Al-doped ZnO (AZO) is a promising earth-abundant alternative to Sn-doped In$_2$O$_3$ (ITO) as an n-type transparent conductor for electronic and photovoltaic devices; AZO is also more straightforward to deposit by atomic layer deposition (ALD). The workfunction of this material is particularly important for the design of optoelectronic devices. We have deposited AZO films with resistivities as low as $1.1 \times 10^{-3} \ \Omega \cdot \text{cm}$ by ALD using the industry-standard precursors trimethylaluminum (TMA), diethylzinc (DEZ), and water at 200$^\circ$C. These films were transparent and their elemental compositions showed reasonable agreement with the pulse program ratios. The workfunction of these films was measured using a scanning Kelvin Probe (sKP) to investigate the role of aluminum concentration. In addition, the workfunction of AZO films prepared by two different ALD recipes were compared: a “surface” recipe wherein the TMA was pulsed at the top of each repeating AZO stack, and an interlamellar recipe where the TMA pulse was introduced halfway through the stack. As aluminum doping increases, the surface recipe produces films with a consistently higher workfunction as compared to the interlamellar recipe. The resistivity of the surface recipe films show a minimum at a 1:16 Al:Zn atomic ratio and using an interlamellar recipe, minimum resistivity was seen at 1:19. The film thicknesses were characterized by ellipsometry, chemical composition by EDX, and resistivity by four-point probe.

I. INTRODUCTION

Most modern devices contain components that leverage an interaction between light and electrons: displays, cameras, many sensors, photovoltaics and more. A material that is transparent to visible light and also electrically conductive is often essential to these devices. Of the materials that fit these requirements, the most commonly used are transparent conducting oxides (TCOs), typically integrated into devices as thin films. Due to its high transparency and conductivity, the most widely used TCO is indium tin oxide (ITO), where tin is the dopant. The relatively low natural abundance of indium drives up the financial and environmental cost of devices employing this conductor. Al-doped ZnO (AZO) is emerging as an earth-abundant replacement for ITO for applications that require transparent conductive n-doped thin films. Due to its high transparency and conductivity, the most widely used TCO is indium tin oxide (ITO), where tin is the dopant. The relatively low natural abundance of indium drives up the financial and environmental cost of devices employing this conductor. Al-doped ZnO (AZO) is emerging as an earth-abundant replacement for ITO for applications that require transparent conductive n-doped thin films. Resistivity values as low as $10^{-3} \ \Omega \cdot \text{cm}$ have been achieved for ZnO films, and doping can yield even lower resistivities. Thin film deposition methods at moderate temperatures have been reported that match the relevant properties of ITO films.

Atomic layer deposition is a well-known layer-by-layer growth method that uses alternating pulses of gases carrying the components of the target film. Alumina is an extremely common film deposited by this technique using trimethylaluminum (TMA) and H$_2$O, and doping zinc oxide with aluminum by ALD is straightforward: a pulse of TMA is interspersed with the diethylzinc (DEZ) and water cycles. The aluminum doping level can be easily altered by changing the ratio of TMA:DEZ cycles. AZO has been deposited by atomic layer deposition in this manner for several applications. For a comprehensive survey of the state of the art (2014) of atomic layer deposition of ZnO and related films, please see the outstanding review by Tynell and Karppinen. The aluminum doping levels reported as optimal for minimum resistivity vary considerably but most reports lie within the 2-5% range. It is likely that the variation of dopant concentration in the literature depends to a significant degree on processing and post-processing details, although in many cases the doping levels are assumed from the TMA:DEZ pulse ratios and not experimentally determined. As a small part of a larger investigation, Kim et al. have reported the workfunctions for three different aluminum concentrations with an eye towards the effect of the annealing process. More work of this type is needed: careful measurement and discussion of AZO’s workfunction, assessing the effect of aluminum concentration and surface treatment.

The workfunction is the energy required to promote an electron from the Fermi level to the vacuum level for a given material, and relates the Fermi levels of materials to one another. Band alignment at interfaces between materials depends on the workfunction, making it an important parameter in the design of devices. The workfunction is determined by both bulk (chemical potential) and interfacial contributions (e.g. crystal orientation, physisorbed or chemisorbed solid, liquid or gas adsorbates). This can allow universal tuning of the workfunction by for example up to 1.3 eV by deposition of ultrathin polymer films on a variety of surfaces.

