

A rapid method for growth of metal nanoparticles on nanowire substrates

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Abstract

The production of nickel and platinum nanoparticles on silica nanowire substrates using plasma-enhanced chemical vapor deposition has been investigated. Determination of particle size and particle size distribution was done using transmission electron microscopy (TEM). Ni nanoparticle diameters were found to be between 2 and 6 nm, with particle size increasing as the substrate temperature increased from 573 to 873 K. The size of Ni nanoparticles was found to be dependent on the chamber pressure during growth. The results indicate a competition between pressure-related diffusion within the vapor and dissociation of the precursor. Pt nanoparticle diameters were consistently found to be 2.5–3.0 nm at all deposition conditions. Insufficient thermal energy within the studied range results in a minimal contribution from surface diffusion, the primary mechanism for nanoparticle growth.

Introduction

The physical properties of metal nanoparticles (NPs) have been widely studied because of their potential for use in applications ranging from chemical sensors to lubricating oils. One of the most important areas for metal NPs is in catalysis because of their increased surface area compared to traditional thin film materials, which results in more reaction sites. Two metals that have been studied for this particular application are Ni and Pt (Che et al., 1999; Boudjahem et al., 2002; Bell, 2003; Wu & Chen, 2003; He et al., 2004; Matsumoto et al., 2004; Tang et al., 2004; Liu et al., 2005). Pt NPs have potential use in the oxidation of hydrocarbons, carbon monoxide (Bell, 2003), and methanol (He et al., 2004). Ni NPs are typically utilized in benzene hydrogenation (Boudjahem

et al., 2002), ketone and aldehyde reduction (Mitchell, 2005), and the decomposition of hydrazine (Wu & Chen, 2003). Controlling the particle size is necessary for many catalysts to enable large surface areas and to produce an optimal size for catalyzing a particular reaction.

Another aspect in the use of NPs for catalysis is the substrate material used to support the metal. One common support used for catalytic materials is carbon black, which offers a large surface area (Matsumoto et al., 2004). However, a problem with carbon black is that the NPs can become trapped in deep cracks in the substrate, effectively making them inactive. Alternative support materials such as carbon nanotubes (CNTs) and various ceramic nanowires (NWs) offer smooth surfaces and provide an optimal substrate for metal NPs.

Several routes have been investigated to obtain metal NPs including sonication (Rojas et al., 2000), supercritical fluid deposition (Ye et al., 2004, 2003), chemical reduction (Ayyappan et al., 1996; Satishkumar et al., 1996; Che et al., 1999; Saravanan et al., 2001; Boudjahem et al., 2002; Chen & Hsieh, 2002; Wu & Chen, 2003; Duan & Li, 2004; Fukuoka et al., 2004; Matsumoto et al., 2004; Panigrahi et al., 2004; Liu et al., 2005), microemulsion-centrifugation (Qiu et al., 2001), adsorption-precipitation (Planeix et al., 1994), electrochemical deposition (Xu et al., 2003), sol-gel processes (Fonseca et al., 2002), physical vapor deposition (PVD) (Zhang et al., 2000, 2001; Pradhan, 2003; Ikuno et al., 2004), arc discharge (Jiao et al., 1996; Suzuki et al., 2004), and electroless plating (Li et al., 1997). One of the most prevalent drawbacks of these techniques is the processing time. For example, the chemical reduction technique used by Fukuoka et al. (2004) requires the substrate material to be left in the reaction solution for 24 h. The chemical reduction process used by Boudjahem et al. (2002) requires 16 h to prepare the NPs. Even the PVD process reported by Zhang et al. (2000) still required a procedure time of almost 1 h. In order for the production of metal NPs to be economical a rapid growth technique must be used that can produce NPs with small sizes and a narrow particle size distribution on a range of substrate materials. In this communication we report a plasma-enhanced chemical vapor deposition (PECVD) process that is capable of producing metal NPs in approximately 10 min.

Experimental

The SiO₂ NW substrates used for this study were produced by a flow furnace technique, similar to that used by Zhang et al. (2003). They were grown on a single crystal Si substrate and have diameters ranging in size from 30 to 180 nm. The NPs were produced in a custom-designed parallel plate PECVD chamber operated at 13.56 MHz. The chamber volume is approximately 1 m³. The parallel plates are 3" in diameter and 1.5" apart. A nozzle protrudes from the center of the anode where the precursor/carrier gas mixture is introduced and the sample holder/heater serves as the

ground plate. Argon gas was used as both the carrier and the background gas.

