Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2018

Supplementary Information: Surface species during ALD of platinum observed with in situ reflection IR spectroscopy

Michiel Van Daele, Christophe Detavernier, and Jolien Dendooven*

Ghent University, Department of Solid State Sciences, CoCooN Research Group, Krijgslaan 281/S1, Ghent 9000, Belgium

E-mail: jolien.dendooven@ugent.be

XRR measurements

X-Ray Reflectivity measurements (XRR) of films grown by a Pt PE-ALD process, using $MeCpPtMe_3$ as precursor and O_2 plasma as the reactant, for a substrate temperature of 100 and 200°C are shown in Fig.1. To obtain these samples a Pt seed layer of 6.9 nm was sputtered on a silicon substrate. The substrate was pretreated inside the ALD chamber before deposition using an O_2 plasma to remove contaminants from the surface. An ALD process of 50 Pt PE-ALD cycles was performed on a plasma pretreated sample for a substrate temperature of 100°C or 200°C.

The XRR fit for the deposition performed at 200°C gives a Pt thickness of 9.4 nm after deposition (Fig. 1b), resulting in a growth of 0.05 nm/cycle. For a substrate temperature of 100°C, the fit for the XRR data gives a platinum thickness of 6.3 nm and an extra Pt:O layer of 4.2 nm (Fig. 1a). This extra Pt:O layer is necessary to get a decent fit of the data. The decrease in thickness of the seed layer, by 0.6 nm, might be due to oxidation of the platinum

top layer by the plasma pretreatment. This yields a Pt:O growth of 0.72 nm/cycle for a substrate temperature of 100°C, when correcting for the oxidation of 0.6 nm.

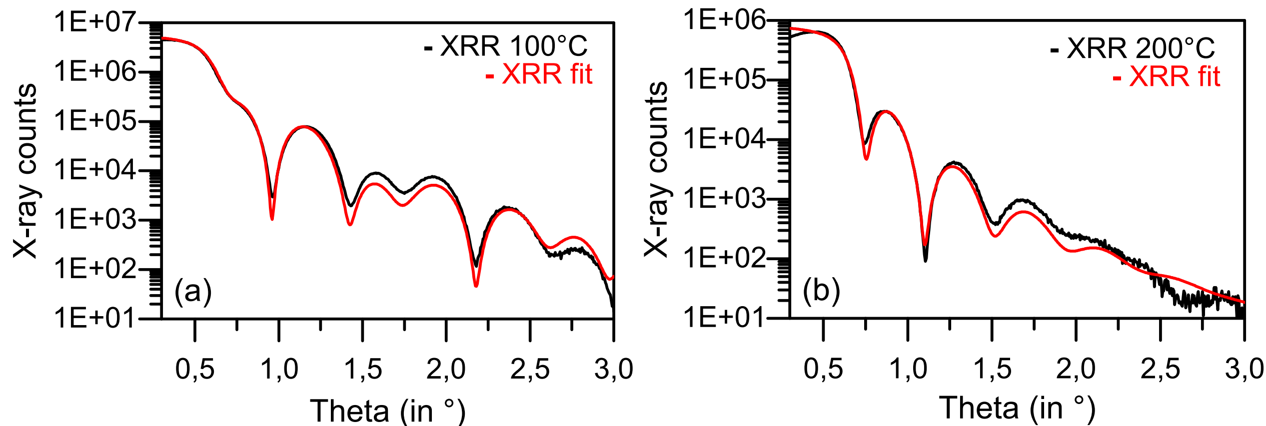

Figure 1: XRR measurements of the Pt layers after 50 cycles of the Pt PE-ALD process for a substrate temperature of 100 and 200°C. The thickness of the Pt seed layer before deposition was 6.9 nm for both samples. (a) Data and fit for a substrate temperature of 100°C, from the fit after deposition a Pt thickness of 6.3 nm and a Pt:O thickness of 4.2 nm is obtained. (b) Data and fit for a substrate temperature of 200°C, the fit after deposition gives a platinum thickness of 9.4 nm.

