Atomic Layer Deposition of Nanoalloys of Noble and Non-noble metals

Ranjith K. Ramachandran,^a Jolien Dendooven,^a Matthias Filez,^{b#} Vladimir Galvita,^b Hilde Poelman,^b Eduardo Solano,^{a##} Matthias M. Minjauw,^a
Guy B. Marin^b and Christophe Detavernier^a

^aDepartment of Solid State Sciences, COCOON, Ghent University, Krijgslaan 281/S1, B-9000 Ghent, Belgium

^bLaboratory for Chemical Technology, Ghent University, Technologiepark 914, B-9052 Zwijnaarde, Belgium

[#] Current address: Inorganic Chemistry and Catalysis group, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

^{##} Current address: ALBA Synchrotron, BL11-NCD, Carrer de la Llum 2-26, 08290 Cerdanyola del Vallès, Barcelona, Spain

We present a novel ALD-based approach for the synthesis of bimetallic materials consisting of a noble metal along with a non-noble metal such as Pt-M (M = In, Ga, Sn, etc.), with a precise control on the composition and size. First, a bilayer consisting of a metal oxide and a Pt film of the desired thickness is deposited on to the substrate. The film is then subjected to a temperature programmed reduction (TPR) under H₂ atmosphere. *In situ* X-ray diffraction (XRD) measurements during TPR revealed the formation of Pt-M bimetallic alloys with a phase determined by the Pt/(Pt + M) atomic ratio of the as-deposited bilayer. Scanning electron microscopic (SEM) analysis revealed the formation nanoparticles after annealing, with the particle size controlled by the initial total thickness of the bilayer.

Introduction

In recent years, there has been an increasing interest in the use of atomic layer deposition (ALD) for the direct synthesis of bimetallic nanoparticles (BMNPs)(1–8). Using sequential self-limiting chemical reactions between gaseous precursor molecules and a solid surface, both core/shell(4,7,8) and alloyed(1–3,5–7) nanoparticles have been fabricated with (sub-)monolayer precision. In these previous studies, typically two noble metal ALD processes were combined, either sequentially(4,8) or in a supercycle approach(1–3,5,6), and the nanoparticle morphology emerges as a result of the nucleation controlled growth of noble metals on oxide surfaces(9). To date, the deposition of Pd-Pt,(4,7,8) Ru-Pt(1,2,6) and Ir-Pt(3) nanoparticles have been demonstrated.

Bimetallic materials consisting of a noble metal along with a non-noble metal, such as Pt-In, Pt-Ga and Pt-Sn, are actively explored in catalysis and gas sensing(10–14) and are usually synthesized by wet chemical methods.(10–15) The direct deposition of such bimetallic materials by ALD is challenging because of the lack of ALD chemistries for

the deposition of the non-noble metals in their elemental state. Here, we report a general ALD-based two-step method for the controlled synthesis of Pt based bimetallic alloys containing non-noble metals such In, Sn, Ga etc.

Figure 1 depicts the basic principle of our approach for synthesizing different Pt-M bimetallic alloys(16,17). Initially, a metal oxide (MO_x) layer with a defined thickness is deposited on the plasma cleaned SiO_2 substrate, which is then followed by the deposition of a controlled amount of Pt. The as-deposited Pt/ MO_x bilayer is then subjected to a TPR up to 700 °C in 10% H_2/N_2 environment at a heating rate of 0.2 °C/s, which results in the formation of alloyed Pt-M particles. It is also demonstrated that the phase and size of the Pt-M alloys can be controlled by changing the MO_x thickness, the Pt thickness and/or the total deposited thickness.

Figure 1. Schematic representation of the ALD based Pt-M BMNPs synthesis.

Experimental

All the depositions were performed in a home-built experimental cold-wall ALD chamber(18,19) connected through a gate valve to a turbo pump backed up by a rotary pump. A second gate valve was installed for pre-evacuation of the chamber *via* a bypass line to the rotary pump. Pieces of silicon wafer covered with 100 nm thermally grown SiO_2 were used as substrates, which were loaded into the vacuum chamber through a load-lock and were heated to 150 °C using a resistive heating plate. Prior to the deposition, the substrates were cleaned *in situ* using an O_2 plasma exposure. Pt and MO_x were deposited using the ALD processes reported elsewhere(20–24). For catalytic experiments, the mesoporous SiO_2 powder, which was used as the support material, was loaded in a molybdenum sample cup and transferred into the ALD reactor through the load-lock and was placed on the heating plate. To ensure the saturation, extended exposure times were used for both precursor and reactants.