The source compound utilized for Ni deposition was bis(cyclopentadienyl)nickel [Ni-(C₅H₅)₂]. For Pt deposition dimethyl(1,5-cyclooctadiene)platinum (II) [(CH₃)₂Pt(C₈H₁₂)] was used as the source. Both materials are powders that are easily sublimated. The precursor was delivered to the chamber by heating to 343 K in an Ar stream flowing at 10 sccm. The process time was 12 min for all samples reported in this study. Due to the fact that the precursor is a powder it is difficult to quantify the amount of material entering the chamber. This is a typical issue with solid precursors since the sublimation rate is either unknown or too difficult to measure. The parameters that are more easily controlled and therefore allow for repeatability are the quantity of the precursor used, the temperature of the precursor, and the flow of argon. The total pressure of the chamber was varied at predetermined settings of 17, 42, and 67 Pa. The substrate temperatures were also varied at fixed values of 573, 723, and 873 K.

The samples were examined using a Philips CM200 transmission electron microscope (TEM) and a JEOL 2010 high-resolution TEM (HRTEM), both operated at 200 kV. Sample preparation for TEM characterization consisted of mechanical transference of a small quantity of the coated NWs from the Si substrate to a copper grid coated with a lacey carbon support film.

Results and discussion

Shown in Figure 1(a-c) are TEM images of Ni NPs formed on SiO₂ NWs, which from this point will be referred to as the substrate. The NW in Figure 1(a) is 100 nm in diameter and the Ni deposit was produced at a total chamber pressure of 17 Pa, while the substrate was heated to 573 K. The average NP size for this deposit was found to be 2 nm with a standard deviation of 0.5 nm. The inset is a HRTEM image of a 5 nm NP showing the {111} planes and the monocrystalline nature of the particle. The NPs shown in Figure 1(b) have an average size of 4 nm with a standard deviation of 1 nm and were produced at 873 K and 67 Pa on a NW with a 70 nm diameter. The distinct rings of the inset diffraction pattern in Figure 1(b) confirm that the Ni NPs are crystalline and that they are

