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Citation for published version (APA):

Kessels, W. M. M., Knoop, H. C. M., Dielissen, S. A. F., Mackus, A. J. M., & Sanden, van de, M. C. M. (2009). Surface reactions during atomic layer deposition of Pt derived from gas phase infrared spectroscopy. *Applied Physics Letters*, 95(1), 013114-1/3. [013114]. <https://doi.org/10.1063/1.3176946>

DOI:

[10.1063/1.3176946](https://doi.org/10.1063/1.3176946)

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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Surface reactions during atomic layer deposition of Pt derived from gas phase infrared spectroscopy

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(Received 30 January 2009; accepted 23 June 2009; published online 10 July 2009)

Infrared spectroscopy was used to obtain absolute number information on the reaction products during atomic layer deposition of Pt from (methylcyclopentadienyl)trimethylplatinum [(MeCp)PtMe₃] and O₂. From the detection of CO₂ and H₂O it was established that the precursor ligands are oxidatively decomposed during the O₂ pulse mainly. Oxygen atoms chemisorbed at the Pt lead to likewise ligand oxidation during the (MeCp)PtMe₃ pulse however the detection of a virtually equivalent density of CO₂ and CH₄ also reveals a concurrent ligand liberation reaction. The surface coverage of chemisorbed oxygen atoms found is consistent with the saturation coverage reported in surface science studies. © 2009 American Institute of Physics.

[DOI: 10.1063/1.3176946]

Atomic layer deposition (ALD) of metals has only been studied to a limited extent despite the growing importance of ultrathin and conformal metal films in a wide variety of applications. One metal ALD process that has become popular is ALD of Pt from (methylcyclopentadienyl)trimethylplatinum [(MeCp)PtMe₃] and O₂ dosing as developed by Aaltonen *et al.*¹ This process has been adopted for a variety of applications,^{2–4} while it also represents a class of ALD processes of noble metals in which the catalytic activity of the film is used to dissociate reactants for the subsequent decomposition of the metal precursor ligands. More specifically, the O₂ dissociates on the Pt surface during the O₂ pulse and oxidatively decomposes the ligands of the (MeCp)PtMe₃. Mass spectrometry studies have revealed that this oxidation takes place during the O₂ pulse for the ligands remaining on the surface after precursor adsorption but also during the precursor adsorption process itself, because oxygen atoms reside at the Pt surface after the O₂ pulse.⁵ A similar reaction mechanism was observed for ALD of Ru from RuCp₂ and O₂.⁵

In this letter additional experimental proof for the reaction mechanism proposed by Aaltonen *et al.*⁵ is presented, while the insight into the mechanism is also extended by more quantitative data on the reaction products. From gas phase transmission infrared spectroscopy the production of CO₂ and H₂O in the oxidation of the ligands is confirmed by absolute density information, while also the production of CH₄ reaction products is observed during the (MeCp)PtMe₃ precursor pulse. On the basis of these data the precursor adsorption reaction including the role of chemisorbed oxygen atoms is addressed.

Figure 1 shows the thickness of a Pt film deposited at 300 °C (reactor wall temperature is 70 °C) as a function of the number of cycles as monitored by *in situ* spectroscopic ellipsometry. This Pt film, with a preferential (111) orientation, was deposited on a Pt seed layer deposited by plasma-assisted ALD (Ref. 4) in order to prevent problems with

nucleation due to the initial absence of catalytic activation of oxygen on Pt-free substrates. Under the experimental conditions used, described in Ref. 4, a growth per cycle of 0.045 ± 0.002 nm/cycle was obtained in good agreement with reports in the literature.^{1–3} Rutherford backscattering spectrometry revealed that $(3.0 \pm 0.2) \times 10^{14}$ cm⁻² Pt atoms, corresponding to 0.2 ML Pt, are deposited per cycle.⁴ As every (MeCp)PtMe₃ molecule consists of nine C atoms and 16 H atoms (cf. Fig. 1) the amount of C and H atoms that need to be removed from the surface by ligand oxidation and other reactions can be calculated when taking the heated substrate area into account.

