行政院國家科學委員會專題研究計畫 成果報告

總計畫

計畫類別：整合型計畫
計畫編號：
執行期間：91年08月01日至92年07月31日
執行單位：國立成功大學材料科學及工程學系（所）

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報告類型：精簡報告

處理方式：本計畫涉及專利或其他智慧財產權，2年後可公開查詢

中華民國92年11月17日
Formation Mechanism and Integral Processing of Carbon Nanotubes

A: Carbon nanowire (CNW) exhibiting crystalline structure was obtained using amorphous Ni thin films as the catalyst. The carbon nanowires were grown in a microwave plasma-enhanced chemical vapor deposition system using methane as the carbon source and hydrogen as the carrier gas. The use of amorphous Ni as the catalyst led to the formation of crystalline CNW but not amorphous CNW. In general, a catalyst can be seen at the tip of each CNW. However, a total of six CNWs grown from a single catalyst were regularly observed. The carbon nanowires were also found to exhibit an interesting microstructure where the basal planes were perpendicular to the wire axial direction and parallel to the closest packing plane of the catalyst. Furthermore, the use of amorphous Ni thin film catalyst resulted in the formation of an interlayer between CNW and the substrate, depending on the film thickness.

B: The detailed relationship between cobalt catalysts and resulting multi-walled carbon nanotubes (CNT) by microwave plasma-enhanced chemical vapor deposition is studied. The Cobalt nanoparticles or films are prepared by magnetron sputtering, molecular beam epitaxy and ion beam deposition and are to be demonstrated to consist of various structural characteristics including phase, crystallinity and morphology. By comparing the resulting CNT, our results show that CNT catalytically-grown by the cobalt of fcc phase with better crystallinity is of high yield and better quality than the cobalt of other phase and crystallinity. Higher yield CNT can be obtained from the fcc Co catalysts of optimized thickness. Finally we show the preliminary results on the imaging simulations of CNT.

結果與討論

A: It is known that the use of Ni as a catalyst in various growth processes would lead to the formation of CNT. However, as mentioned above, growth of amorphous CNW (10 nm to 40 nm in diameter) using a thermal evaporation technique in the presence of graphite and Ni powder mixtures was observed recently [17]. Figure 1A shows TEM bright-field images of CNW obtained. The growth time was 3 min and the microwave power was 500 W. It was observed at a higher magnification (Fig. 1B) that all the one-dimensional nano-carbons are solid nanowires without a hollow center. The average diameter is 40 nm. Interestingly, unlike CNT, the basal planes were found to perpendicular to axial direction, as shown in Fig. 1C where a section of CNW near a catalyst is shown. The crystalline structure of the CNW was determined using selected area diffraction (SAD).

The CNW are polycrystalline with a (0002) preferred orientation to some extend. The crystalline structure of the catalyst was also determined to be NiC with L10 structure. In general, a catalyst can be seen at the tip of each CNW (Fig. 1A). However, multiple growth of CNW from a single catalyst was also observed. In a previous study, we have observed such multiple growth of CNW from a single NiC particle at a microwave power of 1000W and 35 torr [21] (Fig. 2A). It was found that the growth of multiple CNW required a NiC particle larger than 100 nm. An abundance of CNW having the sea urchin structure was obtained. A number of carbon nanowires radiate from a single catalyst particle. A bright field TEM image is shown in Fig. 2B. It was first confirmed that the one-dimensional nano carbons, indicated by the 4 arrows are solid nanowires, which radiate from a
close-packed planes of NiC (represented by dashed lines in Fig. 2D). As a result, a CNW has its graphene planes parallel to the \{111\} planes of NiC. However, the current study has found that by increasing the microwave power to 1500 W and reducing the pressure to 25 torr, multiple growth of CNW would occur on a NiC particle whose diameter is much smaller and near 20 nm. The basal planes were also found to perpendicular to axial direction. It is believed that the formation of the initial basal plane on the NiC occurred on the closest packing plane (111) of the L10 structure NiC [21].