The workfunction of AZO herein was measured herein using a Kelvin probe (KP). This instrument measures the workfunction difference (or contact potential, $V_C$) by bringing a vibrating probe tip in close proximity to the sample being measured (tungsten is used as an example in Figure 1). The instrument uses a current amplifier to measure the charging current (signal) as the distance between tip and the sample oscillates. The traditional KP method involves applying a DC bias (backing potential) between tip and the sample and varying this potential until the signal vanishes at $V_b = V_C$. The instrument used herein employs off-null detection in which the signal is measured at various values of $V_b$ and linear interpolation used to determine $V_C$. In addition to improving signal to noise, the off-null method also enables using the gradient of the signal vs. $V_b$ data to maintain a constant probe-to-sample spacing while scanning across a surface. The off-null KP method enables sensitive ($< 5 \text{ meV}$) measurements of the workfunction of the sample relative to that of the tip.

Here, we examine the effect of changing the Al:Zn ratio on the workfunction of the material. Due to the sensitivity of
received. These precursors and distilled water were held at 

diethylzinc (Advanced deposition tool. Trimethylaluminum (II. EXPERIMENTAL

c) to compare the resistivity measured for the films reported

an effect on the surface dipole of the material, so we com-
pared the workfunction with undoped ZnO. Because the sur-
face dipole is sensitive to surface contamination and adsorbed
surface species, surface cleaning prior to the characterization
of workfunction also demanded special attention. A variety
of surface solvent treatments and their effect of the measured
workfunction will be discussed. The workfunction will be
compared to the resistivity measured for the films reported
here, and compared to literature values.

II. EXPERIMENTAL

ALD depositions were performed using a Picosun R200
Advanced deposition tool. Trimethylaluminum (> 98%) and
diethylzinc (> 95%) were purchased from Strem and used as
received. These precursors and distilled water were held at
18°C in stainless steel bubblers for all depositions. Purge and

line flows used 99.998% N₂ (150 sccm for TMA and DEZ, 200 sccm for H₂O). The pulse and purge times for TMA, DEZ and H₂O were all 0.1 s and 6.0 s respectively, for all depositions. In all depositions the TMA pulse was introduced after a DEZ pulse/purge cycle, as this has been reported to minimize the impact of the TMA pulse on growth rate. All depositions were performed with the chamber temperature set to 220°C, with a measured temperature of 200 °C as the minimum values for (undoped) ZnO film resistivity (10⁻³ Ω cm) are typically achieved in the range of 200-220 °C. To ascertain the impact on workfunction measurements, two pulse program recipes were employed to generate the same dopant levels; in the first, the TMA pulse was introduced at the end of each H₂O/DEZ sub-cycle. In the second recipe, the TMA pulse was introduced half-way through a H₂O/DEZ sub-cycle. All substrates were 50 mm Si (100) wafers with a 1000 Å coating of thermally grown silica; this silica coating was essential for proper evaluation of the deposited films’ electrical properties.

Ellipsometry was performed using a Plasmos SD2000 with
a HeNe laser at λ = 632 nm. The refractive indices were set as follows: \( n_{Si} = 3.882, n_{SiO₂} = 1.457 \), and \( n_{ZnO} = 2.00 \). A refractive index of \( n_{AZO} = 2.00 \) was used for all ZnO and AZO films. The growth rates obtained from these measurements are in reasonable agreement with similar processes in the literature.

Elemental composition was determined using an Oxford Instruments/INCA Energy Dispersive Spectroscopy System, installed on a Tescan Vega-II XMU Scanning Electron Microscope. All spectra were acquired using a beam acceleration of 20 kV, calibrated to a copper standard.

Sheet resistance was evaluated using a home-built four-point probe (4PP), and resistivity values were determined from measurements of \( V \), by Equation 1.

\[
\rho = \frac{W}{V} \ln \left( \frac{I}{4} \right)
\]

where \( I \) was supplied by a constant current source set to 10 mA.

