Fabrication of Ni@Ti core–shell nanoparticles by modified gas aggregation source

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Abstract
Ni@Ti core–shell nanoparticles were prepared by a vacuum based method using the gas aggregation source (GAS) of nanoparticles. Ni nanoparticles fabricated in the GAS were afterwards coated by a Ti shell. The Ti shell was deposited by means of magnetron sputtering. The Ni nanoparticles were decelerated in the vicinity of the magnetron to the Ar drift velocity in the second deposition chamber. X-ray photoelectron spectroscopy and energy dispersive x-ray spectroscopy analysis of the nanoparticles showed the core–shell structure. It was shown that the thickness of the shell can be easily tuned by the process parameters with a maximum achieved thickness of the Ti shell ~2.5 nm. The core–shell structure was confirmed by the STEM analysis of the particles.

Keywords: core@shell nanoparticles, gas aggregation source, magnetron sputtering, nanoparticles flow, XPS, EDX, STEM

(Some figures may appear in colour only in the online journal)

1. Introduction
Nanoparticles (NPs) are receiving continuous attention because of various promising applications in catalysis [1] and the general use of their novel electronic, optical and magnetic properties [2–4]. Usually, these nanoparticles have been based on metals and have been prepared by wet chemical processes [1, 5]. In recent years, vacuum based techniques of preparation have also received increasing attention because of demand by certain technology sectors. Most of them are based on gas aggregation either by vacuum evaporation [6] or sputtering [7]. Gas aggregation sources (GAS) based on planar magnetron became very popular for the production of metallic [8, 9], metal oxide [10] and even polymeric nanoparticles [11]. However, certain applications require so called heterogeneous or core–shell nanoparticles [5, 11]. Sowwan et al [12, 13] put considerable effort in the investigation of core–shell nanoparticles using GAS. Their work has been summarized in a recent review [11]. Originally, Wang et al [14] were studying magnetic nanoparticles and suggested to use composite target Co/Au to prepare nanoparticles composed from the two metals, Co and Au. They pointed out that speed of cooling that is given by the pressure and flow of the working gas (Ar) of compound (mixed) nanoparticles determines if the result is Co–Au, Au–Co or an onion structure. It is rather tricky to get the right window of parameters (power, flow and pressure). Huettel et al [14–16] overcame the obstacle of the difficult cooling of mixed nanoparticles in flight relying on complex diffusion processes and overall thermodynamics by using two or even three magnetrons in different positions with respect to the Ar inlet behind the first magnetron. This enabled them to originate cores above the first magnetron target. These NPs cores are dragged to the next magnetron target where they are overcoated by a shell, and so on. Huetel et al prepared in this way, e.g. Ag–Au and Ag, Au, Pd, using three magnetrons in one aggregation chamber. Because the magnetrons are at the same Ar pressure, the result is not only core–shell but NPs of core metal and NPs of shell metal. There has been an attempt to solve this in [13] by coating core NPs with linear magnetron positioned downstream to the Ar. No complete shell over cores was obtained.
In this paper, we report on the preparation of nanoparticles with Ni core and Ti shell which are fabricated by a hybrid system that is something in between two (three) magnetrons in one aggregation chamber [14–16] and in-line coating of the shell [13].

2. Experimental setup

2.1. Deposition arrangement

The system used for the production of core–shell nanoparticles is schematically depicted in figure 1. It consisted of a primary gas aggregation cluster source (GAS) used for production of Ni NPs and an arrow-like secondary chamber for the coating of Ni NPs by thin film of Ti. The primary GAS that was used for Ni NPs fabrication was developed in our laboratory according to the Haberland concept [7]. It consisted of a water cooled aggregation chamber 100 mm in diameter and DC planar magnetron 81 mm in diameter with a 1.5 mm thick Ni target. The GAS was terminated by the cone. The cone was, in contrast with our previous studies [17–20], ended with a nozzle 4 mm in diameter and length 20 mm. Such a nozzle ensured a gas flow similar to our standard 2 mm orifice but it focused the beam of the Ni NPs leaving the GAS and entering into the secondary arrow-like chamber. The aggregation length of the GAS was set to 8 cm and Ar flow was 10 sccm for all the experiments described in this study. The corresponding working pressure inside the GAS was 48 Pa.