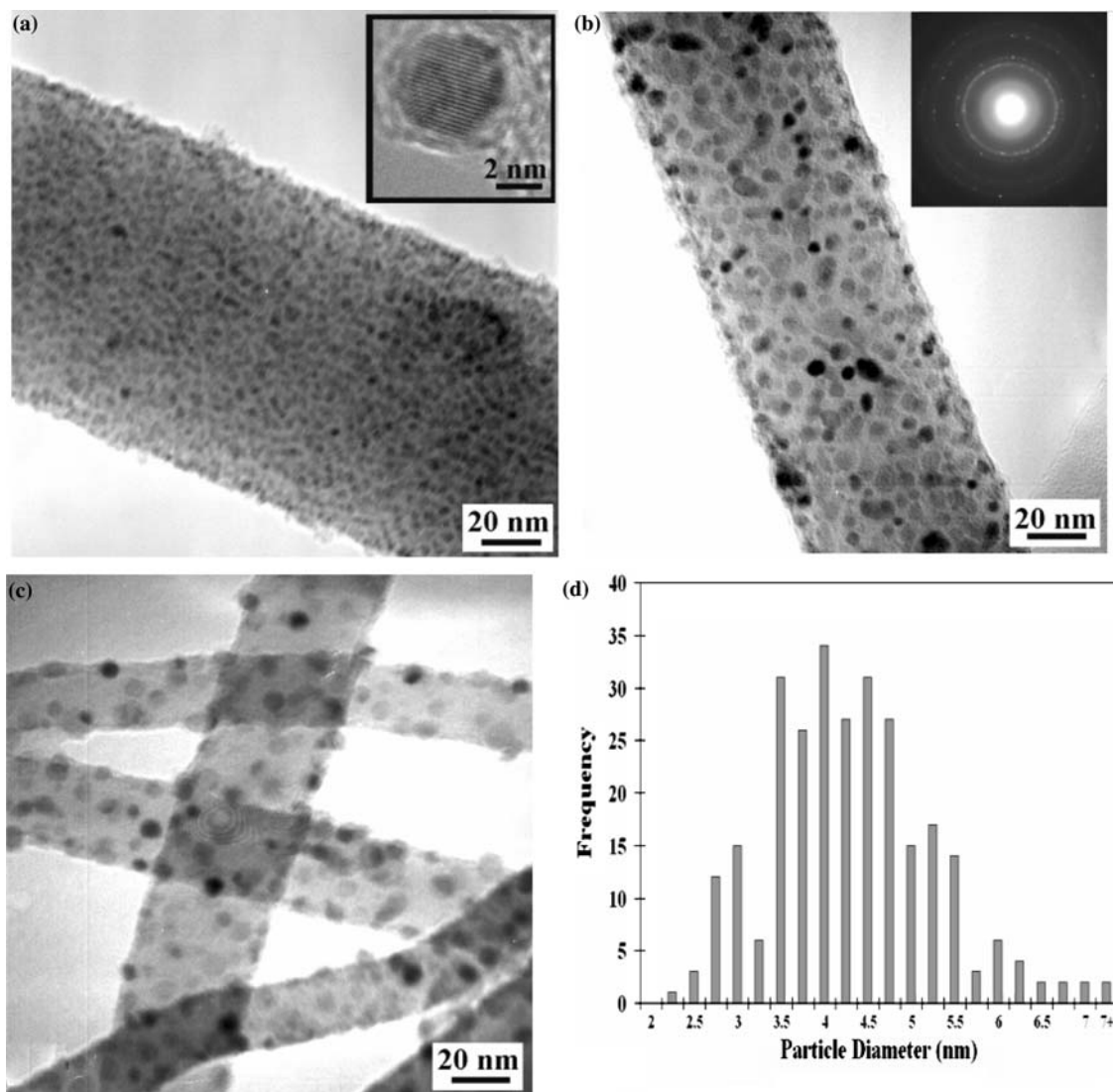


Figure 1. Bright-field images of Ni NPs: (a) on a 100 nm SiO₂ NW, (inset) HRTEM image of Ni NP showing {111} lattice planes; (b) on a 70 nm SiO₂ NW, (inset) diffraction pattern; (c) on 20–40 nm SiO₂ NWs; (d) histogram showing particle size distribution for Ni NPs.

randomly oriented on the substrate surface. Figure 1(c) shows several NWs with diameters ranging from 20 to 40 nm. Deposition conditions in this case were a chamber pressure of 42 Pa and a substrate temperature of 873 K, resulting in an average Ni NP size of 6 nm with a standard deviation of 1 nm. Figure 1(d) shows a histogram of particle size measurements for Ni NPs deposited at 873 K and a chamber pressure of 67 Pa. From a

deposition where the average NP size is approximately 4 nm the total surface area is 168 m²/g.

Depositions were performed at different temperatures and pressures to determine how these variables affected particle size. Higher substrate temperatures resulted in an increase in NP size as might be expected. At a fixed pressure of 42 Pa the average size was 4 nm at 573 K and 6 nm at 873 K. The increase in NP size may be attributed

to surface diffusion effects as more energy is provided at higher temperatures allowing surface diffusion to occur more readily. Several groups have determined the activation energies for Ni surface diffusion. Higai and Ohno (2000) reported an activation energy of 30.9 kJ/mol for Ni on Si(100) substrates, while Hitzke et al. (1997) calculated a value of 50.2 kJ/mol for surface diffusion on (1×2) reconstructed Au(110). The values are quite high but enough thermal energy is available within the studied temperature range for growth to occur.

It was found that as the overall chamber pressure increased there was also an increase in particle size. At a fixed temperature of 873 K the NP diameters reached a maximum of 6 nm at 42 Pa

and subsequently decreased at a pressure of 67 Pa to 4 nm. This result is due to the influence of the chamber pressure on the interactions occurring within the plasma. As the chamber pressure increases more of the precursor material is dissociated making more Ni available for deposition. Simultaneously the diffusion of the species within the plasma decreases, resulting in less material reaching the substrate surface for deposition. The overall effect of the increased chamber pressure is a competition between these two effects resulting in a maximum in NP size followed by a decrease in size at higher pressures.

Figure 2 is a montage of TEM images of Pt NPs on SiO₂ NW substrates. The deposition conditions for the NPs shown in Figure 2(a) were a chamber