Workfunctions were measured with a KP Technology SKP5050 Scanning Kelvin Probe (sKP) housed in a humidity controlled enclosure provided by the manufacturer, and kept in a room with a relative humidity of ≈ 15%. The Au probe tip was set to vibrate at 75 Hz. The workfunction was measured as the sample was scanned using a 10 × 10 grid, taking points every 475 μm. The workfunction difference measured by the sKP was converted to an absolute sample workfunction.

FIG. 1. Principle of work function measurements. (a) When a probe tip (dark grey) and a sample (light grey) are not in contact, they have different Fermi levels and equal absolute vacuum energies \( E_{\text{vac}} \). (b) When the standard and sample are brought into electrical contact, charges flow between them to even their Fermi levels, generating the contact potential difference \( V_c \) equal to the difference in their workfunctions \( V_c = \phi_p - \phi_s \). (c) The workfunction can be measured determined more accurately by applying a bias voltage \( V_b \) across the probe and sample until the read difference is zero.

FIG. 2. Illustration of the (a) surface and (b) interlamellar deposition recipes for AZO. The dark grey lines represent the Al-Zn-O layers, the light grey represents the ZnO lattice, and the black is the substrate. Note that the substrate interface does not change, but the surface does.

\[
\phi_p - \phi_s = E' \neq 0
\]
TABLE I. Pulse programs used for depositions. Each precursor identifier indicates a pulse/N$_2$-purge pair. For example, the AZO (1:17) film used 76 supercycles, each consisting of 17 cycles of DEZ and H$_2$O and one cycle of DEZ and TMA. Cycle values were chosen to deposit a film thickness of approximately 200 nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TMA:DEZ (ratio)</th>
<th>Surface</th>
<th>Recipe Interlamellar</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZO (1:15)</td>
<td>83[15(DEZ,H$_2$O)][(DEZ,TMA)]</td>
<td>83[7(DEZ,H$_2$O)][(DEZ,TMA)][8(DEZ,H$_2$O)]</td>
<td></td>
</tr>
<tr>
<td>AZO (1:17)</td>
<td>76[17(DEZ,H$_2$O)][(DEZ,TMA)]</td>
<td>76[8(DEZ,H$_2$O)][(DEZ,TMA)][8(DEZ,H$_2$O)]</td>
<td></td>
</tr>
<tr>
<td>AZO (1:19)</td>
<td>74[19(DEZ,H$_2$O)][(DEZ,TMA)]</td>
<td>74[10(DEZ,H$_2$O)][(DEZ,TMA)][9(DEZ,H$_2$O)]</td>
<td></td>
</tr>
<tr>
<td>AZO (1:21)</td>
<td>60[21(DEZ,H$_2$O)][(DEZ,TMA)]</td>
<td>60[10(DEZ,H$_2$O)][(DEZ,TMA)][11(DEZ,H$_2$O)]</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>1143(DEZ,H$_2$O)</td>
<td></td>
</tr>
</tbody>
</table>

by assuming a tip workfunction of 5.10 eV.

To ascertain the role of surface species remaining after cleaning, three independent sKP measurements were acquired after three separate surface treatments: 1) as deposited; 2) a 5 s wash with toluene, hereafter referred to as the non-polar rinse; and 3) a series of 5 s washes of 2-propanol, ethanol, acetone, water (the polar rinse). Each sample was thoroughly dried with flowing N$_2$ at room temperature before measurement.

### III. RESULTS AND DISCUSSION

The films were grown from DEZ and water, with intervening pulses of TMA in ratios from 21:1 to 15:1. The films were characterized without annealing. The growth rate of ZnO from water and DEZ was 1.70 Å/cycle (Table 2). This growth rate is in line with, but slightly lower than those reported in the seminal work performed by Elam and George. The growth rate of AZO in this study ranged between 1.40 – 1.59 Å/cycle, which is in agreement with literature.