Figure 2 shows infrared absorbance spectra taken during the (MeCp)PtMe₃ and O₂ pulses. The differential spectra reflect the difference in gas phase species such as precursor molecules and reaction products before and after the pulses. The data are taken with the reaction chamber isolated from the pump to allow for sufficient measurement time, and the signal-to-noise ratio of the data is also improved by averaging.

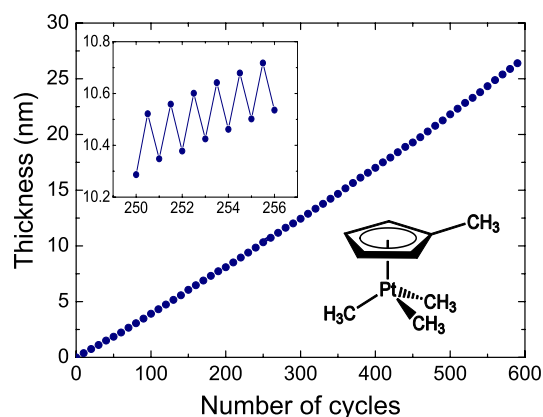


FIG. 1. (Color online) Pt film thickness vs the number of cycles as measured by *in situ* spectroscopic ellipsometry. The substrate was a Pt seed layer deposited by plasma-assisted ALD and the substrate temperature was 300 °C. The insets show the (MeCp)PtMe₃ precursor and the thickness for a few half-cycles with the half-integer and full-integer data points representing the (MeCp)PtMe₃ pulse and O₂ pulse, respectively.

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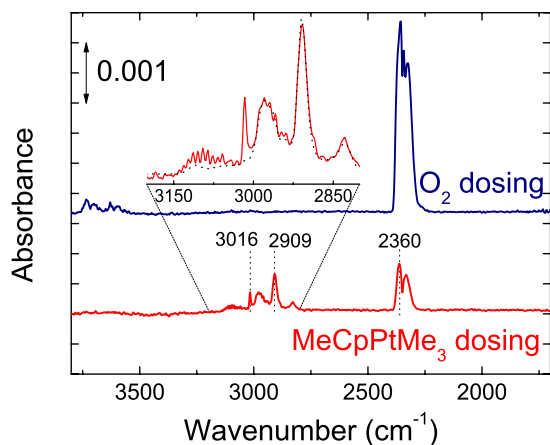


FIG. 2. (Color online) Gas phase absorbance spectra for the (MeCp)PtMe₃ pulse and O₂ pulse. The maximum peak positions of (MeCp)PtMe₃ (2909 cm⁻¹), CO₂ (2360 cm⁻¹), and CH₄ (3016 cm⁻¹) are indicated. In the inset the absorbance due to CH₄ can be distinguished from the absorbance due to (MeCp)PtMe₃ from a comparison with a spectrum measured for (MeCp)PtMe₃ precursor only (dotted line).

ing the data over several ALD cycles. (MeCp)PtMe₃ is dosed by a single long pulse or by several sequential pulses (“micropulses”) with the total pressure remaining below 0.015 Torr while O₂ is dosed in a single pulse at a pressure of 0.7 Torr. The formation of CO₂ during both the (MeCp)PtMe₃ and O₂ pulses can clearly be observed from the absorbance peaks around 2360 cm⁻¹, with most of the CO₂ being produced during the O₂ pulse. During the O₂ pulse the oxidation of ligands is sufficiently large in magnitude such that also the presence of H₂O can be observed from the absorption bands in the regions around 1600 cm⁻¹ (not shown) and 3700 cm⁻¹. These observations confirm the reaction mechanism proposed by Aaltonen *et al.*, i.e., the oxidation of precursor ligands takes place during the O₂ pulse as well as during the precursor pulse, because oxygen atoms, generated by O₂ dissociative chemisorption reactions,^{6–8} reside at the Pt surface after O₂ dosing. Furthermore, the spectrum taken during the (MeCp)PtMe₃ pulse shows that the precursor dosing reached saturation as a nonzero absorbance of (MeCp)PtMe₃ (dominated by C–H stretch at 2909 cm⁻¹ associated with Pt–CH₃ and Cp–CH₃ groups) can clearly be observed. Additionally the *Q* branch (3016 cm⁻¹), and to a lesser extent the *P* and *R* branch, of the C–H stretching mode of CH₄ can be distinguished in the spectrum during the (MeCp)PtMe₃ dosing. This demonstrates the remarkable fact that CH₄ is also produced during the (MeCp)PtMe₃ adsorption step during Pt ALD. This reaction product was not reported so far for the Pt ALD process.

