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Ion and Photon Surface Interaction during Remote Plasma ALD of Metal Oxides

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The influence of ions and photons during remote plasma atomic layer deposition (ALD) of metal oxide thin films was investigated for different O2 gas pressures and plasma powers. The ions have kinetic energies of \( \leq 35 \text{ eV} \) and fluxes of \( \sim 10^{12} \text{ cm}^{-2} \text{s}^{-1} \) toward the substrate surface: low enough to prevent substantial ion-induced film damage, but sufficiently large to potentially stimulate the ALD surface reactions. It is further demonstrated that 9.8 eV vacuum ultraviolet photons, present in the plasma, can degrade the electrical performance of electronic structures with ALD synthesized metal oxide films.

The kinetic energy \( E \) and the electron density \( n_e \) of ions accelerated to the substrate surface with a kinetic energy \( E_i \) of 27.3 \( \pm 1 \) eV, which is the ion energy where the IED is at its maximum value. This kinetic energy obtained by the ions in the plasma sheath is determined by the difference between the plasma potential \( V_p \) and the substrate potential \( V_s \). The energy has a peak value equal to \( eV_p \), as the substrate stage is grounded, and it is distributed due to fluctuations in \( V_p \) and collisions between the ions and other plasma species in the sheath. The corresponding average ion flux \( \Gamma_i \) is \( (5.0 \pm 0.3) \times 10^{11} \text{ cm}^{-2} \text{s}^{-1} \). The energy and flux of the ions can be attributed mainly to singly ionized O2 molecules, as reported by Gudmundsson et al.

The values of \( T_e \) and \( n_e \) are \( 3.4 \pm 1.0 \text{ eV} \) and \( (3.0 \pm 0.6) \times 10^9 \text{ cm}^{-3} \), respectively. The electron density directly above the substrate stage is approximately two orders of magnitude lower compared to the density in the bulk.

The pressure \( p \) and power \( P \) dependence of \( E_i \), \( T_e \), \( \Gamma_i \), and \( n_e \) is illustrated in Fig. 2. For pressures \( \leq 22.5 \text{ mTorr} \), measurements were carried out in the FlexAL reactor, whereas for pressures \( \geq 85 \text{ mTorr} \) data was obtained from measurements in the OpAL reactor. \( E_i \) is given only for \( p \leq 22.5 \text{ mTorr} \), because at higher pressures the ion current was too low to be measured by the RFEA. The change in the peak ion energy and the electron temperature show a similar trend upon a change in \( p \) and \( P \), because the plasma potential depends on the electron temperature. Obviously, the electron density and the ion flux are also related. In electropositive processing plasmas, such as the ones used in this work, the electron density and ion density in the bulk plasma are equal and a change in the electron density directly affects the ion flux. Upon a pressure increase, both \( E_i \) and \( T_e \) decrease due to the fact that more electron–molecule collisions take place at higher pressures increasing the ionization rate. As a result, the plasma can be sustained at a lower electron temperature explaining its decrease with increasing pressure. The electron density and ion flux also decrease at higher pressures for the position directly above the substrate stage, possibly due to a slightly reduced out-diffusion of the plasma species from the plasma source. At higher plasma powers, more power is coupled into the plasma, which also results in a higher ionization rate and lower \( T_e \) and \( E_i \). Obviously, the ion flux and density increase with increasing power as well. The
magnitude of $T_e$ indicates that, although the plasmas in the FlexAL and OpAL are generated remotely, they are still ionizing above the substrate over the complete pressure and power range measured in this study.

The amount of energy the ions provide to the substrate surface can be illustrated by comparing the growth-per-cycle, in terms of atoms deposited per unit area, with the ion dose to the surface within one cycle. Table I summarizes this data for four metal oxide systems deposited in the FlexAL reactor. These materials were deposited under saturated and optimized plasma-assisted ALD conditions as previously reported by Potts et al. and Heil et al. The ion dose per cycle and the average energy per atom deposited are provided for a plasma generated at 15 mTorr O$_2$ gas pressure and 300 W plasma power ($E_0$ = 17.8 eV, $\Gamma_i$ = 3.2 x 10$^{13}$ cm$^{-2}$ s$^{-1}$). Consequently, for every few atoms deposited there is one ion leading to an average ion energy dose of one or a few electron volts per atom. The dose is highest for deposition processes such as TiO$_2$ that provide only a low atomic growth-per-cycle and require a relatively long plasma dosing time. From the data and the fact that good material properties were reported by Potts et al. and Heil et al., it can also be concluded that the ion doses and energies are not high enough to induce substantial ion-induced damage. On the other hand, as reported by Takagi the ion energies and fluxes are within the range to potentially stimulate the ALD surface reactions, e.g., through ligand desorption and adatom migration. As illustrated in Fig. 2, the potential influence of the ions can be limited mainly by increasing the O$_2$ gas pressure.