In both the surface and interlamellar recipes, energy-dispersive X-ray (EDX) analysis showed that the Al:Zn peak ratios were reasonably close to the TMA:DEZ pulse ratios regardless of deposition geometry, with the small discrepancies possibly due to a minor amount of Al-centre etching by subsequent DEZ pulses (Table 2). Since the TMA pulse was followed directly by a DEZ pulse, a simple ligand exchange could occur (※ represents the film surface):

\[
\text{※-OH} + \text{AlMe}_3(g) \rightarrow \text{※-O-AlMe}_2 + \text{CH}_4(g) \quad (2)
\]

\[
\text{※-O-AlMe}_2 + \text{ZnEt}_2(g) \rightarrow \text{※-O-ZnEt} + \text{AlMe}_2\text{Et}_3(g) \quad (3)
\]

Notably, these Al:Zn ratios are averaged through the entire film due to the acceleration of the electrons (20 keV), which results in an interaction volume significantly greater than the thickness of the deposited AZO. This has the added effect of rendering the oxygen signal useless for compositional analysis.

In general, the resistivities were ~5x better in the doped films than in undoped ZnO (Table 2). These resistivities compared favourably to resistivities found by Lee et. al. under similar ALD conditions. In contrast to this reference, however, no minimum in resistivity was found within this dopant range, and the general trend showed a more slightly decreasing resistivity with increasing Al doping levels, regardless of deposition geometry (Figure 3). It should be noted that our doped films showed a resistivity range of 1.053–1.320 x 10$^{-3}$ Ω cm and 5.574 x 10$^{-3}$ Ω cm for undoped ZnO, while the previously reported data showed a range of 3.2–11 x 10$^{-3}$ Ω cm for doped films (with a minimum at 1:19 TMA:DEZ) with 7.6 x 10$^{-3}$ Ω cm for the undoped film. The lowest resistivities reported in the literature for ALD AZO on silicon are 0.77 x 10$^{-3}$ Ω cm. Our results contradict the commonly reported assertion that a 1:19 TMA:DEZ pulse ratio yields minimum film resistivity. It appears that AZO film performance is tool-dependant, with a dopant efficiency being affected by precursor delivery, and number of ZnO pulses between sequential TMA pulses.

Characterization of AZO deposited by different tools should be undertaken for effective integration into devices.

![FIG. 3. Resistivity of ALD-deposited AZO as a function of Al:Zn atomic ratio as measured by EDX. Note that there was no significant difference in resistivity for the two recipes (see Figure 2) and so this chart includes data obtained from both recipes.](image)

The surface recipe yielded higher workfunctions than the interlamellar recipe. Average workfunctions for the surface recipe ranged between 5.06–5.21 eV, and for the interlamellar recipe between 4.97–5.06 eV (Figure 4). This is likely due to the improved doping efficiency (i.e. electron donation to the conduction band) per Al ion when within the ZnO lattice (in-
TABLE II. Growth rates as measured by ellipsometry, elemental composition measured by EDX.

<table>
<thead>
<tr>
<th>Sample Recipe</th>
<th>Growth rate [Å/cycle]</th>
<th>Al:Zn ratio by EDX</th>
<th>Resistivity [mΩ cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA:DEZ (ratio)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AZO (1:17) surface</td>
<td>1.45</td>
<td>1:16</td>
<td>1.053</td>
</tr>
<tr>
<td>AZO (1:17) interlamellar</td>
<td>1.44</td>
<td>1:16</td>
<td>1.085</td>
</tr>
<tr>
<td>AZO (1:19) surface</td>
<td>1.48</td>
<td>1:17</td>
<td>1.091</td>
</tr>
<tr>
<td>AZO (1:19) interlamellar</td>
<td>1.40</td>
<td>1:18</td>
<td>1.212</td>
</tr>
<tr>
<td>AZO (1:21) surface</td>
<td>1.52</td>
<td>1:20</td>
<td>1.262</td>
</tr>
<tr>
<td>AZO (1:21) interlamellar</td>
<td>1.59</td>
<td>1:21</td>
<td>1.162</td>
</tr>
<tr>
<td>AZO (1:23) surface</td>
<td>1.56</td>
<td>1:25</td>
<td>1.315</td>
</tr>
<tr>
<td>AZO (1:23) interlamellar</td>
<td>1.56</td>
<td>1:25</td>
<td>1.315</td>
</tr>
<tr>
<td>ZnO – – –</td>
<td>1.70</td>
<td>–</td>
<td>5.574</td>
</tr>
</tbody>
</table>

KP is a very surface sensitive technique, so the local doping efficiency at the surface is expected to significantly affect the measured workfunction. Improved doping efficiency increases the carrier concentration and the Fermi level of the AZO local environment, resulting in lower workfunctions. These principles have been demonstrated experimentally and theoretically for doped ZnO films deposited by physical methods,\textsuperscript{23–25} and are applicable here.

