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Metal coatings on SiC nanowires by plasma-enhanced chemical vapor deposition

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Coating of nanowires is being investigated to broaden potential uses for future applications. Coatings of Ni and Pt nanoparticles have been synthesized on silicon carbide nanowires by plasma enhanced chemical vapor deposition. Coatings with high particle densities with average particle diameters of 2.76 and 3.28 nm for Pt and Ni, respectively, were formed with narrow size distributions. Plasma enhanced chemical vapor deposition appears to be an efficient method for production of metal coatings on nanowires.

Nanomaterials and their potential applications are among the most pertinent issues on the scientific community's research agenda. Some of the more promising nanomaterials are nanowires (NWs), offering a high degree of versatility for future uses in applications ranging from sensors to biological research. Nanowires present the possibility of a wide range of uses because of their relative ease of production and the numerous types of materials available, including metallic, semiconducting, and dielectric NWs.[1] Nanowires will be able to be tailored to both specific and broad ranging applications and can be used as templates for coatings. These coatings can alter specific properties of the wires and may be utilized to make nanoscale devices. Coated NWs should prove to be useful and enhance their versatility.

Previous research has shown carbon nanotubes (CNTs) used as templates for the deposition of metal particles.[2–9] Possible applications for such coated nanostructures include reinforced metal-nanofiber materials,[10] catalysis,[2,9,11,12] scanning tunneling microscope tips,[6] and chemical sensors.[13,14] Various methods for metallization of CNTs include pulsed laser deposition (PLD),[6] supercritical fluid,[7–9] adsorption,[2] electrochemical deposition,[3] physical vapor deposition (PVD),[5] and electroless plating.[4] For example, Ye et al.[7,9] used hydrogen reduction of metal precursors using supercritical carbon dioxide (CO_2) as a reaction medium to deposit nanoparticles of Pd, Rh, and Ru, on multiwalled CNTs. These experiments yielded well-dispersed nanoparticles of Pd, Rh, and Ru with diameters of approximately 5–10 nm, 3–5 nm, and 1 nm, respectively. A chemical-vapor-deposition method was reported by Xu et al.[3] for Ni coating CNTs utilizing porous anodic aluminum oxide (AAO). In this study, AAO was used to produce CNTs via chemical vapor deposition. Electrochemical deposition was subsequently used to deposit Ni on the CNTs within the AAO. The Ni particles fabricated by this method were approximately 10 nm in diameter. Coating of CNTs has also been accomplished by Zhang et al.[5] using evaporation to synthesize W coatings. These evaporated coatings were uniformly dispersed over the surface of the CNTs, and the spherical W nanoparticles exhibited a range of diameters. Several of the above-mentioned techniques have produced metal coatings with spherical shaped particles. Deposited particles have been shown to be evenly distributed on the CNTs; however, dense coatings have not been produced. Coating times typically vary from 30 min[3,8,9] to nearly 3 days.[2] Although numerous methods have produced metal-coated nanostructures, no single technique has produced coatings with superior density, uniformity, and short production time.

In an analogous manner to these earlier experiments, we report Pt and Ni coatings formed on SiC nanowires

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(NWs) using plasma-enhanced chemical vapor deposition (PECVD). To our knowledge, there exist no previous reports regarding the coating of NWs or CNTs using the PECVD method. Particle geometries produced by PECVD are similar to those previously mentioned; however particle densities are substantially greater. The coatings that we report are relatively simple to produce and require a short processing time. This PECVD method may be a new way to produce superior coatings of metal on NWs and may be applicable to CNTs.

The NWs used for this study were produced as described elsewhere.[15,16] The NWs were grown on a Si substrate and have diameters ranging in size from 40 to 140 nm. The metal coatings were produced in a custom-designed parallel plate PECVD chamber operated at 13.56 MHz. Argon was used as both the carrier gas and the background gas. The nanowire samples were mounted on a heated sample holder, which also acted as the grounded anode.

For the coating process, the NWs remained on the Si substrate as produced. During the Ni coating process, bis(cyclopentadienyl)nickel [Ni–$(C_5H_5)_2$] was used as the source compound. It is a crystalline powder that is easily sublimated and will be referred to as nickelocene. The nickelocene was delivered to the deposition chamber by heating to 343 K in an Ar stream flowing at 2.5 sccm. Pumping was throttled down to give a total chamber pressure of 600 mTorr. The sample substrate was heated and maintained at a temperature of 573 K during the coating process.

