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Citation for published version (APA):

Knoops, H. C. M., Mackus, A. J. M., Donders, M. E., Sanden, van de, M. C. M., Notten, P. H. L., & Kessels, W. M. M. (2009). Remote plasma ALD of platinum and platinum oxide films. *Electrochemical and Solid-State Letters*, 12(7), G34-G36. <https://doi.org/10.1149/1.3125876>

DOI:

[10.1149/1.3125876](https://doi.org/10.1149/1.3125876)

Document status and date:

Published: 01/01/2009

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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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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Manuscript submitted February 20, 2009; revised manuscript received April 7, 2009. Published April 27, 2009.

When deposited with the precise thickness control and high conformality 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.^{1–7} While being less investigated, platinum oxide is of interest because of its optical properties and because PtO_x can be (locally) reduced to Pt.^{8–10} 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.¹ has become the most adopted.^{2,3} This process relies on the dissociative chemisorption of O₂ on the Pt surface for oxidative decomposition of the precursor ligands.^{11,12} For PtO_x only one ALD process has been reported, to the best of our knowledge.¹³ PtO_x films were obtained from the combination of Pt(acac)₂ (acac = acetylacetonate) and O₂ in the small temperature window of 120–130°C.¹³

In this article, ALD processes are reported for Pt and PtO₂ from the combination of MeCpPtMe₃ precursor and O₂ plasma exposure. In the O₂ plasma, O radicals are created, providing atomic O to the surface directly from the gas phase, enhancing oxygen chemisorption and oxidation.¹⁴ 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^{−5} 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),³ 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.¹⁵ 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 1. 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.¹

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.^{1,3} 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

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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.

Material	ALD process	Thickness (nm)		Roughness (nm)	Growth per cycle (Å/cycle)	Mass density (g cm ⁻³)		Atomic composition (atom %)			Electrical resistivity (μΩ cm)
		SE	XRR			XRR	RBS	Pt	O	C	
Pt	5 s O ₂ gas ^a	27.3 ± 0.5	26.6 ± 0.3	0.7 ± 0.3	0.45 ± 0.04	22 ± 1	20.8 ± 0.5	100	<5	<5	13 ± 1
Pt	0.5 s remote plasma	~30 ^b	29.2	0.4	0.47	22	20.0	100	<5	<5	15
PtO ₂	5 s remote plasma	26.7	26.5	0.4	0.47	10	8.9	31	69	<5	>1 × 10 ⁸

^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.

ALD. The remote plasma process of Pt shows a similar growth rate as the thermal process, which in turn is close to that reported by Aaltonen et al. (~0.045 nm/cycle).¹

The PtO₂ process (5 s O₂ plasma) also shows immediate growth with potentially a brief nucleation delay. After ~50 cycles the growth per cycle is constant at 0.047 nm/cycle compared to ~0.055 nm/cycle found by Hämäläinen et al. using Pt(acac)₂ and O₃.¹³ From the difference in Pt atomic density, it is concluded that for PtO₂, fewer Pt atoms are deposited per cycle than for the Pt process (1.1×10^{14} Pt cm⁻² cycle⁻¹ for PtO₂ compared to 3.0×10^{14} Pt cm⁻² cycle⁻¹ for Pt). This is different from the thermal Ru and RuO₂ ALD process where the growth rate increases with the partial O₂ pressure going from Ru to RuO₂ material.¹⁶

The dielectric functions determined by SE for Pt and for PtO₂ are shown in Fig. 2. The two materials result in very distinct dielectric functions, whereas the dielectric functions for Pt obtained by thermal ALD and remote plasma ALD are indistinguishable. The Pt was modeled using a Drude-Lorentz parametrization, where the Drude term, dominant at low photon energies, accounts for the intraband absorption by conduction electrons. Several Lorentz oscillators (at 0.9, 1.5 eV, and higher energies) were used for the interband absorption.¹⁷ In agreement with its semiconductive nature, the dielectric function of PtO₂ could be parametrized by a single Tauc-Lorentz oscillator (0.9 eV bandgap and 4.8 eV peak energy).¹⁸ The optical Tauc bandgap was ~1.5 eV, which is close to the bandgap reported for sputtered amorphous PtO₂ (1.2–1.3 eV).⁸

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.^{1,3} 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.^{1,2} 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).^{1,3} Because island growth is known to promote surface roughening,¹⁹ 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 (PtO_{2.2}). 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 (PtO_{1.6}).^{13,20} The

Figure 1. (Color online) Thickness measured by in situ SE as a function of the number of cycles for the Pt and PtO₂ ALD processes. The process conditions are listed in Table I. The starting substrate at 0 cycles was Si(100) with 400 nm SiO₂. After 150 cycles of remote plasma ALD, the Pt film growth is continued by thermal ALD.

