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Atomic layer deposition of platinum: from reaction mechanisms to direct-write nanopatterning

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Atomic layer deposition (ALD) of Pt thin films [1] and nanoparticles [2] is gaining increasing interest for applications in catalysis and microelectronics. In this presentation, the reaction mechanisms and the nucleation behavior of Pt ALD will be discussed, and it will be demonstrated how this knowledge can be exploited in the development of novel applications of Pt ALD.

First, the surface reactions that can take place at a catalytic Pt surface were evaluated from experiments combined with results reported in surface science literature [3]. As illustrated in Fig. 1, the ligands of the $MeCpPtMe_3$ precursor undergo dehydrogenation reactions on the catalytic Pt surface during the precursor pulse, in addition to the combustion-like reactions that take place when oxygen is present. The occurrence of dehydrogenation reactions has important implications for the self-limiting behavior of the half-reactions, the growth rate, and the temperature-dependence of the process.

The nucleation behavior of Pt ALD on oxide substrates was investigated using transmission electron microscopy (TEM) and spectroscopic ellipsometry (SE). The O_2 exposure employed during the O_2 half-reaction of the Pt ALD process was identified as a key parameter influencing the nucleation behavior [4]. This observation was explained by faster diffusion of deposited Pt atoms in the presence of O_2, which enhances the formation of Pt islands that can catalyze the ALD reactions. It will be discussed that the O_2 exposure can be used as a parameter to tune the nucleation behavior for the various applications of Pt ALD.

Based on the new insights obtained in the reaction mechanism study described above, new three-step plasma-assisted ALD processes ($MeCpPtMe_3$ dosing, O_2 plasma exposure, and H_2 gas or plasma exposure) were developed that allow for Pt ALD at substrate temperatures down to room temperature [5]. It was demonstrated that these processes enable the coating of temperature-sensitive substrates such as polymers, paper, and textile (see Fig. 2).

Furthermore, the study of the nucleation behavior revealed conditions that could be used for selective growth on seed layer patterns in a novel bottom-up nanopatterning approach. The approach combines the patterning capability of the direct-write patterning technique of electron beam induced deposition (EBID) and the material quality of ALD as illustrated in Fig. 3 [6]. A major benefit of this so-called *direct-write ALD* approach is that it does not involve etching, lift-off steps, or the use of resist films, which eliminates compatibility issues with certain sensitive surfaces. Recent work focuses on the application of direct-write ALD to the fabrication of carbon nanotube field effect transistors (CNTFETs).

[1] Aaltonen *et al.*, *Chem. Mater.* **15**, 1924 (2003)
[2] King *et al.*, *Nano Lett.* **8**, 2405 (2008)
[3] Mackus *et al.*, *Chem. Mater.* **24**, 1752 (2012)
[4] Mackus *et al.*, *Chem. Mater.* **25**, 1905 (2013)
[5] Mackus *et al.*, *Chem. Mater.* **25**, 1769 (2013)
[6] Mackus *et al.*, *Nanoscale* **4**, 4477 (2012)

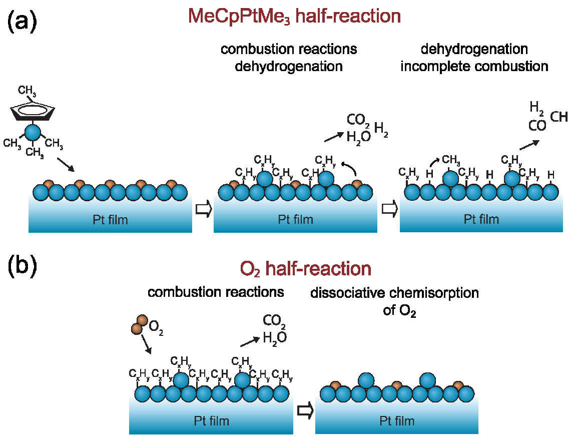

Figure 1 Schematic representation of the reaction mechanism of Pt ALD. (a) The precursor adsorbs on the Pt surface and reacts with chemisorbed oxygen in combustion reactions. In addition, dehydrogenation of the precursor ligands takes place at the catalytic Pt surface, which results in a carbonaceous layer that blocks further surface reactions. (b) During the O_2 pulse, the carbonaceous layer is combusted, and O_2 dissociatively chemisorbs on the Pt surface.

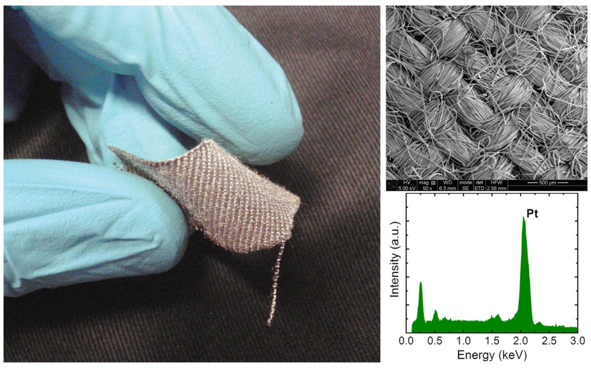

Figure 2 Photograph, scanning electron microscopy (SEM) image, and energy dispersive X-ray spectroscopy (EDX) scan illustrating that the newly developed plasma-assisted ALD processes enable the deposition on temperature sensitive surfaces (woven cotton fabric in this case).

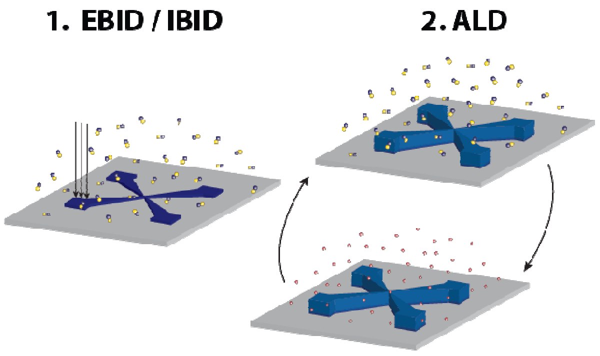

Figure 3 Schematic representation of the direct-write ALD technique comprising the deposition of a thin seed layer by electron beam induced deposition (EBID), or alternatively by ion beam induced deposition (IBID), and area-selective ALD. The ALD step consists in turn of the alternating exposure of the seed layer to two different gases. This technique yields high-quality Pt material (~100% pure, 12 μΩcm), while it allows for patterning of nanoscale line deposits of only ~10 nm in width.