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Remote Plasma ALD of Platinum and Platinum Oxide Films

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Platinum and platinum oxide films were deposited by remote plasma atomic layer deposition (ALD) from the combination of (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe3) precursor and O2 plasma. A short O2 plasma exposure (0.5 s) resulted in low resistivity (15 μΩ cm), high density (21 g/cm³), cubic Pt films, whereas a longer O2 plasma exposure (5 s) resulted in semiconductive PtO2 films. In situ spectroscopic ellipsometry studies revealed no significant nucleation delay, different from the thermal ALD process with O2 gas which was used as a benchmark. A broad temperature window (100–300°C) for remote plasma ALD of Pt and PtO2 was demonstrated.

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When deposited with the precise thickness control and high conformation of atomic layer deposition (ALD), platinum films have a large variety of potential applications in microelectronics and energy technologies due to their chemical stability, catalytic activity, and excellent electronic properties. While being less investigated, platinum oxide is of interest because of its optical properties and because PtOx can be (locally) reduced to Pt. In the research efforts toward the applications of these films deposited by ALD, nucleation properties, material quality, and process temperature window are of key importance.

Few Pt ALD processes have been reported, of which the thermal ALD process using (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe3) and O2 gas described by Aaltonen et al. has become the most adopted. This process relies on the dissociative chemisorption of O2 on the Pt surface for oxidative decomposition of the precursor ligands. For PtOx, only one ALD process has been reported, to the best of our knowledge. PtOx films were obtained from the combination of Pt(acac)2 (acac = acetylacetonate) and O3 in the small temperature window of 120–130°C.

In this article, ALD processes are reported for Pt and PtO2 from the combination of MeCpPtMe3 precursor and O2 plasma exposure. In the PtO2 process, radicals are created, providing atomic O to the surface directly from the gas phase, enhancing oxygen chemisorption and oxidation. The growth and nucleation properties, material properties, and substrate-temperature dependence of the Pt and PtO2 process are investigated for remote plasma ALD and benchmarked against the thermal ALD of Pt.

Experimental

The Pt and PtO2 films were deposited in the open-load ALD-I setup described extensively in Ref. 15. In short, a deposition chamber was connected to an inductively coupled plasma source and a pump unit through gate valves. The pump unit consisted of a turbo molecular pump and a rotary pump reaching a base pressure of <10−9 mbar by overnight pumping. MeCpPtMe3 precursor (98%, Sigma-Aldrich), heated to 70°C, was vapor drawn into the chamber. The substrates were heated to 100–300°C (precursor decomposition starts above 310°C), while the reactor walls were kept at a temperature of 75°C.

For the processes investigated the first half-cycle consisted of MeCpPtMe3 precursor dosing with the bottom valve closed (no pumping) to maximize precursor usage. After the precursor exposure the reaction products were pumped out by opening the bottom valve to the turbo pump. For thermal ALD the second half-cycle consisted of a 5 s O2 exposure at 0.03 mbar. For the remote plasma process the O2 gas flowed through the plasma source (0.01 mbar pressure) while a 100 W plasma power was applied. A 0.5 s O2 plasma exposure was used for Pt deposition, while a 5 s plasma exposure resulted in the deposition of PtO2 films. Si(100) with native oxide or with 400 nm thermally grown SiO2 was used as the substrate.

In situ spectroscopic ellipsometry (SE) with a J. A. Woollam, Inc. M2000U (0.75–5.0 eV) ellipsometer was employed to determine the thickness and the dielectric function of the films during the ALD process. After deposition the optical range was extended to 6.5 eV using ex situ variable-angle measurements with a J. A. Woollam, Inc. M2000D. Electrical resistivity was measured by a four-point probe (FPP), whereas the atomic composition and mass density of the films were determined from Rutherford backscattering spectrometry (RBS) using 2 MeV 4He+ ions. The microstructure of the films was studied using X-ray diffraction (XRD) with a Philips X’Pert MPD diffractometer equipped with a Cu Kα source (1.54 Å radiation). Additionally, the thickness and mass density were determined by X-ray reflectometry (XRR) measurements on a Bruker D8 Advance X-ray diffractometer. The surface roughness of the films was determined by atomic force microscopy (AFM) using an NT-MDT Solver P47 SPM.

Results and Discussion

ALD growth and nucleation delay.— Pt films were deposited by remote plasma and thermal ALD, and PtO2 was deposited by remote plasma ALD at a substrate temperature of 300°C. A summary of the conditions and material properties is given in Table I. For the thermal process a MeCpPtMe3 dosing time of 1 s is necessary to reach saturation of the growth per cycle, while the remote plasma process requires 3 s. The length of the plasma exposure time determines whether Pt or PtO2 is deposited. A short O2 plasma exposure of 0.5 s results in Pt, while a long O2 plasma exposure of 5 s results in PtO2. When using O2 gas, Pt is obtained up to long O2 exposure times in line with the results reported by Aaltonen et al.

