Supporting Information

Atomic Layer Deposition of High-Purity Palladium Films from $Pd(hfac)_2$ and H_2 and O_2 plasmas

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S1: Details on the ALD process using $Pd(hfac)_2$ as precursor and an O_2 plasma followed by H_2 plasma as co-reactant step

For Ir[1] and Pt[2], ALD processes have been reported that employ dosing of a metalorganic precursor in combination with a co-reactant step that consists of exposure to an oxidizing agent followed by exposure to a reducing agent. The rationale behind this approach is that the adsorbed precursor ligands are first combusted by the oxidizing agent after which the oxidized metal atoms in the surface layer can be reduced to the metallic state by the reducing agent. Oxidizing agents such as O_2 plasma or ozone can be used in this approach in combination with H_2 gas or H_2 plasma as reducing agent. For ALD of Pd, this approach has however been rather unsuccessful[3] and so far ALD of Pd is typically only achieved by using a reductive chemistry such as with H_2 or formalin. Nevertheless, in this work several attempts were made to apply this approach for ALD of Pd using $Pd(hfac)_2$ as precursor and O_2 plasma and H_2 plasma in the co-reactant step. However, for all conditions investigated very poor results showing no or almost no growth were obtained.

One example of a result is shown in Figure S1. This figure shows an XPS survey scan of a film after 1000 cycles. The process parameters were similar to those reported in the manuscript with the exception of the reverse order of the co-reactants in this experiment. The substrates were Al_2O_3 films on Si and the substrate temperature was 100°C. The XPS result in Figure S1 was obtained after removing the surface contamination by a mild sputtering step. The XPS peaks reveal that the elements Pd, C, F, but also Al and O are present. The presence of Al peaks, originating from the Al_2O_3 substrate, is a sign that the film is very thin (< 5 nm). The presence of C and F peaks, clearly visible, indicates that the film is strongly contaminated by carbon and fluorine containing species. The film was too thin to enable a decent quantitative compositional analysis and furthermore presented a very high resistivity value of 10^7 μΩ.cm, as measured by FPP.

One hypothesis to explain the fact that this approach is not viable for ALD of Pd from $Pd(hfac)_2$ is the presence of F in the precursor ligands. During the O_2 plasma step the adsorbed precursor ligands will undergo reactions with the plasma species leaving various fragments behind at the surface. It is known from the literature that ALD based on the reaction between fluorinated metal precursors and a strong oxygen source can result in metal fluorides.[4] For example, CaF_2 thin films were prepared by an ALD process based on $Ca(hfac)_2$ and ozone at 300°C.[4] This shows that the hfac ligands are reactive with strong oxidizing agents, and hence it is possible that hfac ligands and O_2 plasma species lead to surface metal fluoride species and other by-products. Moreover, during the H_2 plasma step, H atoms can potentially react with adsorbed F atoms leading to HF species. These could induce etching which is also detrimental for ALD film growth.

For other ALD processes for which the O_2 plasma approach is viable, i.e. for ALD of Pt,[2] Ir[1] or Ru[5], the precursors contain typically no F atoms but only C, H, and O. In these cases exclusively volatile by-products are created in the reaction with O_2 plasma species.[6]