In the secondary chamber, another DC magnetron was installed equipped with 4 mm Ti target (Ti purity 99.2%) 81 mm in diameter. The secondary chamber was also terminated with the cone finished by a nozzle. The nozzle was, in this case, 25 mm long, with 7.5 mm diameter. The higher gas conductivity of this nozzle, as compared to the nozzle of the primary GAS, ensured that the pressure in the second chamber was about ¼ compared to the GAS. The whole system was connected to the main deposition chamber, which was pumped by turbomolecular and scroll pumps.

Both magnetrons were operated in a constant current regime. The first one with the Ni target was powered by a MDX 500 DC power supply, while the second one with the Ti target was powered by a Pinnacle 3000 DC power supply, both from Advanced Energy. Ar (99.996%, Linde Gas) was used as the working gas. The deposition rate of nanoparticles was monitored by means of quartz crystal microbalance (QCM) working at 5 MHz that was positioned in the main deposition chamber perpendicularly to the axis of the output nozzle of the secondary chamber.

2.2. Nanoparticles characterization

One side polished silicon wafers (OnSemi, ⟨100⟩, thickness 525 μm) were used as substrates for x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscopy (AFM—NTMD NTegra Prima). The XPS measurements were performed on a spectrometer equipped with Al Kα x-ray source (Specs, XR-50) and hemispherical electron analyzer (Specs, Phoibos 100). All spectra were acquired at 12 kV and 200 W. The survey spectra were measured with a 0.5 eV step and pass energy 40 eV, while the high resolution spectra were taken with 0.05 eV step and pass energy 10 eV. The data were processed using the CASA XPS software. SEM (Tescan Mira III) was used for the characterization of the NP’s size and for NP’s composition analysis via energy dispersive x-ray spectroscopy (EDX). Carbon coated copper grids (S 160, Agarscientific) were used for scanning transmission electron microscopy (STEM) analysis. The STEM observations were performed on Jeol 2200FS electron microscope equipped with Centurio Large Angle SDD-EDX detector.

3. Results and discussion

3.1. Ni nanoparticles

The first step of this study was the investigation of the deposition process of Ni NPs and their characterization. Primary GAS was solely used in these experiments and the Ni NPs were prepared at magnetron currents in a range from 200 mA to 800 mA with corresponding powers from 55 W to 250 W, respectively. It has been found that the deposition rate of Ni NPs measured by QCM increased linearly within this range
with the magnetron current, as shown in figure 2. The increase of the deposition rate with increasing current on the magnetron in the primary GAS was accompanied by a slight increase of the mean size of the Ni NPs, as can be seen in figure 3, which presents size histograms of the produced NPs.

### 3.2. Deposition of Ti

The second step of this study was the identification of the conditions that assure sufficient deposition rate of Ti shells onto Ni NPs passing through the secondary chamber. As will be shown, the key parameters are pressure in the secondary chamber that affects both the residence time of NPs in the secondary chamber and deposition rate, as well as magnetron current used for Ti deposition.

Gas aggregation sources are normally operated in such way that after the exit orifice, or nozzle in our case, the pressure is as low as possible. The NPs inside the GAS fly with the velocity equal to the drift velocity of the working gas. They are accelerated in the nozzle and the typical speed of metallic NPs leaving the nozzle is in the range of tens m·s⁻¹ depending on the size and mass of NPs and the flow of the gas. Because our magnetron with a Ti target has a diameter of 81 mm, the residence time of the NPs in the vicinity of the magnetron is at low pressure in the range of hundredths of a second. To coat the NPs by a 1 nm Ti shell, the deposition rate of the Ti has to be at least several tens of nm·s⁻¹. It is impossible to reach such a high deposition rate of Ti with our magnetron, so the NPs have to be slowed down at higher pressure by collisions with Ar atoms in order to increase their residence time in the vicinity of the Ti magnetron.

The numerical model describing the deceleration of the NPs in the arrow-like chamber was adapted from [21]. The particle movement was simulated starting from the area close to the nozzle inside the GAS, where the drag of the accelerating gas becomes relevant. The NPs are accelerated in the nozzle and their flux is focused. The velocity of the NPs reaches the maximum when leaving the nozzle and they start to decelerate to the drift velocity of the Ar. The model shows that the deceleration distance for 15 nm nanoparticles, i.e. the distance from the end of the nozzle during which the nanoparticles are slowed down to the Ar drift velocity, decreases from 170 mm at a pressure 5 Pa in the arrow-like chamber down to 50 mm at a pressure 20 Pa. Because the distance from the nozzle to the Ti deposition region is ~4 cm and the gas drift velocity is at a constant flow rate decreasing with the increasing pressure, the highest possible pressure is preferred from this point of view (figure 4).