Quantitative information on the amount of CO₂ and CH₄ produced in both half-cycles of the Pt ALD process was obtained from a calibration of the infrared absorbance intensities of CO₂ and CH₄ gas over the relevant pressure range. For the spectra in Fig. 2, CO₂ densities of $(3.7 \pm 1.4) \times 10^{14}$ and $(2.5 \pm 0.4) \times 10^{13}$ cm⁻³ were found for the O₂ and (MeCp)PtMe₃ pulses, respectively. This implies that approximately fifteen times more carbon atoms are oxidized during the O₂ pulse. This is in good agreement with the qualitative results reported by Aaltonen *et al.*, who also observed that only a very small proportion of the (MeCp)PtMe₃ ligands were decomposed oxidatively during precursor adsorption. In addition, a density of $(3.1 \pm 0.6) \times 10^{13}$ cm⁻³ of

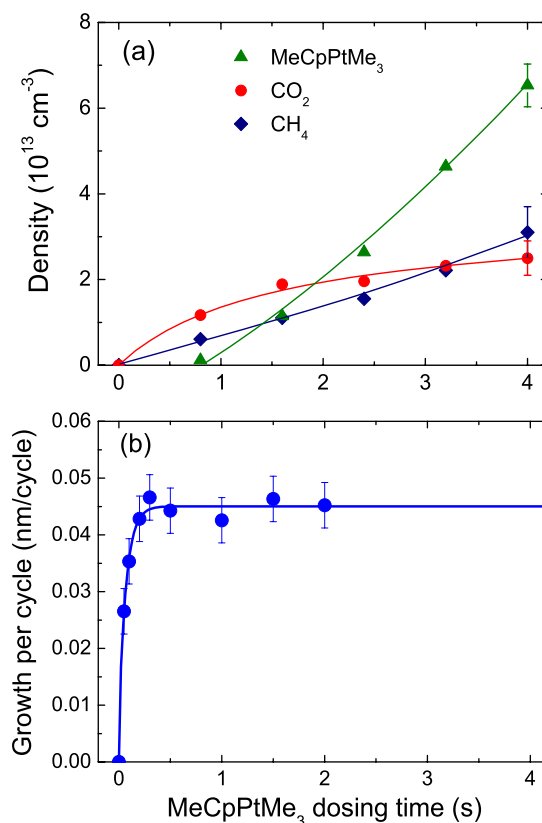


FIG. 3. (Color online) (a) (MeCp)PtMe₃, CO₂, and CH₄ densities during (MeCp)PtMe₃ dosing in which the precursor is dosed by sequential micropulses of 0.8 s. Typical error bars are shown for a total dosing time of 4 s. (b) The saturation of the growth per cycle with (MeCp)PtMe₃ dosing time as measured by spectroscopic ellipsometry for a substrate at 300 °C. The lines serve as a guide to the eye.

CH₄ is produced during the (MeCp)PtMe₃ pulse, i.e., a virtually equivalent amount of carbon atoms decompose into CH₄ and CO₂ during adsorption of the precursor in the ALD cycle.