For the formation of the Pt coating, the conditions were similar to that used for Ni, with the exception of the source compound that was changed to (trimethyl)methylcyclopentadienylplatinum [$(CH_3)_3(CH_3C_5H_4)Pt$]. The precursor and substrate temperatures were the same as well. Coating times for both Ni and Pt ranged from 12 to 15 min. The precursor materials for both Ni and Pt coatings were 99% pure and used as received from the vendor, Strem Chemicals Inc (Newburyport, MA).

The coated NW samples were examined using a Philips CM200 (Hillsboro, OR) transmission electron microscope (TEM) operated at 200 kV. Sample preparation involved mechanically transferring a small quantity of the coated NWs from the Si substrate to a carbon-coated copper grid.

Three TEM images of Pt coated SiC NWs are shown in Fig. 1. The NW in Fig. 1(a) has an approximate diameter of 60 nm, while the NW in Fig. 1(b) has a diameter of nearly 140 nm. In both images it is seen that the NWs have received a complete coating. The presence of distinct rings in electron-diffraction patterns taken from the samples, inset in Fig. 1(b), indicates the polycrystalline nature of the coating. The diffraction pattern was indexed and the coating was confirmed to be metallic Pt. Particle analysis was performed on Pt coated NWs with initial NW diameters of approximately 60, 80, 105, 120, and 140 nm. Particle size distributions are shown in Fig. 1(d). An average overall particle size was determined to be 2.76 nm with a standard deviation of 0.46 nm. The particle density for the Pt coating was found to be nearly 31,000 particles per square micrometer. Particle densities were calculated from wires where the coating thickness appeared to be one particle thick. In cases where the coatings were thicker, the values reported refer to surface density only.

For determination of the average particle sizes and the histogram showing the particle size distribution, several wires for each coating condition were analyzed. For the Pt coating, seven nanowires with varying diameters were analyzed; approximately 100 particle diameters per wire were measured to determine the average particle size and the resultant histogram of particle size distribution. For the Ni coating, four nanowires with varying diameters were analyzed, with approximately 50–60 particle diameters per wire measured to determine the average particle size and the resultant histogram of particle size distribution. It was also determined through these measurements that the particle diameter is independent of the nanowire diameter.

TEM images of Ni coated SiC NWs are shown in Fig. 2. The NW in Fig. 2(a) has an approximate diameter of 45 nm, while the NW in Fig. 2(b) has a diameter of nearly 120 nm. The NW shown in Fig. 2(a) is an asymmetric crystalline core NW with an amorphous shell; the coating is uniform over the surface of the NW. The dark contrast running down the interior of the wire is caused by the crystallinity of the core of the bi-phase SiC nanowire on which the coatings were formed. While the coating of the wire is uniform, it is actually the amorphous shell around the crystalline core of the nanowire that is not uniform. The Ni coating on both the minimum and maximum NW diameters is continuous, showing that the PECVD technique is applicable to coating NWs with a range of diameters. The distinct rings of the inset diffraction pattern in Fig. 2(a) indicate the polycrystalline nature of the coating. The diffraction pattern was indexed to confirm the metallic Ni coating. The bright spots in the diffraction pattern are from the crystalline SiC core of the nanowire, seen as the dark region running through the middle of the NW. Particle analysis was also performed on the Ni coated NWs with wire diameters of approximately 45, 80, 110, and 125 nm. Particle size distributions are shown in Fig. 2(d). The average overall particle size was determined to be 3.28 nm with a standard deviation of 0.74 nm. The particle density for the Ni coating was found to be approximately 12,000 particles per square micrometer.

Previous studies have demonstrated that there is a relationship between grain size and grain morphology as a function of deposition temperature for thin metal films grown on a ceramic substrate.[17] Hentzell el al. reported