However, the increase of the pressure leads not only to slowing down the NPs, but also to a decrease of the deposition rate. It was revealed by measurements performed on films deposited onto Si substrates placed in the intersection of the magnetron axis and Ni NPs beam axis, 10 cm from the Ti magnetron and 16 cm from the nozzle (figure 5).

In order to account for both the deposition rate and speed of NPs, a parameter Δ (nm cm⁻¹) defined as the ratio of the Ti deposition rate and the Ar drift velocity can be used to describe the thickness of the shell deposited on the Ni nanoparticle...
during its flight through the arrow-like secondary chamber. The highest $\Delta$ at fixed Ar flow rate 10 sccm was found in the pressure range from 5 Pa to 12 Pa (figure 5) and the highest pressure of 12 Pa in the secondary chamber was chosen for further experiments.

In addition, due to the geometry of our system, the Ti deposition rate is not the same along the flight of the NPs through the arrow-like chamber. The deposition rate of Ti at the axis of the NPs beam as a function of a distance from the nozzle was estimated experimentally (figure 6). The pressure was set to 12 Pa and the Ti magnetron current was 1 A. The time integration of this function gives the hypothetical thickness of the Ti shell deposited on the Ni nanoparticles, and it is about 0.5 nm. This is the lowest estimation of the shell thickness. A more complicated motion of the charged NPs can be expected in the presence of the electromagnetic field of the magnetron, which will increase the residence time of the NPs in the deposition zone of Ti.

The next step was the measurement of the Ti deposition rate as a function of applied magnetron current. The deposition rate was measured at one point similar to the measurements of the pressure dependence and the pressure was fixed at 12 Pa (figure 7). As can be seen, the thickness of the Ti shell can be easily tuned by the applied DC magnetron current because the Ti deposition rate depends monotonously on it. However, it was found that for magnetron currents above 1.25 A, the deposition rate drops suddenly to zero and no particles reached the QCM. This effect is probably due to intensive heating of the NPs in the vicinity of the magnetron, which leads to their melting.

3.3. Core–shell nanoparticles

After the characterization of the Ti film deposition and Ni NPs production, Ni@Ti core–shell nanoparticles were fabricated. Based on the above-mentioned results, the Ar flow rate was set to 10 sccm with a corresponding 48 Pa pressure in the GAS and 12 Pa pressure in the arrow-like chamber. In the first set of experiments, the flux of Ni NPs was constant (DC magnetron current in the GAS 200 mA) and the deposition rate of Ti was varied by the magnetron current. The current was changed in the range from 0.5 A up to 1 A. The chemical composition of the NPs was investigated by XPS and EDX and Ti/Ni ratios measured for different currents applied on the Ti magnetron are shown in figure 8. This figure clearly shows that a higher magnetron current leads to a higher deposition rate of Ti and hence an increase in the Ti/Ni ratio.

It is important to note that in spite of similar trends observed by XPS and EDX, the Ti/Ni ratios measured by XPS are significantly higher as compared to the ones determined by means of EDX. This difference is due to the different sensing depths of these techniques. The XPS mainly gives information about the chemical structure of the shell, while most of the photoelectrons from the core are screened out. The sensing depth of the EDX is much larger than the size of the NPs, thus the EDX can be used for estimating the Ti/Ni ratio and for the
calculation of the shell thickness when the size of the particle is known. The calculation is as follows: the EDX gives the ratio of the atomic concentrations of Ti and Ni, $C_{\text{Ti}}/C_{\text{Ni}}$. This can be recalculated to the volume ratio $X_V$ using the equation:

$$X_V = \frac{V_S}{V_C} = \frac{C_{\text{Ti}} \cdot (M_{\text{Ti}}/\rho_{\text{Ti}})}{C_{\text{Ni}} \cdot (M_{\text{Ni}}/\rho_{\text{Ni}})}.$$  

(1)

Here, $V_S$ is the volume of the Ti shell and $V_C$ is the volume of the Ni core. $M_{\text{Ti}}$ and $M_{\text{Ni}}$ are then molar weights of the Ti and Ni (47.87 g mol$^{-1}$ and 58.69 g mol$^{-1}$ respectively) and $\rho_{\text{Ti}}$ and $\rho_{\text{Ni}}$ (4.51 g cm$^{-3}$ and 8.91 g cm$^{-3}$ respectively) are their densities. The volume of the spherical nanoparticle $V$ is calculated using the equation:

$$V = \frac{4}{3} \pi \cdot (R_C + T)^3.$$  

(2)