Photons and their surface interaction.—Emission spectra in the VUV (100–200 nm), UV (200–400 nm), and visible (400–800 nm) range of the optical spectrum were recorded at standard conditions. Figures 3a and 3b show a number of emission peaks corresponding to photons emitted after decay of electronically excited atoms and ions. In the visible range (Fig. 3b), the spectrum is similar to what was observed and described in more detail by Mackus et al. In the UV and VUV range (Fig. 3a), an intense peak was observed at 130.5 ± 0.1 nm, corresponding to 9.5 eV photons (transition: 3s $^3$S$^0$ → 2p$^4$ $^3$P). Besides this emission peak, this spectral range does not reveal other intense emission lines (the peak at 261.0 ± 0.1 nm is a second order effect of the diffraction grating used in the monochromator). High energy VUV photons are likely to be re-absorbed by the plasma, so it is expected that the photons emitted toward the substrate surface are produced directly above the substrate surface, e.g., by de-excitation of O atoms in the plasma or by ion-electron recombination at or near the sample surface. The intensity of the 130.5 nm peak, a qualitative measure for its photon flux, decreases when going to higher pressures and increases at higher powers, as illustrated in Figs. 3c and 3d, respectively.

It has been reported that high energy VUV photons have the ability to affect the performance of electronic devices with metal oxide thin films negatively during plasma processing. To investigate the influence of VUV photons on the material properties of films prepared by ALD, a number of plasma exposure experiments were conducted in the FlexAL reactor. During the experiments the minority charge carrier lifetime of c-Si wafers passivated by Al$_2$O$_3$ was monitored using a Sinton WCT-100 tool. This parameter is very sensitive to electrical defects near the c-Si/Al$_2$O$_3$ interface, whereas Al$_2$O$_3$ is a commonly applied dielectric prepared by ALD. For the experiment, double side polished float-zone $<$001$>$ n-type Si wafers were used, double side deposited with a 30 nm Al$_2$O$_3$ passivation layer and annealed for 10 min at 400°C. These Al$_2$O$_3$ layers were deposited by thermal ALD to avoid the influence of plasma photons at the initial stage of the experiment. The resulting effective lifetimes $\tau_{\text{eff}}$, i.e., the minority charge carrier lifetimes at a charge injection level of $10^{15}$ cm$^{-3}$, in the Si substrates were measured to be ~6 ms. The high lifetime is a result of...
Table I. Comparison between the growth-per-cycle in terms of atoms deposited and the ion dose for four metal oxides deposited under optimized ALD conditions in the FlexAL reactor. The precursor [Me is methyl, CH₃; Et is ethyl, C₂H₅; Pr is isopropyl, CH(CH₃)₂], the plasma dosing time per cycle ($t_{\text{plasma}}$), the growth-per-cycle, the ion-to-atom ratio, and the average energy provided to an atom deposited ($E_i$-per-atom) are given for depositions performed at $p = 15$ mTorr and $P = 300$ W. References to publications in which the optimization of the ALD processes and the resulting material properties are described in more detail are indicated. The data demonstrates that the energy provided by the ions can be significant, depending on the growth-per-cycle obtained and/or plasma dosing time required for the process.

<table>
<thead>
<tr>
<th>Material</th>
<th>Precursor</th>
<th>$t_{\text{plasma}}$ (s)</th>
<th>Growth-per-cycle (cm⁻² cycle⁻¹)</th>
<th>Ion dose per cycle (cm⁻² cycle⁻¹)</th>
<th>Ion-to-atom ratio (→)</th>
<th>$E_i$-per-atom (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>Al(MeC₂)</td>
<td>2</td>
<td>$1.1 \times 10^{15}$</td>
<td>$6.4 \times 10^{14}$</td>
<td>0.06</td>
<td>1.1</td>
<td>3</td>
</tr>
<tr>
<td>HfO₂</td>
<td>Hf(MeC₂Et)₂</td>
<td>3</td>
<td>$8.5 \times 10^{14}$</td>
<td>$9.6 \times 10^{13}$</td>
<td>0.11</td>
<td>2.0</td>
<td>4</td>
</tr>
<tr>
<td>TiO₂</td>
<td>TiO(Pr)</td>
<td>12</td>
<td>$3.7 \times 10^{14}$</td>
<td>$3.8 \times 10^{14}$</td>
<td>1.03</td>
<td>18.4</td>
<td>3</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>Ta(MeC₂)₃</td>
<td>5</td>
<td>$6.3 \times 10^{14}$</td>
<td>$1.6 \times 10^{14}$</td>
<td>0.26</td>
<td>4.6</td>
<td>3</td>
</tr>
</tbody>
</table>