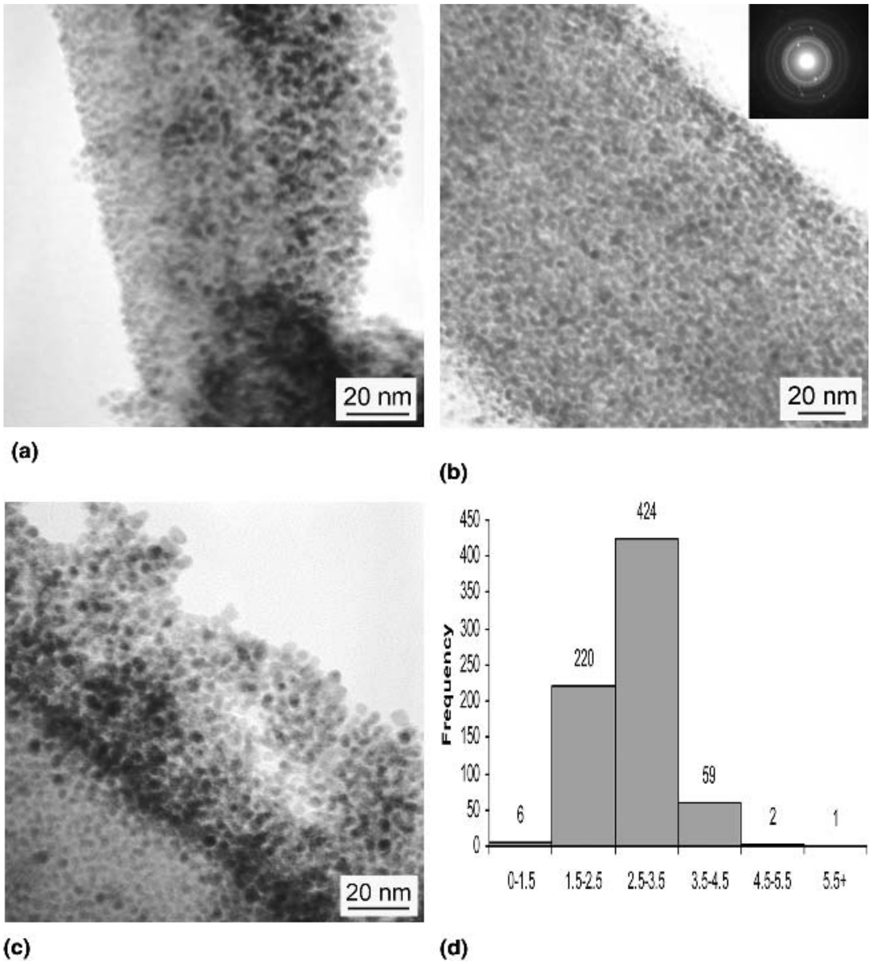

FIG. 1. TEM characterization of Pt coated nanowires. All images are bright-field TEM images: (a) coated nanowire with 60 nm diameter, (inset) diffraction pattern verifying metallic Pt as the coating; (b) coated nanowire 140 nm in diameter; (c) higher magnification image showing particle density; and (d) histogram showing particle size distribution.

the existence of four zones in the film growth, Zones I, T, II, and III, in a structure-zone diagram. In the diagram where the substrate to melting temperature ratio (T_s/T_m) is less than 0.2 (this includes Zone I and the lower half of Zone T) the grains are equiaxed and less than 20 nm in diameter. In the second half of Zone T, $T_s/T_m = 0.2$ to 0.3, the grain size increases to as large as 50 nm. Zone III starts at T_s/T_m equal to 0.3, and at T_s/T_m approximately equal to 0.37, the grains start to become columnar. From this point on, the grains continue to grow with bulk grain growth and surface recrystallization occurring at T_s/T_m greater than 0.5 in Zone III. The current results for Pt and Ni coatings on NWs are qualitatively consistent with these previous studies on thin films. The values of T_s/T_m for the coatings reported here is 0.17 and 0.21 for Pt and Ni, respectively. These values of T_s/T_m correspond to a smaller grain size, less than 20 nm, within Zone T microstructures, from the structure-zone diagram.[17]

Higher magnification images of the coated NWs shown in Figs. 1(c) and 2(c) show that the coatings are very dense, with no uncoated areas. In several previous studies of coatings on CNTs, complete and uniform coatings were not achieved.[2,7–9] It can be seen clearly in Figs. 1(c) and 2(c) that the particle size distribution for both Ni and Pt is small, with all the particles appearing very similar in shape and size. In comparison with the previous studies of metal coatings,[2–5,7–9,12] the coatings produced in this present study appear to exhibit significantly higher particle densities. For example, the coatings produced by Ye et al.[8] exhibited a particle density of approximately 1500 particles per square micrometer, while deposits made by Che et al.[12] achieved roughly 100 particles per square micrometer.

Shown in Fig. 3 is a scanning electron microscopy (SEM) image of Pt-coated nanowires. The coatings appear homogeneous and are evidenced by an increase in surface roughness (uncoated nanowires appear smooth). This image is representative of the bulk of the samples that were examined. It should also be noted that the images presented in Figs. 1 and 2 are representative of the

