ALD and AS-ALD of Metallic Films with New Precursors and Approaches

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Metal ALD is a topic where high industrial importance and inspiring and challenging scientific questions meet. As always, the success of ALD builds on chemistry. There is constant need for new precursors to enable ALD of metals of interest with improved characteristics. Major challenge arises from the strong tendency of metals to agglomerate, hence making it difficult to achieve continuous films at the smallest thicknesses. Lowering of the deposition temperature is of utmost importance to tackle this issue. This requires highly volatile and reactive metal precursors and reducing agents. Overall, the lack of an efficient universal reducing agent is a major challenge for metal ALD. In this presentation examples will be shown from our recent work on both metal precursors and reducing agents, including also reaction mechanism studies on selected processes.

Sustainability is one more parameter to be taken into account when developing new ALD precursors. This is however challenging considering all the other requirements and limitations there are for the ALD precursors. Metal chlorides are controversary precursors that are often avoided because they and the resulting byproducts can be corrosive, yet metal chlorides are thermally stable, reactive, inexpensive and probably the greenest precursor compounds because of the small number of synthesis steps involved. Many metal chlorides are nonvolatile but here it will be shown that these can be converted volatile by adding proper neutral adduct ligands. One of the metal chloride adducts, $PdCl_2(PEt_3)_2$, was found to be fully recyclable: unused molecules can be condensed and collected from the exhaust tube of the reactor by dissolving into acetone, purified by recrystallization, and reused for ALD of Pd and Pd_2Ge [1].

Area-selective ALD (AS-ALD) of metals, and also other materials, is an important topic for self-aligned thin-film patterning. Ideally, the selectivity should be inherent with no need for passivation or activation of the surfaces. Here noble metal processes using metal β-diketonates and O_2 will be shown to have excellent inherent selectivity (Fig. 1) [2].

As an entirely new approach to self-aligned thin-film patterning area-selective etching of polymers will be presented (Fig. 1) [3, 4]. In these etching processes the selectivity arises from the materials underneath the polymer layer. Both O_2 and H_2 can be used as an etchant gas. The etching gas molecules diffuse through the polymer film, and upon reaching a catalytic surface underneath, they dissociate into the respective atoms which then react with the polymer etching it away. On noncatalytic surfaces the polymer film remains. When combined with AS-ALD, self-aligned etching of polymers opens new avenues for the fabrication of semiconductor devices. Fig. 2 shows an example where area-selective etching of polyimide from Pt is followed by area-selective ALD of iridium using the patterned polymer as a growth-inhibiting layer on SiO_2, eventually resulting in dual side-by-side self-aligned formation of metal-on-metal and insulator(polymer)-on-insulator.

References

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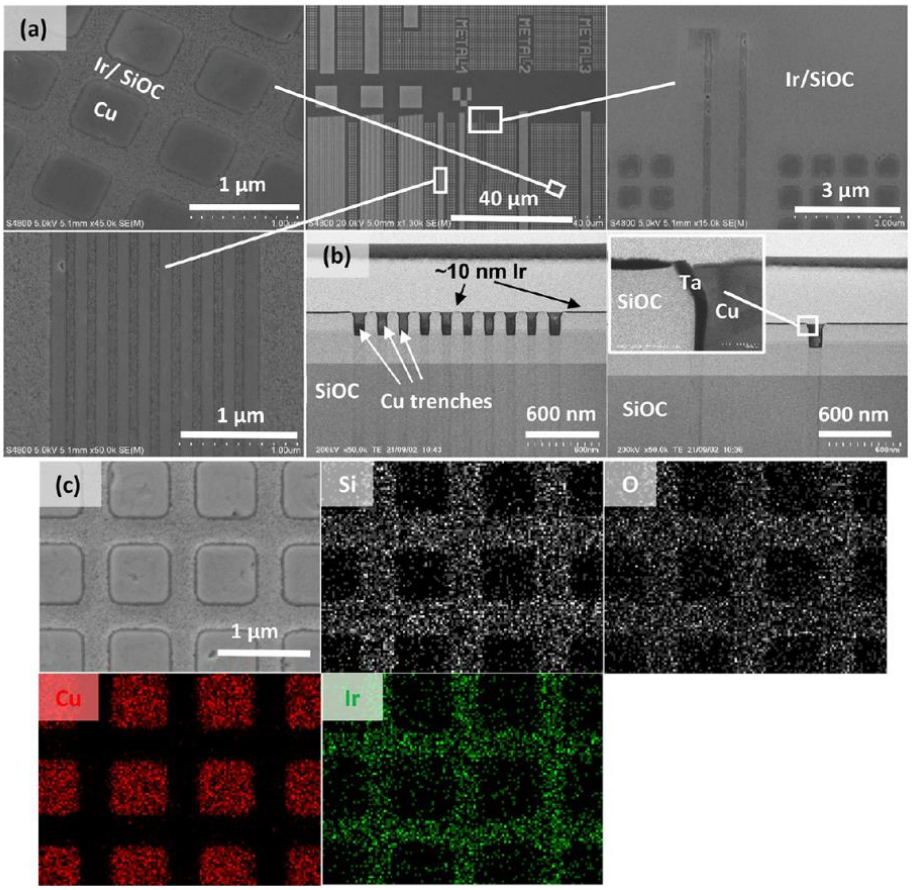