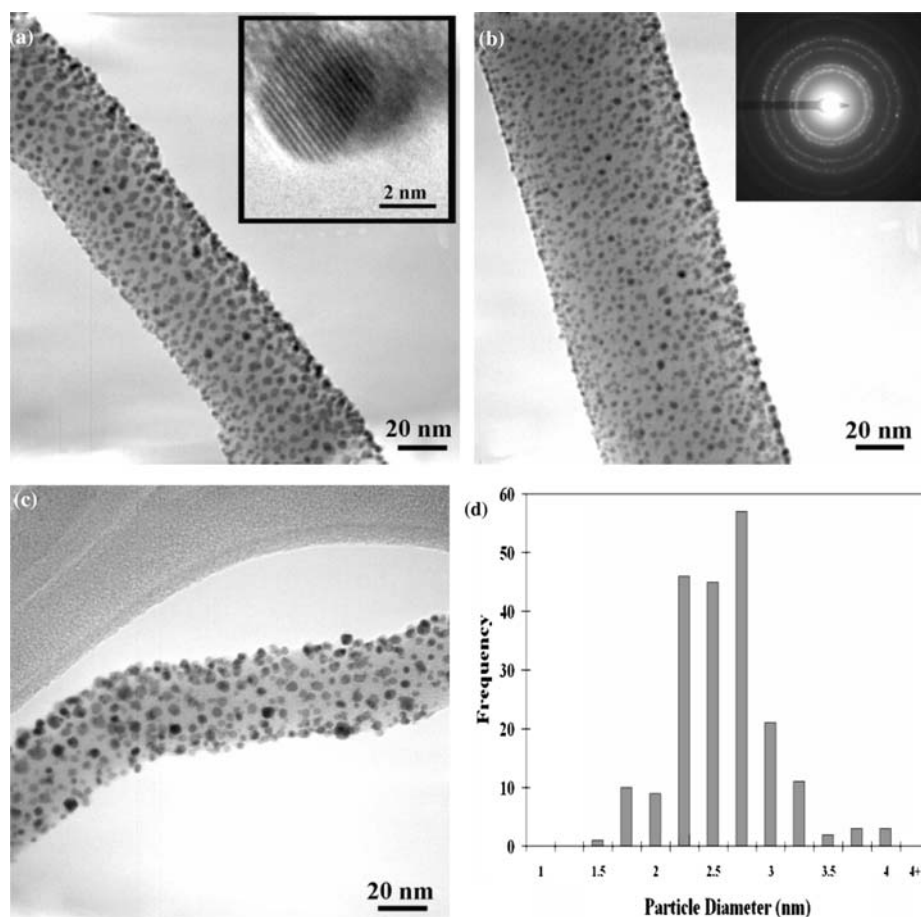


Figure 2. Bright-field images of Pt NPs: (a) on a 40 nm SiO₂ NW, (inset) HRTEM image of Pt NP showing {111} lattice planes; (b) on a 70 nm SiO₂ NW, (inset) diffraction pattern; (c) on a 35 nm SiO₂ NW; (d) histogram showing particle size distribution for Pt NPs.

pressure of 17 Pa with a substrate temperature of 573 K. The inset HRTEM image is of a 4 nm particle exhibiting a single crystal domain with lattice fringes corresponding to the {111} planes. The NPs in Figure 2(b) were produced at 42 Pa and 723 K on a NW of 70 nm diameter. The distinct rings of the inset diffraction pattern in Figure 2(b) indicate the crystalline nature of the Pt NPs. The deposition shown in Figure 2(c) was made at 67 Pa and 873 K on a NW 35 nm in diameter. Figure 2(d) shows a histogram for particle size measurements of Pt NPs deposited at 723 K at a chamber pressure of 42 Pa. The average particle size of all the Pt depositions was near 3 nm, corresponding to a surface area of 95 m²/g.

The effects of both temperature and pressure variations on the size of Pt NPs were found to be small. The NP diameter varied at most by 0.8 nm as the smallest particles had an average size of 2.5 nm and the largest averaged 3.3 nm. As mentioned previously, diffusion plays an essential role in the growth of NPs on the substrate surface. The limited effect of substrate temperature within the range 573–873 K can be understood in terms of the very high activation energies for surface diffusion. Kolaczkiwicz and Bauer (1991) reported a value of 65.6 kJ/mol for Pt diffusion on the W(110) surface and Kellogg (1993) determined a value of 88.8 kJ/mol for diffusion on Rh(100). Taking these activation energies into consideration it is not surprising that the temperature range used in this study does not significantly affect Pt growth rates and temperatures > 1100 K would be required (Ahn et al., 1981). The size of Pt NPs also showed little dependence on chamber pressure. A different precursor compound was used in the case of Pt and it may be that the dissociation behavior differs from that used for Ni. Further work is being undertaken in this regard.

Conclusions

In summary, PECVD is a method allowing rapid formation of metal NPs on nanowire substrates. We have demonstrated the formation of Ni and Pt NPs on SiO₂ nanowires. NPs with average sizes ≤ 3 nm and narrow size distributions are possible using this method. Changing the deposition parameters allowed the size of the Ni NPs to

be varied. The Pt NP size was relatively unaffected by the deposition parameters over the ranges explored in this present study. A further advantage of PECVD is that it is amenable to the formation of a range of different metal NPs on a wide variety of substrate materials.

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