The aforementioned results hold for ALD cycles with a large (MeCp)PtMe₃ overdose. The reaction products and the depletion of precursor were also investigated when dosing the precursor by micropulses as shown in Fig. 3(a). The spectra in Fig. 2 correspond with a total (MeCp)PtMe₃ dosing time of 4 s. The data were also compared with a saturation curve measured by spectroscopic ellipsometry at the 300 °C heated substrate holder as shown in Fig. 3(b). Although care needs to be taken when comparing results from local ellipsometry measurements with global infrared measurements, it is clear that the growth per cycle saturates at a much smaller precursor dose than the density of the reaction products. Moreover, the CO₂ density shows a clear saturation behavior but such a behavior is not evident for the CH₄ density. The ratio of CH₄ and CO₂ density increases with (MeCp)PtMe₃ dosing time when going to precursor overdosing conditions.

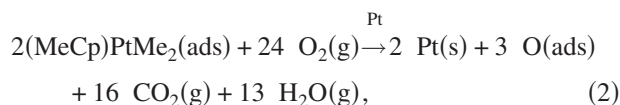
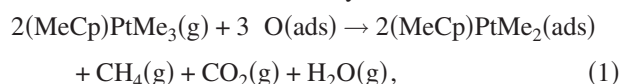
The discrepancy between the results in Figs. 3(a) and 3(b) can be attributed to several effects, for example, by a (relative) change in the reaction products produced when reaching saturation. Possibly somewhat colder parts of the 300 °C heated substrate holder play a role and contribute to a slower saturation behavior. Another explanation is that the surplus of (MeCp)PtMe₃ precursor reacts with reaction prod-

uct species, such as H₂O, produced during initial (MeCp)PtMe₃ adsorption. This can occur either directly with H₂O molecules or indirectly, for example, through –OH surface species generated by the interaction of H₂O with (colder) surfaces. For one (MeCp)PtMe₃ micropulse, corresponding to a dosing time of 0.8 s, the precursor is fully depleted by the surface reactions, while for two micropulses some of the precursor remains unreacted. For a dosing time of 0.8 s, the growth per cycle at the substrate [Fig. 3(b)] is also saturated and, therefore, it is expected that the densities reported for 1–2 micropulses reflect the reaction products produced during ALD of Pt at 300 °C well. More support for this conclusion is obtained when calculating the number of C atoms liberated into the gas phase as reaction products per ALD cycle. A number of $(2.4 \pm 0.9) \times 10^{18}$ C atoms can be calculated from the number of Pt atoms deposited per cycle at the heated substrate holder, whereas a calculation on the basis of the CO₂ and CH₄ densities during both half-cycles and the reactor volume reveals that this number is obtained for 70% after one (MeCp)PtMe₃ micropulse, for 111% after two micropulses, and for 153% after five micropulses. Notwithstanding a large experimental uncertainty, this comparison indicates that sufficient (MeCp)PtMe₃ precursor is dosed into the reaction chamber between one and two micropulses to achieve ALD saturation conditions for the heated substrate holder. It also provides support for the aforementioned additional reactions possibly taking place during precursor overdosing.

From the relative densities of CH₄ and CO₂ obtained during the (MeCp)PtMe₃ and O₂ pulses, it can be derived that approximately one C atom per precursor molecule is liberated from the precursor as volatile reaction product during adsorption of the precursor on the Pt surface in the ALD cycle. The other eight C atoms of the precursor molecule remain at the surface and are oxidatively decomposed during the O₂ pulse. This conclusion is virtually independent of the number of micropulses considered however the CH₄:CO₂ ratio during precursor adsorption is approximately 1:2 at one to two micropulses and 1:1 at five micropulses. These observations can be used to discuss the precursor adsorption mechanism. Considering the fact that the Pt in (MeCp)PtMe₃ is bonded to three CH₃ groups and one CpCH₃ group it can be hypothesized that one of the CH₃ groups is liberated during precursor adsorption. This CH₃ group can either be oxidized by chemisorbed oxygen or it can react to form CH₄ by ligand exchange.⁹ The other two CH₃ groups as well as the CpCH₃ group will subsequently be oxidized during the O₂ pulse. From the stability of covalent (substituted) cyclopentadienyl groups, it is also expected that the CpCH₃ group remains intact during precursor adsorption. In addition, the case that the precursor adsorbs with most of the (large) ligands remaining unreacted on the surface is consistent with the ellipsometry data obtained for the ALD half-cycles as shown in the inset of Fig. 1. When film and surface groups are analyzed with one single dielectric function, the (“apparent”) thickness,¹⁰ shows a large increase after precursor adsorption as well as a large, albeit somewhat smaller, decrease after ligand oxidation by O₂.