Figure 1. (a) SEM and (b) TEM images showing the selective growth of Ir on UV irradiated test chip at 225 °C for 1000 cycles. (c) EDS maps show the distributions of Si, O, Cu, and Ir elements [2].

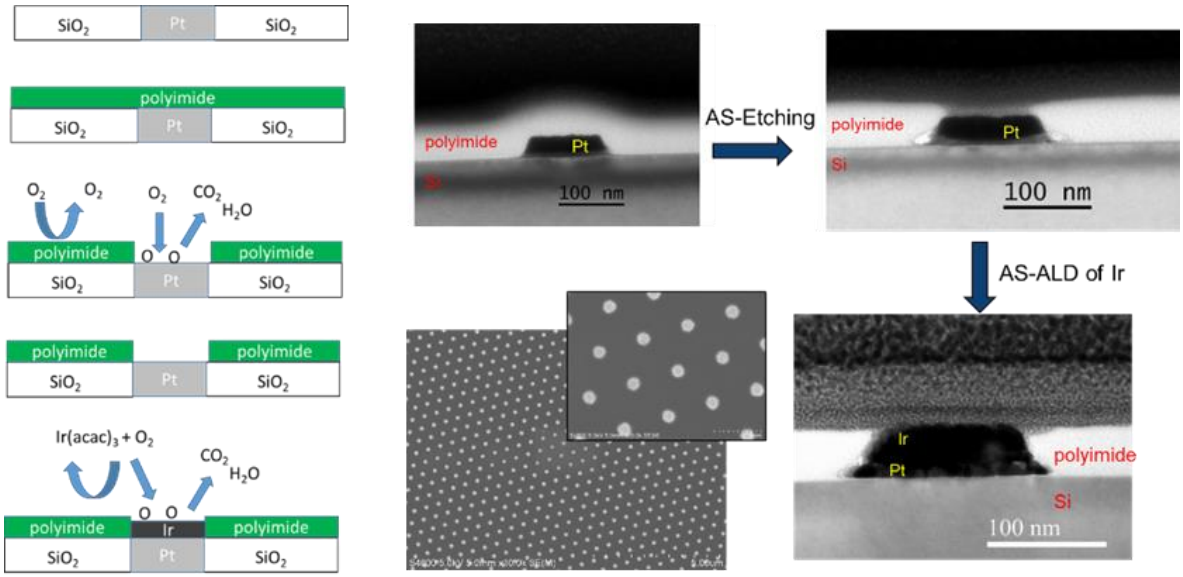

Figure 2. Principle of area-selective etching followed by AS-ALD (left), and cross-sectional SEM images before and after area-selective etching of polyimide from Pt and after AS-ALD of Ir (right).