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# Low temperature atomic layer deposition of noble metals using ozone and molecular hydrogen as reactants

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ABSTRACT

Atomic layer deposition (ALD) of noble metals by thermal processes has relied mostly on the use of molecular oxygen as a reactant at temperatures of 200 °C and above. In this study, the concept of using consecutive ozone and molecular hydrogen pulses with noble metal precursors in ALD is introduced for palladium, rhodium, and platinum metals. This approach facilitates the growth of noble metal thin films below 200 °C. Also the ALD of palladium oxide thin films is demonstrated by the ozone-based chemistry. The growth rates, resistivities, crystallinities, surface roughnesses, impurity contents, and adhesion of the films to the underlying $Al_2O_3$ starting surface are reported and the results are compared with the most common noble metal ALD processes.

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## 1. Introduction

Noble metal and noble metal oxide thin films have been proven suitable for various applications. One of the most controlled methods to make these films is atomic layer deposition (ALD) [1–3], which is a modification of the chemical vapor deposition (CVD) method. In ALD, precursors are pulsed into a reactor chamber separately, one at a time, and surface reactions proceed in a saturative, self-limiting manner. Repeatability, conformality, uniformity and thickness controllability of the deposited films are the characteristics of ALD.

The most common thermal ALD noble metal processes use oxygen as a reactant. The noble metals grown with such combustion type processes include ruthenium [4–6], osmium [7], rhodium [8], iridium [9,10], and platinum [11]. The metal precursor type, but also the starting surface, affects the deposition temperature required for the noble metal deposition to proceed. This threshold temperature is usually 200 °C and above, but can be as high as over 300 °C [6,7]. In comparison, thermal noble metal ALD processes using reducing agents are quite few in number, except in the case of Pd where the ALD processes reported use all $Pd(hfac)_2$ (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonato) and reducing agents such as molecular $H_2$ and formalin at low deposition temperatures [12–14]. By contrast, $Pd(thd)_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionato) and β-ketoiminato precursor $Pd(keim2)_2$ [keim2 = $CF_3C(O)CH^-C(CF_3)NBu^n$] have been tested in oxygen-based processes with limited success [15,16]. The $Pd(keim2)_2$–$O_2$ process did not show saturation with increasing pulse length and thermal decomposition of $Pd(keim2)_2$ was seen at 250 °C although the deposited films were uniform [15]. On the other hand, the $Pd(thd)_2$–$O_2$ process resulted in non-uniform films at 250–275 °C and it was concluded that the poor film quality could be related to etching reactions [16].

We have recently reported ozone based ALD processes for the low temperature growth of oxides of rhodium [17], iridium [18,19], and platinum [20]. At the same low deposition temperatures where the iridium oxide films are grown, iridium metal films can also be obtained by using molecular hydrogen as a reducing agent in every ALD cycle after the ozone pulse [19,21]. Thus, with the $O_3$–$H_2$ processes the deposition temperatures for growing ALD noble metals can be lowered below the temperatures required in the corresponding $O_2$-based processes [9,10,19,21]. As an example, with the highly volatile (MeCp)Ir(CHD) (Me = methyl, Cp = cyclopentadienyl, CHD = cyclohexadiene) precursor one can deposit Ir films with the (MeCp)Ir(CHD)–$O_3$–$H_2$ cycling sequence at 120 °C as compared to 225 °C needed with the corresponding conventional $O_2$-based chemistry [(MeCp)Ir(CHD)–$O_2$] [10,19].

Knapas and Ritala have compared reaction mechanisms in oxygen and ozone-based ALD chemistries of Ir using $Ir(acac)_3$ (acac = acetylacetonato) as the noble metal precursor [22]. In the $O_2$-based ALD Ir process, combustion of the ligands of $Ir(acac)_3$ occurs in two steps; the $O_2$ pulse combusts all the ligands on the Ir surface and most importantly leaves adsorbed oxygen atoms on the surface [22]. The following $Ir(acac)_3$ pulse then reacts with these adsorbed oxygen atoms and the ligands are partially combusted in this step also [22]. In contrast to the $O_2$-based ALD Ir process, the $Ir(acac)_3$ adsorbs stoichiometrically (molecularly or dissociatively) on the surface in the $O_3$-based ALD $IrO_2$ process below 200 °C and the oxygen atoms on the $IrO_2$ are not reactive towards $Ir(acac)_3$ [22]. When $H_2$ is used to remove oxygen from the