The excellent passivation of silicon by the ALD-prepared Al₂O₃ films. The effect of the high energy VUV radiation was demonstrated by exposing the samples to an O₂ plasma for different time intervals. The resulting effective lifetime versus the plasma exposure time is illustrated in Fig. 4, for three samples exposed at different plasma conditions. The results clearly show a decrease in the effective lifetimes for samples under plasma exposure. The decrease in lifetime depends on the intensity of the VUV radiation (see Figs. 3c and 3d) as it is evident that the lifetime decreases faster for exposures at higher plasma powers, but slower when higher gas pressures are employed. This automatically also implies that the effect of plasma radiation on the lifetime can be controlled by choosing the right plasma parameters.

The experiments were repeated under standard conditions for the situation in which samples were exposed to the radiation through 5.0 mm thick MgF₂ and quartz windows (blocking plasma radiation <110 nm and <140 nm, respectively). In this way the potential influence of ion bombardment on the lifetime degradation can be excluded and the role of the 9.5 eV photons can be identified. The transparency of the MgF₂ window for 130.5 nm radiation is approximately 60%, and after correcting for the resulting lower photon flux through this window the results were included in Fig. 4. For sample exposure through the MgF₂ window, the lifetime as a function of the plasma exposure time is comparable to the situation in which no window was used at all. For the case with the quartz window virtually no lifetime degradation was observed. Therefore, it is obvious that the VUV photons are responsible for the plasma exposure damage.

According to the literature 9.5 eV photons have enough energy to depassivate hydrogen-passivated Si dangling bonds at the interface between the Si and the Al₂O₃ and/or to create charge traps in dielectric materials whose bandgap is lower than the VUV photon energy. For 9.5 eV photons, the latter holds for the Al₂O₃, but also for the 1–2 nm thick interfacial SiO₂ layer that generally forms between the Si and the Al₂O₃. The decrease in the minority charge carrier lifetime observed during the experiments reported on in this work, can therefore be attributed to an increased density of defect states at the interface, induced by VUV photons. These results explain the observations by Dingemans et al. who compared the lifetime of as-deposited c-Si substrates coated with Al₂O₃ films deposited by thermal ALD and by plasma-assisted ALD. In their study, lifetimes in the microsecond range were found for substrates coated with Al₂O₃ deposited by plasma-assisted ALD, whereas lifetimes in the millisecond range were observed for Al₂O₃ deposited by thermal ALD. The difference in lifetimes can therefore be attributed to the fact that the plasma-assisted ALD samples were exposed to VUV radiation. After a post-deposition anneal the lifetimes were similar for the plasma-assisted and thermal ALD deposited substrates, which implies that the photon-induced lifetime degradation can be repaired by such a postdeposition anneal. It was verified that this holds for the thermal ALD Al₂O₃ samples (shown in Fig. 4) degraded by the VUV radiation as well. This confirms that the results in Fig. 4 reflect the influence of VUV photons during plasma-assisted ALD, despite the fact that the experiments reported in this work were carried out on substrates with thermally deposited Al₂O₃ films. More evidence for the detrimental influence of VUV photons during plasma-assisted ALD of Al₂O₃ (as-deposited) on silicon is also provided by the recent observation that the lifetime degradation during plasma-assisted ALD is lower for shorter plasma exposure steps.

![Figure 3](image-url)
Conclusions

The potential influence of ions and photons during plasma-assisted ALD was investigated for different O2 gas pressures and plasma powers. The ions present in the remote O2 plasma have kinetic energies of \( \frac{1}{35} \text{eV} \) and fluxes of \( \frac{10^{12} - 10^{14} \text{cm}^{-2} \text{s}^{-1}}{2} \). The energy provided by the ions can vary from one up to a few electron volts per atom deposited, depending on the growth-per-cycle of the process and the plasma exposure time required to reach saturation of the ALD cycle. The energy dose is low enough to prevent substantial ion-induced film damage, but sufficiently large to potentially stimulate the ALD surface reactions. The electron temperature and electron density reveal that for the remote plasma systems employed, the plasma is still ionizing at the substrate stage level for the pressure (3.8–187.5 mTorr) and power (100–500 W) range studied. The emission spectrum of the plasma revealed the presence of photons with energies of 9.5 eV in the plasma. These VUV photons are energetic enough to create electrical defects during plasma-assisted ALD processes, which have unambiguously been demonstrated in this work. The plasma-induced damage can be reduced by tuning the gas pressure and plasma power.

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