would contribute to a reduction in the barrier height. In fact, in support of this possibility, we have observed reversible breakdown/resistive switching behavior in the Au/SiO$_2$/TaWSi devices, whereas the Al/SiO$_2$/TaWSi devices did not show switching.

To assess whether Au may be impacting the extracted barrier heights of the opposing Ta-based electrodes, Al was...
used as a top electrode for devices with a TaWSi bottom electrode and either Al2O3 or HfO2. Shown in Fig. 4 are representative yield plots of $Y^{1/2}$ vs. $h\nu$ for Al top electrode MIM devices with (a) Al2O3 and (b) HfO2 insulators and TaWSi bottom electrodes. Schottky plots of the $\Phi_{\text{thresh}}$ values vs. $E_{\text{g}}^{1/2}$ for these devices are shown in (c). Note that the yield curve for the HfO2 barriers in (b) shows tailing at photon energies below the indicated spectral threshold and, as is typically reported for IPE of metal/insulator interfaces, the slopes of the Schottky plot of electric field barrier lowering in (c) do not correspond to the dielectric constant of the insulator.29 Both of these observations are consistent with our previous IPE measurements on ZrCuAlNi amorphous metal bottom electrode/Al top electrode devices14 and have been attributed to either conduction band tailing/defects, charged defect levels, or an interfacial layer (IL) oxide at the injecting electrode/Al top electrode devices, suggesting that Au+ ion migration may indeed play a role in reducing opposing electrode barrier heights.31,32 Conduction band tailing is likely not solely responsible for the observed IPE threshold tailing as the energy spread of the tail is about 1 eV, larger than what would be typically expected for band tailing, though oxygen vacancy related defects have been detected using REELS at roughly 2 eV above the valance band edge in Ar+ sputtered HfO2.9

Potential contributions from ILs would be either an Al2O3 IL at the top Al interface and a TaOx IL at the Ta-based metal interface.47 Given that the tailing was also seen with Al top electrodes and ZrCuAlNi bottom electrodes (which do not contain Ta), both TaOx and Al2O3 ILs can be ruled out as the major source of tailing. Charge in the dielectric seems the most likely explanation as lateral charge non-uniformities can cause IPE threshold tailing. As previously discussed, Au+ charge in the insulator may also be responsible for the reduction of the barrier height in the Au top electrode devices. In addition, charge at the interface can reduce influence of electric field on the barrier height.28 The $\Phi_{\text{thresh}}$ values for each insulator are listed in Table II. In Fig. 4(d), energy band diagrams of the Al top gate devices based on the experimentally determined $\Phi_{\text{thresh}}$ values from Table II (solid lines) are superimposed on band diagrams predicted by $\Phi_{\text{thresh}} = \Phi_M - \chi_i$ (dashed lines). We find much larger (−0.7 to −0.8 eV) TaWSi/insulator barriers than for Au top electrode devices, suggesting that Au+ ion migration may indeed play a role in reducing opposing electrode barrier heights.

The TaWSi/Al2O3 $\Phi_{\text{thresh}}$ (3.8 eV) is within error equivalent to that predicted by the ideal Schottky model. The TaWSi/HfO2 $\Phi_{\text{thresh}}$, on the other hand, is higher than the Schottky model prediction by about 0.9 eV. For HfO2, the $\Phi_{\text{thresh}}$ increase over the ideal model for both TaWSi bottom and Al top electrodes is similar, with an approximately 0.8–0.9 eV increase. This points to a negative fixed charge in the HfO2 or perhaps the formation of an Al2O3 IL at the top Al electrode. Comparing the Al with the Au top electrode devices, it is seen that the Al/insulator barrier heights are smaller than the Au/insulator barrier heights for all insulators. For both HfO2 and Al2O3, this difference is roughly equal to the expected $\Phi_{\text{Au-Au}}$ difference between Au and Al ($\Delta \Phi_{\text{Au-Au}} \sim 0.9$ eV). Comparing to our previous work with a ZrCuAlNi bottom electrode, the Al/insulator barrier heights are equal, within experimental error.14 The TaWSi barriers are 0.8 eV and 0.6 eV greater than that measured for ZrCuAlNi with Al2O3 and HfO2, respectively,14 confirming that TaWSi has a larger effective work-function than ZrCuAlNi.