The thicknesses of the Pt and MO_x films grown on the SiO_2 substrate were determined by X-ray reflectivity (XRR) measurements using a Bruker D8 Discover system with $\text{Cu K}\alpha$ radiation. Alternatively, the deposited thicknesses were extracted from calibrated X-ray fluorescence (XRF) measurements. From the thickness, the specific weight of the Pt and M was calculated by assuming the densities of the films equal to that of bulk Pt and MO_x , respectively(16,17). The XRF intensity counts and specific weight of materials were plotted against the thickness of the films (Figure 2), yielding a relationship that was used for determining the composition of the bilayer materials.

Figure 2. Variation of Pt (a), In (b), Ga (c) and Sn (d) XRF intensity (left y-axis) and weight (right axis) against the Pt, In_2O_3 , Ga_2O_3 and SnO_2 film thickness, respectively.

The TPR treatment of the deposited bilayers in 10% H_2/N_2 was performed in a home-built heating chamber mounted on a Bruker D8 diffractometer(25,26) to enable *in situ* XRD characterization. A linear detector was used to collect the diffracted X-rays at 2 s time intervals.

Morphology of the bimetallic alloys formed after the annealing process was examined by scanning electron microscopy (SEM) measurements performed on a FEI Quanta 200F and a FEI Sirion instrument. Bright field (BF) scanning transmission electron microscopy (STEM BF) were performed using a JEOL JEM-2200FS, Cs-corrected microscope operated at 200 kV, which was equipped with a Schottky-type field-emission gun (FEG) and EDX JEOL JED-2300D. All samples were deposited by immersion onto a lacey carbon film on a copper support grid.

Results and discussion

Phase tuning

Pt-In system. Pt-In system was taken as a case study to demonstrate the phase tuning, which is achieved by controlling the ratio of the thickness of Pt to the thickness of In_2O_3 respectively(16). Three different samples were prepared with a constant Pt thickness of 6 nm, while the In_2O_3 thickness was varied. With In_2O_3 thicknesses of 5.5 nm, 10.6 nm and

22 nm the as-deposited bilayers had a Pt/(Pt+In) atomic ratio of 72% (sample A), 58% (sample B) and 38% (sample C), respectively. Figure 3 (a), middle shows the time-resolved *in situ* XRD patterns recorded during H₂/N₂ TPR on sample A. Initially the pattern shows two diffraction peaks. A first peak at a 2 θ angle of 30.6° corresponds to In₂O₃ (222). The second peak at 40° originates from metallic Pt. Recently, we reported that the crystallinity of In₂O₃ ALD films grown at lower temperatures (100-150 °C) can be increased by a temperature treatment(21), which explain why the In₂O₃ (222) peak intensity is moderate initially and is intensified around 300 °C. As the temperature increases further, a complete reduction of In₂O₃ to metallic In takes place at around 350 °C, which is indicated by the disappearance of the XRD peak at 30.6°. Metallic In is liquid,(27) explaining the absence of diffraction peaks. At the same temperature of 350 °C, a gradual shift of the Pt (111) peak towards a lower 2 θ angle occurs. This is indicative of a progressive insertion of In in the Pt fcc structure. In incorporation causes the fcc lattice to expand which results in a concomitant decrease of the Pt (111) 2 θ angle. The insertion of In into the Pt lattice facilitates the alloying between these two metals, and the stabilization of the diffraction peak at 39° indicates the formation of an InPt₃ fcc structure. The InPt₃ phase is also confirmed in the 20° to 60° 2 θ scan that was measured after the TPR experiment [Figure 3 (a), right].

Figure 3. (Left) *In situ* XRD patterns during H₂/N₂ TPR of Pt/In₂O₃ bilayer samples with a Pt/In atomic ratio of (a) 72% (sample A), (b) 58% (sample B), and (c) 38% (sample C). Note the different 2 θ range in (c). (Right) 20-60° 2 θ scans measured after the annealing experiment.

