Ni-W-P Catalyzed Growth of Carbon Nanotubes on SiC Whiskers

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Abstract

Ni-W-P nanoislands deposited on the surface of semiconducting SiC whiskers were investigated on its role in a catalytic growth of carbon nanotubes during thermal pyrolysis of acetylene. Experimental results indicated that a large quantity of carbon nanotubes formed although complex chemical reactions among the transition metals (Ni and W), SiC and carbon source had occurred to yield nickel silicides and tungsten carbide (WC). Multi-element catalytic growth of carbon nanostructures was found with the Ni-W-P catalyst. Favorable heterostructures made up of carbon nanotube/semiconducting SiC whisker are expected.

Introduction

Transition metals and their alloys are important catalysts for a catalytic growth of carbon nanotubes [1-3]. These catalysts could be prepared on various substrates such as silicon wafer, zeolite, and even carbon nanotube. At elevated temperatures, metallic catalysts tend to aggregate and grow into large catalyst particles, which will be unfavorable for the growth of ultrafine nanostructures. Thus, controlling the surface morphology, size, and distribution of the catalyst particles by using appropriate preparation processes and supporting materials is of great importance [4-6]. To meet such a requirement, electroless plating shows its many advantages such as realizing a simple and flexible deposition of highly dispersed binary or ternary alloy catalysts on various materials [7,8].

Moreover, nanodevices made up of one-dimensional heterojunctions and heterostructures [9,10] are of great interest with rapid development of nanoscale science and technology. Hu et al. reported a rectifying behavior of CVD heterojunctions between multi-walled carbon nanotubes and Si nanowires. Zhang et al. used a solid-solid reaction method to fabricate heterostructures made up of single-walled carbon nanotubes and nanorods or particles of silicon carbide and transition metal carbides. To fabricate SiC semiconductor /carbon nanotube

heterostructure, we used sub-micrometer-sized SiC whiskers to support Ni-W-P nanoparticles for a catalytic growth of carbon nanotubes. The role of the multi-element catalyst during the pyrolysis reaction was examined.

Experimental Procedure

β -SiC whiskers (10-30 μm in length and 0.1-1.0 μm in diameter) were sensitized in a SnCl_2 solution and then activated in a PdCl_2 solution. Ni-4.5W-19.9P (at %) (with a high melting point about 1240°C) nanoislands were deposited on the surfaces of the SiC whiskers by electroless plating (Figure 1) [11,12]. A silica plate covered with the Ni-W-P/SiC powders was put in a quartz tube, which was heated to 700°C in Ar atmosphere. Pyrolysis of C_2H_2 (20-30 ml/min) was then carried out with Ar as the dilute gas (at a flow rate of 200-500 ml/min). After 10-60 minutes of reaction, pyrolysis products were collected and then ultrasonically dispersed in absolute alcohol for 5-30 minutes for examination with X-ray diffraction (XRD, Rigaku D/MAX-III) and field emission transmission electron microscope (TEM, JEM 2010F) equipped with energy dispersive spectroscopy (EDS).

Results and Discussion

The pyrolysis reaction yielded a large quantity of carbon

Figure 1: TEM images of Ni-W-P nanoislands deposited on the surface of a SiC whisker.

nanotubes with diameters around 40 nm. Quite a few of the carbon nanotubes consisted of highly compartmentalized structures (Figure 2). The carbon nanotubes could be connected to the semiconducting whisker due to short reaction time or incomplete diffusion of the nanostructures away from the whisker (Figure 3). Corresponding HREM observations revealed that the compartmentalized structures were composed of short graphene layers, which formed a certain degree of alignment along both the longitudinal direction of the nanotubes and the stacking cones in the center of the carbon nanotubes. TEM observations of the multiple kinks and fracture of the nanotubes (Figure 2) revealed that, during the ultrasonic vibration of the carbon nanotubes, a severe deformation or fracture of the carbon nanotubes had occurred. For the fractured carbon nanotube shown in Figure 2b, it was impossible for this fractured nanotube to have formed during the CVD process. A vibration-induced tensile force along the highly compartmentalized nanotube should have been responsible for the fracture of the nanotube. A weak link between neighboring fractured surfaces in the compartmentalized nanotube suggests some similarity to the fracture of pure single- or multi-walled carbon nanotubes reported in previous works

Figure 2: TEM images of carbon nanotubes grown by pyrolyzing acetylene on the Ni-W-P deposited whiskers. (a) Carbon nanotubes with multiple kinks that present circular images (marked by arrows). (b) Stacking cone-related fracture of the compartmentalized carbon nanotube left with a weak linkage between the separated parts. The arrows point to the fractured surfaces.

Figure 3: TEM images of carbon nanotubes grown from a Ni-W-P deposited whisker.

[13,14]. The failure here should be ascribed as a stacking cone-related fracture since the walls of the two separated parts were self-accommodated. The peculiar physical properties observed with these compartmentalized nanotubes suggest potential properties such as deformation- and kink-related transportation properties [15,16] as well as high-strain-rate deformation ability [17].