Figure 2. (Color online) The imaginary part of the dielectric function (ϵ_2) for Pt and PtO₂ as determined by in situ SE measurements evaluated using Drude-Lorentz and Tauc-Lorentz parametrizations, respectively.

Figure 3. (Color online) Grazing incidence XRD spectra for a remote plasma ALD Pt film (29 nm thickness), a thermal ALD Pt film (27 nm thickness), and a remote plasma ALD PtO₂ film (27 nm thickness). The Miller indexes of cubic Pt are indicated.

PtO₂ film is amorphous or nanocrystalline,¹³ and no diffraction peaks from the α and β PtO₂ phases can be identified in the XRD spectra.⁸

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 $\sim 200^\circ\text{C}$. The fact that the growth per cycle is reduced at lower substrate temperatures is not yet understood.²¹ From surface science studies, it can be inferred that the dissociative chemisorption of O₂ [on Pt(111)] should not be the limiting factor.¹² On the other hand, the remote plasma ALD process which uses atomic oxygen from the gas phase has a higher growth rate than the thermal process at 200°C . The higher resistivity ($\sim 500\ \mu\Omega\ \text{cm}$) found for this temperature, however, suggests incomplete removal of O and C impurities from the material. The poorer material properties could be overcome by an H₂ plasma treatment. Exposure of the film to 300 s H₂ plasma at 100°C reduced the resistivity to $61\ \mu\Omega\ \text{cm}$. Moreover, tests with

Figure 4. (Color online) The growth per cycle for remote plasma and thermal ALD of Pt and remote plasma ALD of PtO₂ as a function of the substrate temperature. At 100°C the growth rate of the remote plasma process including a H₂ gas exposure step in the ALD cycle is shown. For thermal ALD of Pt, deposition took place on 10 nm thick Pt starting surfaces prepared by remote plasma ALD at 300°C . The lines serve as guides to the eye.

an ALD cycle containing a H₂ gas exposure step (no plasma power applied) of 2 s after the O₂ plasma step resulted in excellent materials properties for Pt at 100°C (mass density of $19.8\ \text{g cm}^{-3}$, no C and O impurities detected, and a resistivity of $19\ \mu\Omega\ \text{cm}$ at 22 nm film thickness). These results demonstrate that the temperature window for remote plasma ALD of Pt can effectively be extended down to 100°C . For PtO₂ the growth per cycle decreases slightly with increasing substrate temperature between 100 and 300°C , demonstrating that this process also has a large temperature window. At the substrate temperature of 300°C , decomposition of PtO₂ is reported to start for sputtered films, while in air decomposition starts at 550°C due to the higher partial pressure of oxygen.²⁰ For the process employing Pt(acac)₂ and O₃, only a small temperature window was observed ($120\text{--}130^\circ\text{C}$).¹³ Therefore, the large temperature window of our PtO₂ process suggests a higher stability of the material, which can most likely be related to the higher oxygen content (PtO_{2.2} compared to PtO_{1.6}).

Conclusions

Remote plasma ALD processes of Pt and PtO₂ were developed from the combination of MeCpPtMe₃ precursor and O₂ plasma, and compared to the thermal ALD process of Pt using the same precursor and O₂ gas. High purity Pt can be obtained by a short O₂ plasma exposure, whereas PtO₂ can be obtained by a long O₂ 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 surface or a high O₂ pressure is employed. A broad temperature window of $100\text{--}300^\circ\text{C}$ was achieved for both materials when deposited by remote plasma ALD. For Pt a H₂ gas exposure step was included in the ALD cycle to obtain high purity films at 100°C .

Acknowledgments

This work was sponsored by the Materials Innovation Institute M2i under project no. MC3.06278, and by the Netherlands Technology Foundation STW.

Eindhoven University of Technology assisted in meeting the publication costs of this article.

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