Finally, the goal of this work is to use IPE to directly measure metal/insulator $\Phi_{\text{thresh}}$ in a device stack so as to be able to better predict device behavior. For high quality ALD Al2O3, thick enough so that conduction is not dominated by direct tunneling, and moderate to high $\Phi_M$ electrodes, Fowler–Nordheim tunneling (FNT) dominates conduction. The onset of FNT appears as a distinct “knee” in the current density vs. voltage curve, at a voltage dependent on $\Phi_{\text{thresh}}$ of the

![Image](image.png)

**FIG. 4.** Representative plots of $Y^{1/2}$ vs. $h\nu$ for (a) Al2O3 and (b) HfO2 in MIM devices with Al top electrodes and TaWSi bottom electrodes, where the dashed lines show the linear $\Phi_{\text{thresh}}$ vs. $E_{\text{g}}^{1/2}$ extraction for each interface. Each plot shown was taken at an applied field in the range of 0.4 to 0.7 MV/cm. (c) Schottky plots of $\Phi_{\text{thresh}}$ vs. $E_{\text{g}}^{1/2}$ used to extrapolate the $\Phi_{\text{thresh}}$ from IPE-derived spectral thresholds for the indicated interface, and (d) the IPE based (solid lines) vs. ideal (dashed lines) band diagrams.

**TABLE II.** Barrier heights extracted from devices in this work with Al top electrodes, compared to literature values for the respective Al barrier height. Measured barrier heights are given with an expected error of ±0.1 eV.

<table>
<thead>
<tr>
<th>Insulator (z)</th>
<th>TaWSi</th>
<th>Al</th>
<th>$\Phi_{\text{thresh}}$ (±0.1 eV)</th>
<th>Literature $\Phi_{\text{Al}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3 (1.4 eV)</td>
<td>3.8</td>
<td>3.0</td>
<td>2.9</td>
<td>2.5</td>
</tr>
<tr>
<td>HfO2 (2.25 eV)</td>
<td>3.8</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
consistent with previous IPE reports for each insulator. For the Ta-based metal bottom electrodes with Al2O3, \( \varphi_{\text{ln}} \) increases with increasing \( \varphi_{\text{m}} \). \( \varphi_{\text{ln}} \approx 2.9, 3.1, \) and 3.3 eV for TaN, TaWSi, and TaNiSi, respectively. For HfO2, however, the barrier heights are relatively independent of \( \varphi_{\text{m}} \). \( \varphi_{\text{ln}, \text{TaN}} \approx \varphi_{\text{ln}, \text{TaWSi}} \approx \varphi_{\text{ln}, \text{TaNiSi}} \approx 3.0 \) eV. The difference between HfO2 and Al2O3 is attributed to enhanced Fermi-level pinning due to a larger dielectric constant—confirmed by the slope parameter, \( S \), which was found to be 0.89 and 0.44–0.69 for Al2O3 and HfO2, respectively. In devices with a TaWSi bottom electrode, an Au top electrode leads to significantly lower barrier heights than were obtained with Al, 0.6 eV and 0.8 eV lower for HfO2 and Al2O3, respectively. Measurements of the current-voltage asymmetry of MIM diodes are consistent with the IPE measured barriers, whereas the asymmetry is inconsistent with the Schottky model predictions of barrier heights.

A comparison to previous work with amorphous ZrCuAlNi bottom and Al top electrodes indicates that the electron barriers for TaWSi with HfO2 and Al2O3 are 0.8 eV and 0.6 eV greater, respectively, than the same barriers with ZrCuAlNi. This confirms that for Al2O3, TaWSi has a larger effective work function than ZrCuAlNi, ~5.2 eV vs. ~4.7 eV, respectively. Combined with low roughness and significantly higher temperature stability than ZrCuAlNi (greater than 900 °C vs. less than 400 °C), TaWSi appears promising for use as a high work function bottom electrode in MIM device applications.

**ACKNOWLEDGMENTS**

This work was supported by NSF Center for Sustainable Materials Chemistry, Grant No. CHE-1606982. The authors thank C. Tasker for equipment support and T. Klarr (now at Micron, Boise, ID) for device fabrication assistance. Part of this work was conducted at the Materials Synthesis and Characterization (MaSC) Center, a National Nanotechnology Coordinated Infrastructure (NNCI) Northwest Nanotechnology Infrastructure (NNWI) user facility at Oregon State University, which is supported in part by the National Science Foundation (NSF) (Grant No. ECC-1542101) and Oregon State University.

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