The *in situ* XRD patterns recorded during H₂/N₂ TPR on samples B and C [Figure 3 (b) and (c)] behave initially more or less similar to that of sample A. Due to the higher In₂O₃ film thicknesses, the peak corresponding to In₂O₃ (222) is more intense and an additional peak at 35.5°, corresponding to In₂O₃ (400), is visible in the case of sample C. Even below In₂O₃ reduction temperatures, In is gradually incorporated into the Pt lattice, which is indicated by the shift of Pt peak to a lower angle before the disappearance of the In₂O₃ peak. Once the whole In₂O₃ layer is reduced to metallic In, the high availability of metallic In is likely to further enrich and saturate the pre-existing Pt phase. This results in a phase transformation from InPt₃ alloys into more In-rich In₉Pt₁₃ and In₂Pt intermetallic compounds, respectively.

In summary, by varying the In₂O₃ layer thickness and thus changing the Pt/In atomic ratio, the phase of the In_aPt_b alloy that is formed upon TPR in H₂/N₂ can be controlled. Moreover, comparison of our results with the In-Pt phase diagram confirms that the obtained phases are in agreement with the predicted phases for the considered Pt/(Pt+In) atomic ratios(27,28). These experiments show that, in spite of the complex nature of the In-Pt phase diagram, our approach enables a high level of composition and phase control.

Pt-Ga and Pt-Sn systems. To illustrate the generality of the presented method, phase tuning of two more systems(16,17), Pt-Ga and Pt-Sn, was demonstrated. Series of Pt/Ga₂O₃ and Pt/SnO₂ bilayer samples with different Pt/(Pt + Ga) and Pt/(Pt + Sn) atomic ratios were prepared by using the respective ALD processes(20,22,23). These bilayers were then subjected to a temperature programmed reduction (TPR) to 700 °C in 10% H₂/N₂ at a heating rate of 0.2 °C/s. Figure 4 (a) and (b) show the *ex situ* XRD measurements after TPR and cool down of the Pt/Ga₂O₃ and Pt/SnO₂, respectively, which reveals the formation of different Pt-Ga and Pt-Sn alloys depending on the composition of the bilayers. For detailed information on this experiment, the reader is referred to the recent articles by R. K. Ramachandran *et al.*(16,17). These experiments show that, similar to Pt-In, the ALD of Pt/Ga₂O₃ and Pt/SnO₂ bilayers followed by thermal reduction in hydrogen enables a high level of Pt-Ga and Pt-Sn phase control.

Figure 4. *Ex situ* XRD patterns measured after the TPR to 700 °C in 10% H₂/N₂ of a) Pt/Ga₂O₃ and b) Pt/SnO₂ bilayer samples with different Pt/(Pt+M) atomic ratios, where M = Ga and Sn, respectively.

Size tuning

In addition to phase control, the presented method enables tuning of the BMNP's size. Here, we demonstrate the precise control over the particle size of Pt-In BMNPs while keeping the composition of the alloy constant, which is achieved by controlling the total deposited thickness of the Pt/In₂O₃ bilayer. To demonstrate this, films with a fixed Pt/In atomic ratio of 38% but with a different total thickness were deposited: (a) 27.8 nm (5.8 nm Pt + 22.0 nm In₂O₃), (b) 10.4 nm (2.1 nm Pt + 8.3 nm In₂O₃), (c) 2.46 nm (0.61 nm Pt + 1.85 nm In₂O₃) and (d) 1.33 nm (0.33 nm Pt + 1.0 nm In₂O₃). SEM characterization of the as-deposited samples showed relatively smooth surfaces. TPR of the samples a, b and c in H₂/N₂ to 700 °C resulted in the formation of the expected In₂Pt phase, as confirmed by XRD (Figure 5). The sample d was too thin to be detected by XRD. The SEM images in Figure 6 confirm the formation of particles upon reduction in H₂/N₂. With decreasing total thickness of the deposited bilayer, the size of the particles decreased from micrometer range to *ca.* 4 nm particles. More detailed SEM analysis confirmed a particle size distribution of 2-7 nm for the sample d (total thickness = 1.33 nm), which is promising towards applications such as catalysis.

Figure 5. XRD patterns of annealed bilayered films with a Pt/(Pt+In) atomic ratio of ca. 38% and total thicknesses of (a) 27.8 nm (dashed) and 10.4 (solid) nm and (b) 2.46 nm (dashed) and 1.33 nm (solid).

