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

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Infrared spectroscopy was used to obtain absolute number information on the reaction products during atomic layer deposition of Pt from (methylcyclopentadienyl)trimethylplatinum [(MeCp)PtMe$_3$] and O$_2$. From the detection of CO$_2$ and H$_2$O it was established that the precursor ligands are oxidatively decomposed during the O$_2$ pulse mainly. Oxygen atoms chemisorbed at the Pt lead to likewise ligand oxidation during the (MeCp)PtMe$_3$ pulse however the detection of a virtually equivalent density of CO$_2$ and CH$_4$ 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*.
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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)PtMe$_3$] and O$_2$ 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 O$_2$ dissociates on the Pt surface during the O$_2$ pulse and oxidatively decomposes the ligands of the (MeCp)PtMe$_3$. Mass spectrometry studies have revealed that this oxidation takes place during the O$_2$ 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 O$_2$ pulse.[5] A similar reaction mechanism was observed for ALD of Ru from RuCp$_2$ and O$_2$.[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 CO$_2$ and H$_2$O in the oxidation of the ligands is confirmed by absolute density information, while also the production of CH$_4$ reaction products is observed during the (MeCp)PtMe$_3$ 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)PtMe$_3$ 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)PtMe$_3$ and O$_2$ 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 averag-

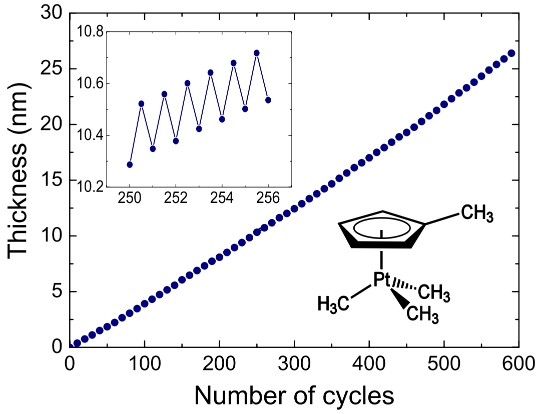

FIG. 1. (Color online) Pt film thickness vs the number of cycles as measured by *in situ* spectroscopic ellipsometry. The substrate was a Pt seed layer deposited by plasma-assisted ALD and the substrate temperature was 300 °C. The insets show the (MeCp)PtMe$_3$ precursor and the thickness for a few half-cycles with the half-integer and full-integer data points representing the (MeCp)PtMe$_3$ pulse and O$_2$ pulse, respectively.

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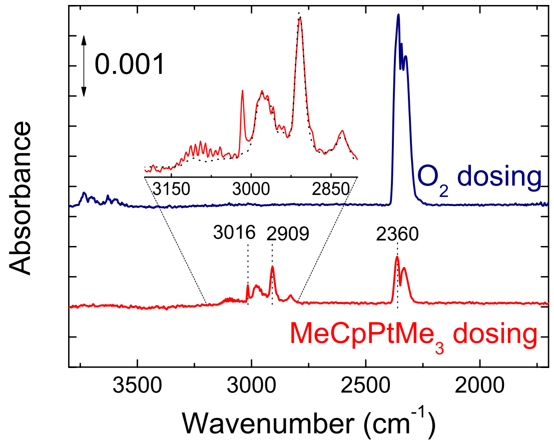

FIG. 2. (Color online) Gas phase absorbance spectra for the (MeCp)PtMe$_3$ pulse and O_2 pulse. The maximum peak positions of (MeCp)PtMe$_3$ (2909 cm^{-1}), CO_2 (2360 cm^{-1}), and CH_4 (3016 cm^{-1}) are indicated. In the inset the absorbance due to CH_4 can be distinguished from the absorbance due to (MeCp)PtMe$_3$ from a comparison with a spectrum measured for (MeCp)PtMe$_3$ precursor only (dotted line).