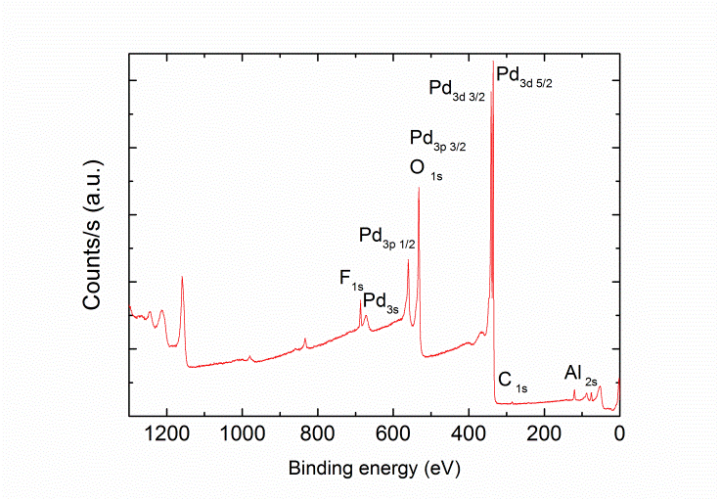

Figure S1. XPS survey scan of a film after carrying out 1000 cycles of the ALD process consisting of $Pd(hfac)_2$ dosing, O_2 plasma exposure and subsequently H_2 plasma exposure. The substrate was a Si wafer covered with a 250 nm ALD Al_2O_3 film. The deposition temperature was 100ºC.

S2: Properties of Pd films deposited by the (thermal) ALD process using $Pd(hfac)_2$ and H_2 gas dosing

Table S1. Properties of Pd films deposited by ALD using $Pd(hfac)_2$ as precursor and H_2 gas as co-reactant. Data obtained with H_2 plasma as co-reactant (i.e., the AB process in the manuscript) are given for easy comparison. The substrates were Si wafers with 250 nm thick Al_2O_3 films and the substrate temperature was 100°C. The process with H_2 gas as co-reactant took place on a 15 nm thick Pt seed layer. In situ spectroscopic ellipsometry (SE), atomic force microscopy (AFM), Rutherford backscattering spectroscopy (RBS) and four-point probe (FPP) measurements were used for analysis of the films. The films were ~30 nm thick.

Properties	Analysis technique	$Pd(hfac)_2$ with H_2 gas	$Pd(hfac)_2$ with H_2 plasma (AB process)
Growth-per-cycle (Å/cycle)	SE	0.16±0.05	0.17±0.05
Growth-per-cycle ($atoms.cm^{-2}.cycle^{-1}$)	RBS	$(0.9\pm0.1)\times10^{14}$	$(0.9\pm0.1)\times10^{14}$
Mass density (g/cm^3)	XRR	10.5±0.5	11.0±0.5
Resistivity (μΩ.cm)	FPP	65±5	48±5
C content (at. %)	XPS	-	14±3
	RBS	12±5	11±5
RMS roughness (nm)	AFM	2.3±0.3	1.0±0.3
	XRR	-	1.3±0.3

S3. Growth-per-cycle during steady-state film growth for the AB and ABC processes at 100°C

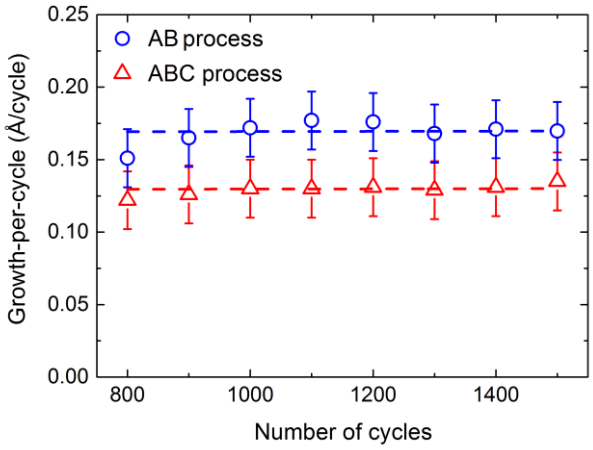

Figure S3. Growth-per-cycle (GPC) of Pd during steady-state ALD growth for the AB and ABC processes as determined by in situ spectroscopic ellipsometry. Data during the nucleation phase are omitted as the GPC as it is difficult to extract reliable data from spectroscopic ellipsometry when there is island growth. The GPC observed with the AB and the ABC processes are 0.13±0.02 and 0.17±0.02 Å/cycle, respectively. The substrates were Si wafers covered with a 250 nm ALD Al_2O_3 film. The deposition temperature was 100ºC.

References:

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