The oxidative decomposition reaction when (MeCp)PtMe₃ adsorbs at the surface during the precursor pulse takes place via the chemisorbed oxygen atoms. Because only one CH₃ group is liberated per Pt atom during this pulse, and because the reaction products are CO₂, H₂O, and CH₄; the amount of oxygen atoms required on the surface per deposited Pt atom can be calculated. This calculation shows that for every Pt atom, approximately 1.5 oxygen atoms need to be available as surface-bound oxygen. As ~0.2 ML Pt is deposited per cycle, this implies that a surface coverage of 0.3 ML of oxygen atoms after the O₂ pulse is sufficient for the precursor adsorption reaction to take place. This surface coverage of oxygen atoms is in very good agreement with the 0.25 ML saturation coverage of chemisorbed oxygen atoms found in surface science studies on Pt(111) exposed to O₂.^{6,7} This illustrates the consistency of the analysis and it provides more evidence that the Pt ALD reaction proceeds through chemisorbed oxygen atoms present at the Pt surface. Contrary to the reaction mechanism for Ru,⁵ the involvement of subsurface oxygen^{5,11} is therefore not required.

In conclusion, quantitative insight into the reaction mechanism of Pt ALD from (MeCp)PtMe₃ and O₂ has been obtained and can be summarized by the reactions:



for (MeCp)PtMe₃ dosing [Eq. (1)] and O₂ dosing [Eq. (2)]. For simplicity, it has been assumed that CH₄ and CO₂ are produced in equal amounts during precursor adsorption in Eq. (1), whereas in Eq. (2) the catalytic activity of the Pt is important for the dissociative chemisorption of the O₂. This reaction mechanism for Pt, which is ruled by the saturation surface coverage of chemisorbed oxygen atoms, can serve as a model system for ALD processes of noble metals.

The Dutch Technology Foundation STW is acknowledged for their financial support (STW-TFN 10018).

¹T. Aaltonen, M. Ritala, T. Sajavaara, J. Keinonen, and M. Leskela, *Chem. Mater.* **15**, 1924 (2003).

²X. Jiang and S. F. Bent, *J. Electrochem. Soc.* **154**, D648 (2007).

³Y. Zhu, K. A. Dunn, and A. E. Kaloyeros, *J. Mater. Res.* **22**, 1292 (2007).

⁴H. C. M. Knoop, A. J. M. Mackus, M. E. Donders, M. C. M. van de Sanden, P. H. L. Notten, and W. M. M. Kessels, *Electrochem. Solid-State Lett.* **12**, G34 (2009).

⁵T. Aaltonen, A. Rahtu, M. Ritala, and M. Leskela, *Electrochem. Solid-State Lett.* **6**, C130 (2003).

⁶J. L. Gland, B. A. Sexton, and G. B. Fisher, *Surf. Sci.* **95**, 587 (1980).

⁷C. T. Campbell, G. Ertl, H. Kuipers, and J. Segner, *Surf. Sci.* **107**, 220 (1981).

⁸R. B. Getman, Y. Xu, and W. F. Schneider, *J. Phys. Chem. C* **112**, 9559 (2008).

⁹The exact nature of the ligand exchange reaction cannot be assessed on the basis of the current data. Possible involvement of –OH surface groups can only be established by surface spectroscopic studies.

¹⁰E. Langereis, S. B. S. Heil, H. C. M. Knoop, W. Keuning, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Phys. D* **42**, 073001 (2009).

¹¹J. F. Weaver, J.-J. Chen, and A. L. Gerrard, *Surf. Sci.* **592**, 83 (2005).