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surface in the $O_3$-based Ir ALD process [$Ir(acac)_3$–$O_3$–$H_2$], the $Ir(acac)_3$ adsorption is also stoichiometric as in the ALD of $IrO_2$ [22]. In addition, all the reaction steps in the $Ir(acac)_3$–$O_3$–$H_2$ process advance as far as possible, i.e. ozone completely combusts the acac ligands of the $Ir(acac)_3$ and $H_2$ completely deoxidizes the surface left after ozone [22]. Similar to the $O_2$-based ALD Ir process, the $O_3$-based Ir and $IrO_2$ processes result also in $CO_2$ and $H_2O$ as the only byproducts [22].

The use of consecutive oxidation and reduction steps has not been limited to thermal ALD only. Knoops et al. [23] deposited Pt films at a low temperature (100 °C) by using oxygen plasma followed by molecular hydrogen. It should be emphasized that plasma was not used in the $H_2$ exposure step. This PEALD (plasma enhanced ALD) Pt process and the above mentioned $O_3$-based thermal ALD processes for $IrO_2$ and Ir metal imply that molecular $H_2$ would be sufficient to reduce also other noble metal oxides to the corresponding noble metals at low temperatures, thereby allowing the ALD of these noble metals at lower temperatures than achieved so far with the $O_2$-based processes.

In this study we will demonstrate the possibility to use ozone for ALD of palladium oxide in addition to the previously reported $IrO_2$, $Rh_2O_3$, and $PtO_X$ [17–20]. Similar to the previously reported $O_3$–$H_2$-based ALD Ir processes [19,21], molecular hydrogen is now used for the reduction of the corresponding noble metal oxides to metallic palladium, rhodium, and platinum at low temperatures. Our results indicate that the $O_3$–$H_2$ chemistry is general for those noble metals which do not form volatile higher oxidation state oxides, i.e. excluding ruthenium and osmium, and which have suitable precursors for thermal ALD with reasonably high volatility combined with sufficient thermal stability and reactivity, i.e. currently excluding silver and gold.

## 2. Experimental details

Noble metal and noble metal oxide film growth were examined in a commercial hot-wall flow-type F-120 ALD reactor (ASM Microchemistry Ltd., Finland) operated under a nitrogen pressure of about 1 kPa. Nitrogen was produced with a Domnick Hunter G2100E nitrogen generator and used as both a carrier and a purging gas. The noble metal and noble metal oxide films were grown on $Al_2O_3$ films [3] deposited in situ from trimethylaluminum (TMA) and water. Both $5\times5$ cm$^2$ silicon (111) and soda lime glass substrates were used. $Rh(acac)_3$ (99 %, ABCR), $Pd(thd)_2$ (Volatec), and $Pt(acac)_2$ (99.9 %, ABCR) were all sublimed from open boats held inside the reactor at 150, 120, and 110 °C, respectively, and pulsed with inert gas valving. Ozone was produced with a Wedeco Ozomatic Modular 4 HC Lab ozone generator from oxygen (99.999 and 99.9999 %, Linde Gas) and pulsed into the reactor through a needle valve and a solenoid valve from the main ozone flow line. The estimated ozone concentration output of the generator was about 100 g/Nm$^3$ with a flow rate of 30 l/h. Flow rate of $H_2$ (99.999 %, Aga) was set to 15 sccm by a needle valve and a mass flow meter during continuous flow and $H_2$ was pulsed into the reactor with a solenoid valve. For rhodium depositions $H_2$ flow rate of about 7 sccm was applied. Palladium oxide thin films were grown using ozone as the oxidant [$Pd(thd)_2$–$O_3$ pulsing sequence], while Pd, Rh, and Pt metals were deposited adding a molecular $H_2$ pulse after the ozone in each deposition cycle, i.e. using noble metal precursor–$O_3$–$H_2$ pulsing sequence. $N_2$ purge followed all the precursor pulses. Because the nitrogen flow was constantly on at a rate of 500 sccm, both $H_2$ and $O_3/O_2$ were strongly diluted by $N_2$. Anyhow, care should be taken to avoid simultaneous supply of $O_3$ and $H_2$ as this combination can be potentially explosive. Also, application of these processes without inert carrier gas may lead to hazardous mixing of $H_2$ and $O_3/O_2$.