Figure 6. SEM images and particle size distribution curves of annealed bilayered films with a Pt/In atomic ratio of ca. 38% and total thicknesses of (a) 27.8 nm, (b) 10.4 nm, (c) 2.46 nm and (d) 1.33 nm.

Catalysis

Finally, in view of catalytic applications, the activity of a reduced Pt–In loaded porous silica with Pt/(Pt+In) atomic ratio of 75% is tested in the industrially important dehydrogenation of propane and compared to the activity of an ALD-prepared monometallic reference sample containing the same amount of Pt, as determined by inductively coupled plasma mass spectrometry (ICP–MS).

Catalytic activity measurements were performed at atmospheric pressure in a quartz micro reactor with an internal diameter of 10 mm, which was placed inside an electric furnace. Typically, 120 mg of catalyst was packed between quartz wool plugs. The temperature of the catalyst bed was measured with K-type thermocouples touching the outside and inside of the reactor at the position of the catalyst bed. The inlet gas flow rates were maintained by means of calibrated Brooks mass flow controllers. The feed and product gas streams were monitored online using a calibrated OmniStar Pfeiffer mass spectrometer (MS). MS signals were recorded for all major fragments of C_3H_8 , C_3H_6 , C_2H_6 , C_2H_4 , and CH_4 species. Carbon balance with a maximum deviation of 15% was obtained.

The as-deposited samples were reduced in 1 ml/s flow of 5 % H_2/Ar at 650 °C for 0.5 h. The nanoparticle nature of the ALD-deposited material after TPR in hydrogen is evidenced by scanning transmission electron microscopy (STEM) in figure 7.

Then, an activity measurement was conducted for 10 min at 600 °C. The site-time yield (Y , $\text{mols}^{-1} \cdot \text{mol}_{Pt,s}^{-1}$) was calculated from the difference in the inlet and outlet molar flow rates, as measured relative to an internal standard (Ar) using an online quadrupole mass spectrometer, i.e.,

$$Y_i = (F_{0,i} - F_i) / N_{Pt,s} \quad [1]$$

where $F_{0,i}$ and F_i , in $\text{mol} \cdot \text{s}^{-1}$, are the inlet and outlet molar flow rates of component i , and $N_{Pt,s}$, in $\text{mol}_{Pt,s}$, is the amount of exposed (surface) Pt atoms in the sample. The latter was determined by H_2 chemisorption using an AutoChem II 2920 (Micromeritics Instrument Corporation).

Figure 7. STEM bright field micrographs showing the overall morphology of the reduced catalysts, Pt/SiO₂ (left) Pt-In/SiO₂ (right).

Figure 8 show the space time yield (Y) of propylene and hydrogen, which were the only detectable products, as a function of time-on-stream for both samples. The activity measurements clearly indicate that Pt-In bimetallic catalyst is more active, more selective and was less prone to coking than monometallic Pt catalyst.

Figure 8. Catalytic propane dehydrogenation at 600 °C ($W_{\text{cat}}/F_{\text{C}_3\text{H}_{8,0}} = 20 \text{ kg}_{\text{cat}} \cdot \text{s} \cdot \text{mol}^{-1}$ and $P_{\text{C}_3\text{H}_{8,0}} = 20 \text{ kPa}$ at a total pressure of 101.3 kPa) using Pt-In/SiO₂ (Solid symbol) and Pt/SiO₂ (Open symbol) catalysts.

Conclusion

ALD processes have been successfully employed for the synthesis of bimetallic materials consisting of a noble metal along with a non-noble metal, with a precise control on the composition and size. First, thin films of MO_x (M = In, Ga or Sn) and Pt were sequentially deposited using ALD, yielding a Pt/MO_x nanocomposite. These bilayer structures were then subjected to a H₂/N₂ temperature programmed reduction (TPR) treatment, which resulted in the formation of alloyed Pt-M particles. The XRD measurements revealed the formation of different bimetallic alloys, which depends on the initial composition of the deposited films. It is shown that the composition and the size of the bimetallic alloys formed after TPR could be precisely controlled by changing the initial composition and thickness of the bilayers. Finally, the catalytic application of the bimetallic nanoparticles was demonstrated by propane dehydrogenation reactions, which revealed a better conversion for the Pt/In bimetallic nanoparticles compared to the monometallic Pt.

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