When measuring the thickness as a function of the number of cycles by in situ SE for the three processes (Fig. 1), no growth was observed for thermal ALD on c-Si substrates with 400 nm SiO2 or native oxide for the conditions employed. Pt growth on these substrates could only be achieved by using a higher O2 pressure (>0.8 mbar) as also typically used in the literature. On the contrary, remote plasma ALD of Pt (0.5 s O2 plasma) leads to immediate growth without a substantial nucleation delay. From the ellipsometry measurements, which have a reduced accuracy in the first 1–2 nm, it is concluded that growth per cycle is constant after the first 50 cycles. On the Pt film deposited by remote plasma ALD, the thermal ALD process continues without nucleation delay, demonstrating the possibility to deposit a Pt seed layer by remote plasma deposition.
Table I. The material properties of Pt and PtO₂ films deposited at 300 °C by thermal and remote plasma ALD from MeCpPtMe₃ and O₂ gas or O₂ plasma. In situ SE, XRR, AFM, RBS, and FPP measurements were used for analysis. The typical experimental errors are given in the first row.

<table>
<thead>
<tr>
<th>Material</th>
<th>ALD process</th>
<th>Thickness (nm)</th>
<th>Roughness (nm)</th>
<th>Growth per cycle (Å/cycle)</th>
<th>Mass density (g cm⁻³)</th>
<th>Atomic composition (at %)</th>
<th>Electrical resistivity (µΩ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>5 s O₂ gas</td>
<td>27.3 ± 0.5</td>
<td>0.7 ± 0.3</td>
<td>0.45 ± 0.04</td>
<td>22 ± 1</td>
<td>100 &lt; 5 &lt; 5</td>
<td>13 ± 1</td>
</tr>
<tr>
<td>Pt</td>
<td>0.5 s remote plasma</td>
<td>~30</td>
<td>0.4</td>
<td>0.47</td>
<td>22</td>
<td>100 &lt; 5 &lt; 5</td>
<td>15</td>
</tr>
<tr>
<td>PtO₂</td>
<td>5 s remote plasma</td>
<td>26.7</td>
<td>0.4</td>
<td>0.47</td>
<td>10</td>
<td>31 69 &lt; 5</td>
<td>&gt;1 × 10⁸</td>
</tr>
</tbody>
</table>

a Includes a 7 nm Pt seed layer deposited by the remote plasma ALD process.
b Thickness determination less accurate due to opacity of the film at SE wavelengths.

Material properties — As shown in Table I both the remote plasma and thermal ALD process result in very similar material properties for the Pt films. In both cases high density (~21 g/cm³), low resistivity (~15 µΩ cm), and high purity Pt films were deposited. The density and resistivity for these ~30 nm thick films are close to the bulk values of 21.4 g/cm³ and 10.8 µΩ cm, and they are similar to the values reported for thermal ALD of Pt. The O and C contents remain below the RBS detection limit (<5%) and grazing incidence XRD spectra (Fig. 3) revealed a cubic phase composition for both the thermal and remote plasma ALD Pt films. The relatively high intensity of the (220) peak indicates that the Pt crystallites have a preferred orientation with their (111) lattice planes parallel to the sample surface as also reported for the thermal ALD process. The remote plasma ALD Pt film, which is only slightly thicker than the thermal ALD film, shows much stronger diffraction peaks, indicating a higher crystallinity. Both processes resulted in smooth films and had generally lower root-mean-square roughness values (0.4–0.7 nm) than reported (0.75–4 nm). Because island growth is known to promote surface roughening, the fast nucleation and, consequently, more pronounced layer-by-layer growth can be related to the lower surface roughness obtained for the remote plasma ALD process.

The platinum oxide has a lower density and is slightly overstoichiometric (PtO₂). The resistivity is very high as it is above the detection limit of the FPP (>100 Ω cm). For the process employing Pt(acac)₂ and O₃, a lower resistivity (1.5–5 Ω cm) was reported most probably due to a lower O content (PtO₁.₅). The
PtO$_2$ film is amorphous or nanocrystalline, and no diffraction peaks from the $\alpha$ and $\beta$ PtO$_2$ phases can be identified in the XRD spectra.

**Temperature dependence.**—Figure 4 shows the growth per cycle for the three processes over a wide temperature range. The thermal ALD Pt process has a temperature window starting at 200°C. The growth per cycle for remote plasma and thermal ALD processes of Pt and PtO$_2$ were developed from the combination of MeC$_5$H$_{11}$Mg, precursor and O$_2$ gas. High purity Pt can be obtained by a short O$_2$ plasma exposure, whereas PtO$_2$ can be obtained by a long O$_2$ plasma exposure. In situ SE revealed that the remote plasma processes lead to immediate growth without substantial nucleation delay, whereas the thermal ALD process leads to no growth at all unless a Pt starting material is included in the ALD cycle to obtain high purity films at 100°C.

### Conclusions

Remote plasma ALD processes of Pt and PtO$_2$ were developed to start for sputtered films, while in air decomposition starts at 120–130°C. Therefore, the large temperature window of our PtO$_2$ process suggests a higher stability of the material, which can most likely be related to the higher oxygen content (PtO$_2$ compared to PtO$_{1.5}$).

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**References**