XPS measurements

At low substrate temperatures (<150°C) the use of O_2 plasma as the reactant in the Pt PE-ALD process results in the growth of Pt:O instead of pure Pt. To confirm this, an XPS depth profile was taken of a Pt PE-ALD film grown at 100°C on a Pt seed layer to determine if oxygen was present in the deposited film. A Thermoscientific XPS was used equipped with a thetaprobe and an aluminium anode. The XPS measurements were performed with a pass energy of 20 eV, the achieved FWHM of the instrument is 0.63 eV. In Figure 2 the XPS regions for the C1s, O1s, and Pt4f peaks are shown for three levels of the depth profile of the sample: the surface, the Pt:O layer, and the Pt seed layer. Carbon is only present on the surface and can be sputtered away. Oxygen is present on the surface and throughout the deposited film, the sputtered Pt seed layer has no oxygen and the binding energy of the Pt 4f

peaks match to metallic Pt. The surface of the Pt film is in an oxidised state. The deposited film itself has an oxidised component and a metallic component for the Pt 4f peaks. The atomic concentrations can be found in Table 1.

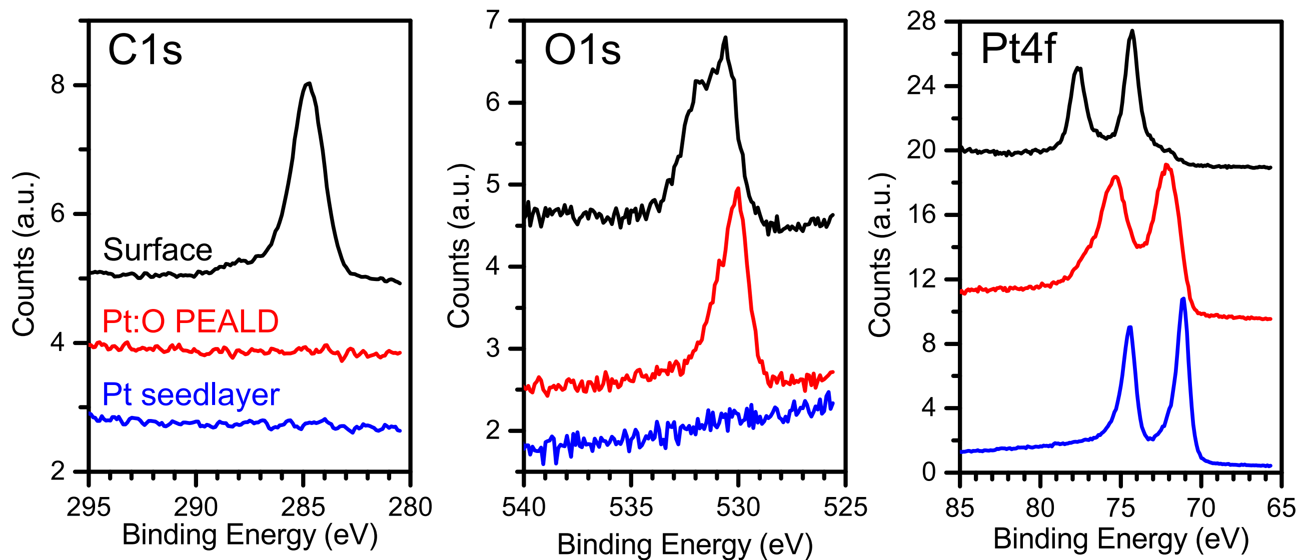

Figure 2: C1s, O1s, and Pt4f regions for a PE-ALD grown Pt film at 100°C on a Pt seed layer.

Table 1: Atomic percentage of C, O and Pt in PE-ALD grown Pt films at 100°C. Oxygen is present in the bulk of the grown film and not only on the surface.

	C (at. %)	O (at. %)	Pt (at. %)
Surface	15.76	20.15	64.09
Bulk	0	10.4	89.6
Seed	0	0	100