Crystal structures of the films were identified from X-ray diffraction (XRD) patterns measured with a PANalytical X′Pert Pro X-ray diffractometer (Cu $K_\alpha$ radiation source). Both θ–2θ and grazing incidence XRD (GIXRD) (incidence angle 1°) configurations were used. Film thicknesses were determined from X-ray reflectivity (XRR) patterns measured with a Bruker AXS D8 Advance diffractometer (Cu $K_\alpha$ radiation source) and from energy-dispersive X-ray spectroscopy (EDX) data. The EDX spectra were measured using an Oxford INCA 350 microanalysis system connected to a Hitachi S-4800 field emission scanning electron microscope (FESEM) with an operating voltage of 20 kV. The EDX results were analyzed using a GMR electron probe thin film microanalysis program [24].

Surface morphology of the films was examined by the FESEM, and atomic force microscopy (AFM). Tapping mode AFM studies were performed in air with a Veeco Instruments Multimode V equipped with Nanoscope V controller. Phosphorus-doped rotated tapping mode etched silicon probes delivered by Veeco Instruments were used and scanning was done under area of $2\times2$ μm$^2$ with a scanning frequency of 0.5 Hz and no image processing except flattening was made. Roughness values were calculated as root-mean-square values ($R_q$).

Resistivities of the films were calculated from sheet resistances measured with a four-point probe technique from the center area of the grown samples and from the film thicknesses. Adhesion of the films was tested with a common Scotch tape test. Elemental compositions of the $PdO_X$ and Pd, Rh, Pt metal films were determined by time-of-flight elastic recoil detection analysis (TOF-ERDA) [25] with a Pelletron accelerator using 8.015 MeV $^{35}Cl^{4+}$ ion beams with an exception of Pt with which 10.2 MeV ion beam was used.

## 3. Results and discussion

### 3.1. Palladium oxide

Palladium oxide thin films were grown using $Pd(thd)_2$ and ozone (Fig. 1). As the sublimation temperature needed for the $Pd(thd)_2$ precursor was 120 °C, the lowest possible deposition temperature for palladium oxide was 130 °C where the growth rate was 0.1 Å/cycle. From 140 to 160 °C the growth rate was about 0.2 Å/cycle. The substantial decrease in the growth rate while the deposition temperature was decreased to 130 °C suggests that also from the precursor reactivity point of view the low temperature limit for the ALD of palladium oxide is close to 130 °C. In contrast the high temperature limit is reached at 160 °C as the film deposited at 170 °C was already partly metallic palladium. The resistivity of the about 20 nm thick film grown at 130 °C was 270 mΩ cm, while the about 40 nm thick films deposited at higher temperatures had resistivities between 20 to 30 mΩ cm (Fig. 1).

Palladium oxide has two stoichiometric forms, namely tetragonal PdO and $PdO_2$ [26], of which $PdO_2$ is quite labile. The θ–2θ XRD shows weak PdO reflections (Fig. 2(a)), while the GIXRD measurements confirm that the films are crystalline PdO (Fig. 2(b)). All the reflections in the θ–2θ XRD and GIXRD patterns match to the tetragonal PdO.

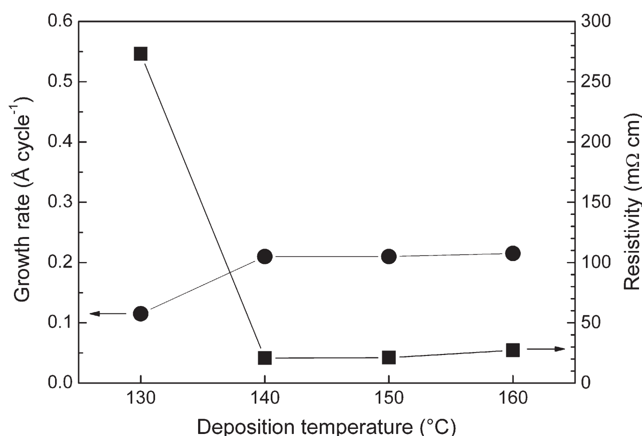


**Fig. 1.** Growth rates and resistivities of the palladium oxide films on $Al_2O_3$ film as a function of deposition temperature. 2000 cycles were applied using 2 s precursor pulses and purges. Substrate was Si(111). Film thicknesses were determined with EDX.

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