During the formation of carbon nanotubes, there occurred complex chemical reactions among the Ni-W-P, SiC and acetylene. Different from the Ni-W-P deposited SiC whiskers (Figure 4a), diffraction peaks corresponding to partially graphitized carbon nanotubes, nickel silicides ($\text{Ni}_{31}\text{Si}_{12}$ and $\eta\text{-NiSi}$) and WC could be observed simultaneously (Figure 4b). It could be inferred that, at elevated temperatures, the Ni atoms reacted with the SiC whiskers to form the silicides by following Equation 1. Our heat-treatment of the Ni-W-P deposited whiskers in Ar atmosphere did not yield any traces of WC, which verified the findings in other reports that the reaction between W and SiC could not occur under temperatures below 800°C [18,19]. Thus, C atoms yielded from the reaction of Equation 1 contributed little to the formation of WC. Whereas, activated carbon atoms provided by the pyrolysis of acetylene (Equation 2) were believed to have combined with the W atoms to form the WC (Equation 3) under a C-rich environment (at 700°C). Considering the reported carburization reaction of W with methane (at 800°C) to form WC [20], we inferred that the formation of WC during a pyrolysis of acetylene here could be expressed as Equation 4.

HREM analyses of the catalysts encapsulated with as-grown carbon nanostructures indicated that the formation of nickel silicides and WC here had not consumed all of the Ni and W elements of the Ni-W-P deposition. Elemental diffusion and separation occurred throughout the pyrolysis reaction. The carbon nanostructures could grow from a Ni nanoparticle (Figure 5), (Ni, P) nanoparticle (Figure 6) and (Ni, W, P) (Figures 7 and 8) nanoparticle. EDS analyses of the composition of the double-element (Ni, P) nanoparticle showed that the contents of elemental Ni and P were 70.5 at% and 29.5 at%, respectively. The (Ni, P) nanoparticle had a much higher P content than the original Ni-W-P deposition containing 19.9 at% of P element. As a formation of Ni_3P phase by consuming all of the Ni element (due to well-known crystallization of amorphous Ni-P to Ni_3P at temperatures above 300°C) in the (Ni, P) particle only needed 23.5 at% of the P element, we take the above (Ni, P) nanoparticle as a composite catalyst which may contain Ni, Ni_3P and excess P in the form of either simple substance or phosphide.

For the triple-element (Ni, W, P) nanoparticle, the incorporation of carbon atoms in it could only reach a certain

Figure 4: XRD patterns of the (a) Ni-W-P deposited whiskers used for the pyrolysis reaction, and (b) pyrolysis products including nickel silicides and WC.

Figure 5: HREM image of the tip of a carbon nanotube with encapsulated Ni nanoparticle.

Figure 6: HREM image of non-graphitic structures grown from a (Ni, P) nanoparticle.

level. The carbon nanostructures formed from this nanoparticle consisted of two regions, amorphous or nongraphitic layers at the outer surface and graphitic layers neighboring to the (Ni, W, P) nanoparticle (Figure 7). It could be found that there was no trace of elemental Ni, W and P detected in the graphitic and amorphous layers (Figure 8), which suggests a different catalysis

mechanism from that of the double-element (Ni, P) nanoparticle.

As a candidate material for micro or nano-electronics, the nickel silicide formed at the Ni-SiC interface could provide low-resistivity metal contact and interconnect [21-23] between the semiconducting SiC whisker and the carbon nanotube. The contact or interconnect quality here should be further investigated by adjusting the reaction temperature and time, the yield of the silicides and the quantity of residual catalysts at the connecting areas. In addition to the diffusion of elemental Ni, W and P away from the whisker, our HREM observations indicated

Figure 7: HREM image of nongraphitic/graphitic layers grown from a (Ni, W, P) nanoparticle.

Figure 8: (a) Dark-field TEM image of the (Ni, W, P) nanoparticle coated with pyrolytic carbon shown in Figure 7. (b) EDS patterns showing the distribution of elemental Ni, W, P and C within the range from the amorphous layer to the (Ni, W, P) nanoparticle.

Figure 9: (a) Dark-field TEM image of carbon nanotubes and (b) EDS pattern showing the doping of nickel silicides at point M marked in (a). Cu element detected here was from copper grid used for supporting the carbon nanotubes.

that a few of the nickel silicides could also diffuse, (presumably with the Ni-based catalyst particles) away from the whisker surfaces and dope in the as-grown carbon nanotubes (Figure 9).

Conclusions

Carbon nanotubes were grown with the SiC-supported Ni-W-P nanoislands as the catalysts. The compartmentalized nanotubes could fracture with a stacking cone-related mode. The pyrolysis reaction could provide activated carbon atoms and thus result in a C-rich atmosphere favorable for the formation of WC. Carbon nanostructures were found to grow from nanoparticles made up of either single element (Ni) or multiple elements (Ni-P, Ni-W-P). The findings here should contribute to an establishment of multi-element catalysis mechanism when various alloy catalysts are involved in a pyrolysis reaction, and the fabrication of ideal low-dimensional heterostructures for favorable nanodevices.

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