ing the data over several ALD cycles. (MeCp)PtMe$_3$ is dosed by a single long pulse or by several sequential pulses ("micropulses") with the total pressure remaining below 0.015 Torr while O_2 is dosed in a single pulse at a pressure of 0.7 Torr. The formation of CO_2 during both the (MeCp)PtMe$_3$ and O_2 pulses can clearly be observed from the absorbance peaks around 2360 cm^{-1}, with most of the CO_2 being produced during the O_2 pulse. During the O_2 pulse the oxidation of ligands is sufficiently large in magnitude such that also the presence of H_2O 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 O_2 pulse as well as during the precursor pulse, because oxygen atoms, generated by O_2 dissociative chemisorption reactions,[6–8] reside at the Pt surface after O_2 dosing. Furthermore, the spectrum taken during the (MeCp)PtMe$_3$ pulse shows that the precursor dosing reached saturation as a nonzero absorbance of (MeCp)PtMe$_3$ (dominated by C–H stretch at 2909 cm^{-1} associated with Pt–CH_3 and Cp–CH_3 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 CH_4 can be distinguished in the spectrum during the (MeCp)PtMe$_3$ dosing. This demonstrates the remarkable fact that CH_4 is also produced during the (MeCp)PtMe$_3$ adsorption step during Pt ALD. This reaction product was not reported so far for the Pt ALD process.

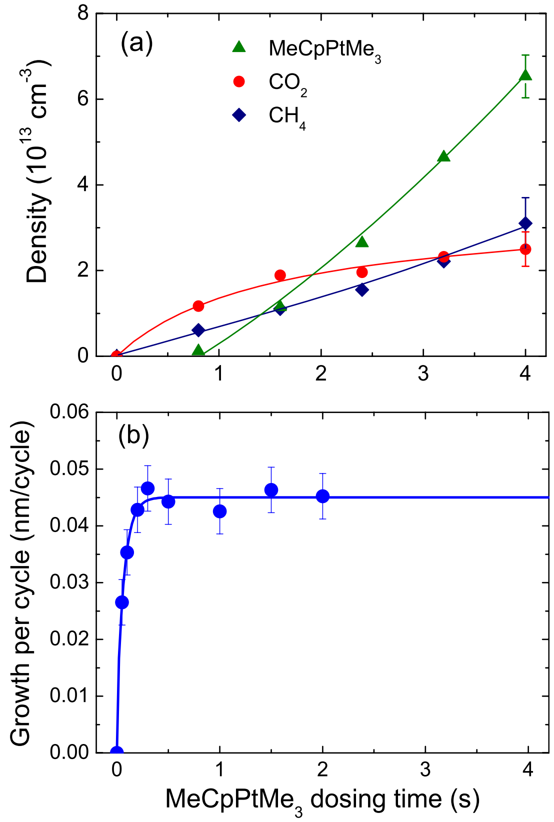

FIG. 3. (Color online) (a) (MeCp)PtMe$_3$, CO_2, and CH_4 densities during (MeCp)PtMe$_3$ dosing in which the precursor is dosed by sequential micropulses of 0.8 s. Typical error bars are shown for a total dosing time of 4 s. (b) The saturation of the growth per cycle with (MeCp)PtMe$_3$ dosing time as measured by spectroscopic ellipsometry for a substrate at 300 °C. The lines serve as a guide to the eye.

Quantitative information on the amount of CO_2 and CH_4 produced in both half-cycles of the Pt ALD process was obtained from a calibration of the infrared absorbance intensities of CO_2 and CH_4 gas over the relevant pressure range. For the spectra in Fig. 2, CO_2 densities of $(3.7\pm1.4)\times10^{14}$ and $(2.5\pm0.4)\times10^{13}$ cm^{-3} were found for the O_2 and (MeCp)PtMe$_3$ pulses, respectively. This implies that approximately fifteen times more carbon atoms are oxidized during the O_2 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)PtMe$_3$ ligands where decomposed oxidatively during precursor adsorption. In addition, a density of $(3.1\pm0.6)\times10^{13}$ cm^{-3} of CH_4 is produced during the (MeCp)PtMe$_3$ pulse, i.e., a virtually equivalent amount of carbon atoms decompose into CH_4 and CO_2 during adsorption of the precursor in the ALD cycle.