The measured workfunction was significantly affected by the condition of the surface. When deposited with the surface recipe (i.e. a TMA pulse was the terminal pulse in the deposition), the as-deposited workfunction showed a range of 4.97–5.18 eV, whereas the range of the as-deposited film using the interlamellar recipe was 4.92–5.03 eV (Figure 5). The surface recipe yielded films that were more sensitive to surface treatment than the interlamellar films. The surface-bound species interacting with surface Al-dopant atoms, changed the local electronic environment at the surface thus changing the observed workfunction. It is known that changes in the Fermi energy or charge concentration of AZO surfaces can dramatically change its observed workfunction.\textsuperscript{24} This is supported by the insensitivity of the interlamellar recipe to surface treatment, as the buried Al ions are unable to interact with adsorbates, unlike the films terminating with exposed Al species.\textsuperscript{26} The electronic nature of adsorption of common solvents with Al or ZnO terminated AZO surfaces, and so their effect on the conduction band electrons, is uncertain. This is the subject of an ongoing investigation.

Kelvin probe force microscopy (KPFM), a modified AFM technique, has been used previously to investigate AZO films deposited by sputtering. The reported workfunction by KPFM was $\phi = 4.85$ eV,\textsuperscript{24} which is in good agreement with our results of $\phi = 4.92–5.18$ eV considering the difference in film morphology, dopant distribution and efficiency, and surface termination obtained via the two fundamentally different techniques. The theoretical value determined by DFT was $\phi = 4.978$ eV which also agrees with our results.\textsuperscript{23}

The workfunction of AZO deposited by magnetron sputtering was also found by ultraviolet photoelectron spectroscopy (UPS) to be 4.26 eV for UV-ozone treated AZO and 3.94 eV for acetone-treated AZO; the authors also reported that the workfunction was highly dependent on at.\% content of Al and surface carbon content.\textsuperscript{27} Additionally, UPS measurements provide an altogether different measurement of workfunction: it is expected that this technique would yield different and lower workfunctions. Specifically, UPS probes the Fermi-edge to low-energy cut-off of secondary electrons, which is an absolute minimum workfunction value for a surface. The macroscopic Kelvin probe provides a workfunction averaged over the whole probe tip, which will always be greater than that obtained by UPS.\textsuperscript{9,26}

IV. CONCLUSIONS

Scanning Kelvin Probe (SKP) and four-point probe measurements revealed small but significant changes in the workfunctions and resistivities of Al-doped zinc oxide films deposited by ALD. These changes were observed to result from two very different types of surface modification: the formulation of the ALD recipe used to generate the film, and the solvents used to wash the film immediately before KP measurements. Two ALD pulse program recipes were employed.
to establish the role that the TMA pulse placement plays in the films’ ultimate properties; one recipe terminated each DEZ/H₂O subcycle with a TMA pulse and the other recipe buried the TMA pulse half-way into each DEZ/H₂O subcycle. The TMA-terminated recipe generated films with, on average, higher workfunctions at Al:Zn ratios higher than 1:21, and lower resistivities at ratios above 1:19. The lowest resistivities observed were 1.05 × 10⁻³ Ω cm for TMA-terminated films and 1.095 × 10⁻³ Ω cm for the interstitial TMA recipe, each with a 1:16 Al:Zn atomic ratio. Surface washing prior to measurement demonstrated that the workfunction of AZO is dependent on the local electronic environment of the surface. The buried Al-dopant layer in the interlamellar samples were less sensitive to adsorbates than the surface doped samples, as they interact with fewer surface species. Scanning Kelvin Probe under ambient conditions provides an accessible method for the determination of thin films’ workfunctions, and the results reported above corroborate the data in the literature.

FIG. 5. The workfunctions of different Al:Zn atomic ratios with varying surface treatments for the surface (a) and interlamellar (b) recipes (see Figure 2). The light grey with circular marks represents the as-deposited film, the grey line with triangular marks represents the non-polar surface treatment, and the black line with square marks represents the polar surface treatment. Error bars are included but are too small to see on the plot.


