Room Temperature Sensing of O_2 and CO by ALD Prepared ZnO Films Coated with Pt Nanoparticles

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Because metal oxide (MOx) gas sensors generally operate at temperatures ranging from ~100-400°C for sensitivity reasons, heating of the gas sensitive layer consumes a relatively large portion of overall power. To reduce heating-power for ultralow power-consumption sensors (operating preferably at ~100 µW), room temperature (RT) gas detection is required. This in turn requires a significant increase in sensitivity at RT. One way to increase the sensitivity is to make use of thin-film MOx layers, thereby increasing the surface to volume ratio of the MOx. It has also been demonstrated that the addition of catalytic Pt nanoparticles (NPs) onto a sensing MOx layer can provide the performance increase required for RT sensing.(1) The improved sensitivity can be linked to the ability of Pt to catalytically dissociate certain gas molecules. Here, the size distribution and the surface loading of the Pt NPs are key parameters.(2) In our contribution, we demonstrate that ALD can be used to both create thin-film Al-doped ZnO sensing structures, and to deposit Pt NPs on these structures, achieving RT sensing of O_2 and CO.

ZnO ALD films of 50 nm thickness, deposited at 180°C using diethyl-zinc ($ZnEt_2$) and H_2O vapor, were doped with Al by alternating every 20 ZnO-ALD cycles with one ALD cycle of trimethyl aluminum ($AlMe_3$) and H_2O vapor. The conductance of the obtained Al-doped ZnO is favorable for gas sensing applications.

ALD of Pt using $(MeCp)PtMe_3$ and O_2 plasma is characterized by the formation of NP islands during the nucleation regime. Figure 1 shows transmission electron microscopy (TEM) images of a ZnO substrate, exposed to 0, 30, 60, and 75 cycles of plasma-assisted Pt ALD respectively. For 0 cycles (i.e. the bare ZnO substrate) the ZnO grains can be seen. After 30 cycles, small Pt nanoparticles appear as bright spots, most of which have an area of approximately ~1 nm^2. For 60 and 75 cycles the NPs have grown and coalesced to form increasingly fewer though larger islands. This demonstrates that ALD can be used to deposit Pt NPs on ZnO with control over their size distribution and surface loading through the number of cycles.

A gas sensing structure was prepared based on an ALD-grown Al-doped ZnO sensing layer with ALD-Pt NPs grown on top. The results for the detection of O_2 at RT are plotted in Figure 2, which shows the change in current through the ZnO layer upon exposure to different concentrations of O_2 in N_2 for, (a) the Pt coated structure, and (b) a reference structure without Pt NP. The Pt-coated structure shows a reversible, proportional conductivity change of up to 40% at RT for O_2, while the reference structure without Pt NPs shows no response. Clearly, the addition of Pt NPs enhances the performance for O_2 detection at RT. For the detection of CO at RT, a conductivity change with similar sensitivity was observed only in the presence of O_2 and H_2O vapor.

The mechanism governing the enhanced performance at room temperature will be discussed based on the obtained results. We anticipate that in the future, the extremely high conformality of ALD could enable the deposition of NPs on ZnO-based sensing structures on 3-D substrates, which will lead to even better performance due to the increased surface to volume ratio.

This work is supported by NanoNextNL, a micro and nanotechnology programme of the Dutch ministry of economic affairs, agriculture and innovation (EL&I) and 130 partners.

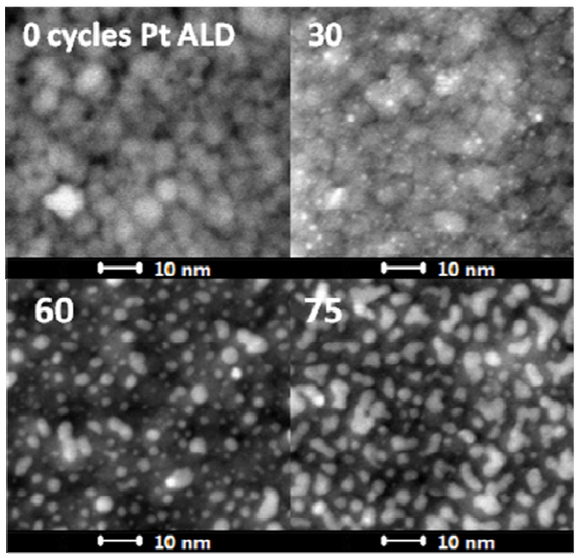

Fig. 1 Plan-view Z-contrast STEM images of ZnO films with Pt NPs deposited by 0, 30, 60, and 75 cycles of plasma-assisted ALD of Pt.

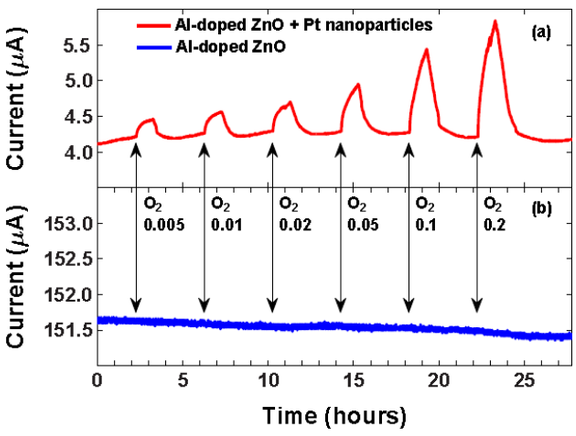

Fig. 2 Electrical response for O_2 in N_2 at RT for (a) Al-doped ZnO with Pt NPs, and (b) Al-doped ZnO without Pt NPs. Arrows indicate when the O_2 gas flow was turned on, with the O_2/N_2 fractions used.

References:

1. **D. Haridas, K. Sreenivas, and V. Gupta, *Sensors and Actuators B-Chemical* 133, 270 (2008).**
2. **D. Haridas, A. Chowdhuri, K. Sreenivas, and V. Gupta, *Sensors and Actuators B-Chemical* 153, 89 (2011).**