The aforementioned results hold for ALD cycles with a large (MeCp)PtMe$_3$ 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)PtMe$_3$ 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 CO_2 density shows a clear saturation behavior but such a behavior is not evident for the CH_4 density. The ratio of CH_4 and CO_2 density increases with (MeCp)PtMe$_3$ 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)PtMe$_3$ precursor reacts with reaction product species, such as H_2O, produced during initial $(MeCp)PtMe_3$ adsorption. This can occur either directly with H_2O molecules or indirectly, for example, through –OH surface species generated by the interaction of H_2O with (colder) surfaces. For one $(MeCp)PtMe_3$ 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 CO_2 and CH_4 densities during both half-cycles and the reactor volume reveals that this number is obtained for 70% after one $(MeCp)PtMe_3$ micropulse, for 111% after two micropulses, and for 153% after five micropulses. Notwithstanding a large experimental uncertainty, this comparison indicates that sufficient $(MeCp)PtMe_3$ 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 CH_4 and CO_2 obtained during the $(MeCp)PtMe_3$ and O_2 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 O_2 pulse. This conclusion is virtually independent of the number of micropulses considered however the $CH_4 : CO_2$ 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 $(MeCp)PtMe_3$ is bonded to three CH_3 groups and one $CpCH_3$ group it can be hypothesized that one of the CH_3 groups is liberated during precursor adsorption. This CH_3 group can either be oxidized by chemisorbed oxygen or it can react to form CH_4 by ligand exchange.[9] The other two CH_3 groups as well as the $CpCH_3$ group will subsequently be oxidized during the O_2 pulse. From the stability of covalent (substituted) cyclopentadienyl groups, it is also expected that the $CpCH_3$ 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 O_2.

The oxidative decomposition reaction when $(MeCp)PtMe_3$ adsorbs at the surface during the precursor pulse takes place via the chemisorbed oxygen atoms. Because only one CH_3 group is liberated per Pt atom during this pulse, and because the reaction products are CO_2, H_2O, and CH_4; 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 O_2 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 O_2.[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 $(MeCp)PtMe_3$ and O_2 has been obtained and can be summarized by the reactions:

$$2(MeCp)PtMe_3(g) + 3\ O(ads) \rightarrow 2(MeCp)PtMe_2(ads) + CH_4(g) + CO_2(g) + H_2O(g), \quad (1)$$

$$2(MeCp)PtMe_2(ads) + 24\ O_2(g) \xrightarrow{Pt} 2\ Pt(s) + 3\ O(ads) + 16\ CO_2(g) + 13\ H_2O(g), \quad (2)$$

for $(MeCp)PtMe_3$ dosing [Eq. (1)] and O_2 dosing [Eq. (2)]. For simplicity, it has been assumed that CH_4 and CO_2 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 O_2. 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.

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[1] T. Aaltonen, M. Ritala, T. Sajavaara, J. Keinonen, and M. Leskela, Chem. Mater. **15**, 1924 (2003).
[2] X. Jiang and S. F. Bent, J. Electrochem. Soc. **154**, D648 (2007).
[3] Y. Zhu, K. A. Dunn, and A. E. Kaloyeros, J. Mater. Res. **22**, 1292 (2007).
[4] H. C. M. Knoops, 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).
[5] T. Aaltonen, A. Rahtu, M. Ritala, and M. Leskela, Electrochem. Solid-State Lett. **6**, C130 (2003).
[6] J. L. Gland, B. A. Sexton, and G. B. Fisher, Surf. Sci. **95**, 587 (1980).
[7] C. T. Campbell, G. Ertl, H. Kuipers, and J. Segner, Surf. Sci. **107**, 220 (1981).
[8] R. B. Getman, Y. Xu, and W. F. Schneider, J. Phys. Chem. C **112**, 9559 (2008).
[9] The 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.
[10] E. Langereis, S. B. S. Heil, H. C. M. Knoops, W. Keuning, M. C. M. van de Sanden, and W. M. M. Kessels, J. Phys. D **42**, 073001 (2009).
[11] J. F. Weaver, J.-J. Chen, and A. L. Gerrard, Surf. Sci. **592**, 83 (2005).