Here, $R_C$ is the Ni core diameter and $T$ is the unknown thickness of the Ti shell. The volume of the nanoparticle $V$ is of course also the sum of the $V_C$ and $V_S$, which can be expressed using the $X_V$ from equation (1):

$$V = V_S + V_C = V_C \cdot (1 + X_V).$$  

(3)

A combination of equations (2) and (3) gives the final cubic equation:

$$\frac{T^3}{R_C^3} + 3 \frac{T^2}{R_C^2} + 3 \frac{T}{R_C} - X_V = 0$$  

(4)

from which the thickness of the shell may be calculated for a known size of core diameter and volume ratio of Ti and Ni. Figure 9 gives the thickness of the Ti shell calculated by equation (4) as a function of the Ti/Ni atomic ratio. Three different particle diameters were taken into account, 13.6 nm, which is the mean size of Ni NPs deposited at 200 mA, and the mean size ± standard deviation of the size distribution of the NPs. Taking into account the maximum of measured Ti/Ni ratio 0.92, which corresponds to the current on Ti magnetron 1 A (figure 8), these calculations then give the theoretical Ti shell thickness of 2.4 nm for Ni core with diameter $d = 13.6$ nm (3.5 nm for $d = 19.9$ nm and 1.3 nm for $d = 7.3$ nm).

The Ti magnetron current was fixed at 1 A in the next experiments and the flux of Ni NPs was varied by the Ni magnetron current. Figure 10 shows the Ti/Ni ratio obtained by XPS and EDX as a function of the Ni magnetron current. A relative decrease of titanium with the increasing Ni magnetron current corresponds with the fact that higher current leads to the linear increase of the deposition rate of the Ni NPs (see figure 2). The deposition rate was measured by QCM, so the data are proportional to the mass of deposited NPs and the ratio between deposition rates at 200 mA and 800 mA is 6.1. Taking into account the size of Ni NPs, this ratio can be recalculated in the sense of amount of the NPs and surface of the NPs leaving the primary GAS per time; those ratios are 3.6 and 5.1 respectively. It means that at 800 mA, the surface of Ni NPs passing the Ti magnetron per unit of time is five times
larger than in case of Ni magnetron current of 200 mA. Such a high increase means that there is not enough sputtered titanium for shell deposition and the thickness of the Ti shell thus decreases with increasing Ni magnetron current. So, it may be concluded that there are three important parameters affecting the thickness of the NPs shell. The first two, the Ti deposition rate and residence time of the nanoparticle in the vicinity of Ti magnetron, are quite obvious, but also the third one, the amount of the NPs which has to be coated, has to be taken into account as well. Up to now, all of the above mentioned results give only indirect evidence that the NPs have a core–shell structure. The last step was thus the STEM analysis of the core@shell nanoparticles. The analysed particles were prepared at Ni magnetron current 200 mA and Ti current 1 A. Both STEM bright field (BF) and high angle annular dark field (HAADF) images confirmed the core–shell structure of the NPs (figure 11). The thickness of the Ti shell is about 2.6 nm, which is in very good agreement with the 2.4 nm calculated from the chemical analysis of the NPs. The core shell structure with the Ni core and Ti shell was confirmed also by the STEM EDX analysis, which is presented in figure 12. The EDX analysis also definitely excluded the possibility that the shell presented in figure 11 is not the Ti shell but just carbon contamination, which arises as an artefact of the STEM measurement. The experimentally obtained thickness of the Ti shell is much larger compared to 0.5 nm calculated from the known deposition rate profile of Ti and velocity of the NPs. As mentioned earlier, the possible explanation is that the NPs are recharged in a Ti magnetron discharge [22]. Their motion becomes more complicated and, as a result, the trajectory of the nanoparticle and hence the residence time in the vicinity of the Ti magnetron is much longer compared to the simple linear motion along the axis of the arrow-like chamber.

4. Conclusions
The possibility of fabrication of core–shell NPs by modified GAS was demonstrated. The Ti shell was successfully deposited on the Ni NPs produced in GAS by magnetron sputtering of Ti during the flight of the NPs through the second deposition chamber. The comparison of the Ti/Ni ratio measured by XPS and EDX showed the core–shell structure of the NPs. The thickness of the shell can be calculated from those two ratios and can be effectively driven by the Ti magnetron current. However, the maximum obtained shell thickness was ~2.5 nm. The core–shell structure was confirmed by STEM analysis of the NPs and the measured thickness of the Ti shell was in very good agreement with the one obtained from XPS/EDX measurements.

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References