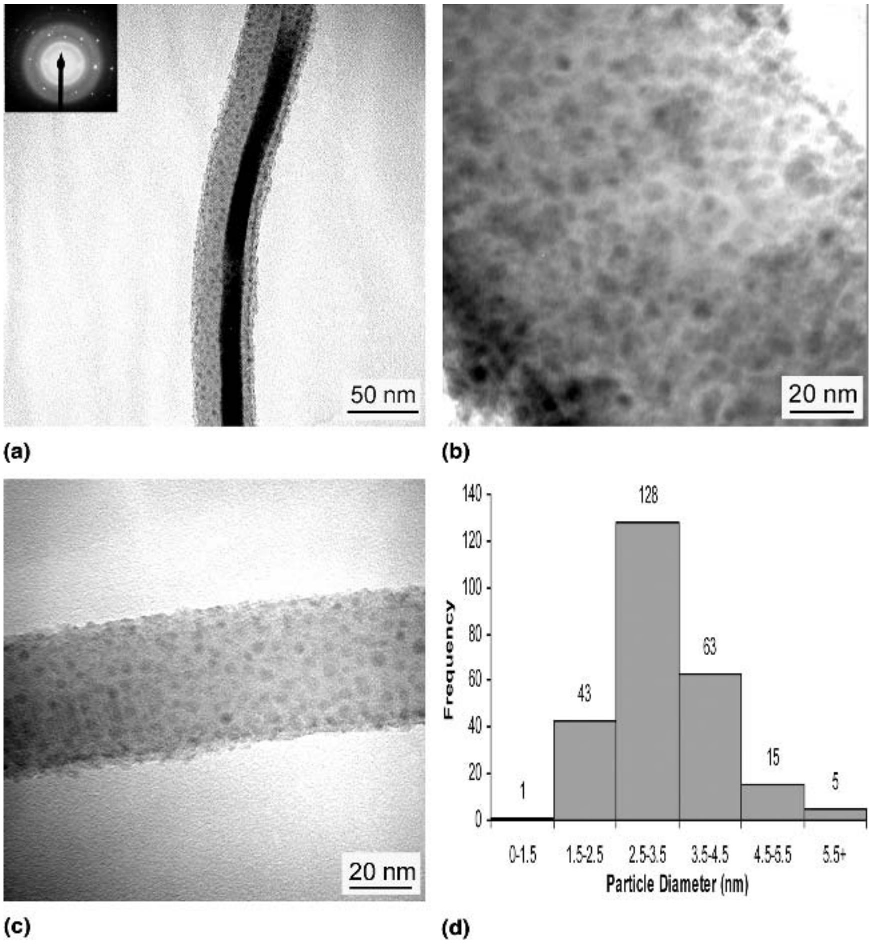

FIG. 2. TEM characterization of Ni coated nanowires: (a) coated nanowire with 45 nm diameter, (inset) diffraction pattern verifying metallic Ni as the coating; (b) coated nanowire 120 nm in diameter; (c) higher magnification image showing particle density; and (d) histogram showing particle size distribution. All images are bright-field TEM images.

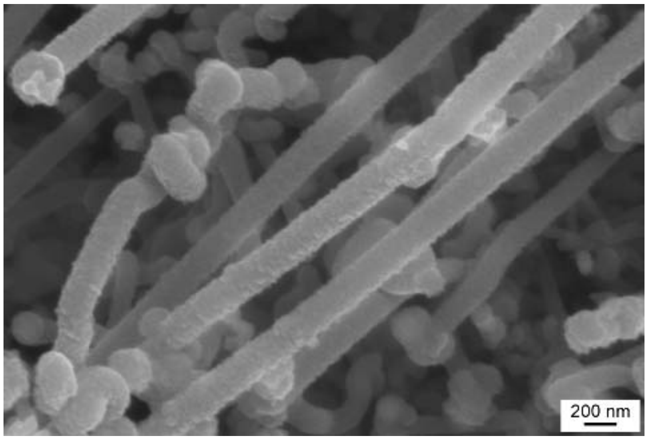

FIG. 3. SEM image of several Pt coated NWs showing homogeneous coatings.

several hundred coated nanowire samples that have been examined by TEM.

The adhesion of the coatings to the nanowires has not been determined at this time. The coatings appear continuous and adherent over the vast majority of the observed wires; only in a very few cases did the coatings show any evidence of having separated from the nanowire. One such example of this separation is seen in Fig. 1(a). It should be noted that the wires are mechanically transferred from the substrate to TEM grids for the subsequent microscopy studies; this may account for the isolated instances where separation of the coating from the nanowire appear to have occurred. In addition, it should be noted that the temperature effects on the particle size and quality have not been studied in depth in this report. The initial trend appears to be that increased substrate temperature produces larger particle sizes. A detailed investigation of possible trends is the subject of future work.

The catalytic properties of Pt and Ni are well documented.[11,12,18] The coatings reported in this study offer the possibility of excellent catalytic properties because of the large surface area created by large particle densities and small particle size. The use of highly stable support materials, taking advantage of excellent mechanical and thermal properties, is also a motivation for using SiC NWs as a template for metal coated nanostructures. The goal of forthcoming work from our group will be to investigate the catalytic properties of metal coated NWs that have been produced as a result of the current study.

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