Fig. 2. Carbon nanowires with new micro-structures, (A) SEM image showing 4 CNW growing from a single catalyst particle. (B) TEM images with bright field showing the multiple growth and the solid nature of the wires. (C) SAD patterns show that the catalyst is single crystal of L10 NiC. (D) A ball model showing the growth of graphene planes on a (111) close-packed plane of NiC.

The amorphous Ni thin films used in the current study led to the formation of not only polycrystalline CNW with an unusual microstructure (Fig. 1C) but also an interlayer between the CNW and the silicon substrate. The appearance of such an interlayer, the interlayer thickness, and the interlayer microstructure depend on the thickness of the Ni thin films, as well as the microwave power. Figure 3 shows the specimens obtained at 500 W, 25 torr, and Ni thin film catalysts with different thickness of 15 nm, 36 nm, 74 nm, and 286 nm. The growth time was 3 min. For the 15 nm-Ni specimens, only CNW were observed as discussed above and shown in Fig. 3A. The interlayer starts to appear as the Ni thin film thickness exceeds 15 nm (Figs. 3B, 3C, and 3D). A TEM bright field cross-sectional image of the interlayer formed on 74 nm Ni thin film is given in Fig. 3. The interlayer has a thickness of 380 nm and consists of polycrystalline carbon with nickel carbide inclusion. The nickel carbide inclusion increases with the thickness of the Ni thin film. The interlayer thickness also increases with the thickness of the thin film Ni catalyst, while the height of the CNW above the interlayer decreases with the thickness of the thin film Ni catalyst.

Fig. 3. SEM images showing cross-sectional views of CNW grown (A) an 10 nm-thick (B) a 36 nm-thick (C) a 74 nm-thick and (D) a 286 nm-thick Ni thin film under 500 W and 25 torr pressure for 3 min growth time. The cliff-like interlayer is saw on 36 nm, 74 nm, and 286 nm-thick Ni film.

As mentioned above, an interlayer appears when the Ni thin film catalyst exceeds a certain thickness. In other words, when there is an excess amount of Ni, the growth of an interlayer would be favored. This is then followed by the growth of CNW, as shown in Fig. 3. We therefore propose a growth model as follows. In the beginning of the growth, the competition between hydrogen etching and carbon deposition may occur. The hydrogen ions may still etch the already-etched thin film catalyst until the catalyst is etched to a condition allowing the formation of CNW or is simply embedded in pyrolytic carbon film. In the mean time, radicals containing carbon in the plasma would lead to the formation of CNW or pyrolytic carbon film, depending on the catalyst condition. It is believed that an excess amount of Ni thin film requires extra time for further etching for the formation of CNW. Therefore, a layer of pyrolytic carbon forms while the Ni is etched. During this stage, Ni could also react with carbon to form nickel carbide. As a result, a thicker Ni thin film catalyst would give a thicker interlayer, which also contains more nickel carbide inclusions as mentioned above. After this stage, the remaining Ni would then serve as catalyst for the growth of CNW on top of the interlayer. The above discussion therefore suggests that the competition of carbon film formation and CNW growth would occur and depends on the etching status of the Ni catalyst. The current scenario is such that the delayed formation of CNW is due to time is required for the etching of excess Ni. This also suggests that an excess amount of carbon species in the plasma would lead to the formation of an interlayer when a thinner thin film catalyst is used. This scenario can be created by increasing the microwave power to allow the formation of more carbon-containing radicals. As mentioned above, specimens obtained using a 15-nm Ni thin film as the catalyst and a microwave of 500 W have no interlayer
Co nanoparticles and films by MS

While investigating the effect of substrate bias, it was found that the surface is continuous but damaged seriously at negative bias. At negative substrate biases, ions receive additional kinetic energies, which cause more surface diffusions and resputtering of adatoms from the surface. In addition, the surface suffers from ion bombardments, which then induce many surface defects accounting for the rough surface. As a consequence, the island/nanoparticle nucleus would be destroyed by the bombardment of energetic ions and the resulting films turns out to be continuous. Moreover, by varying the substrate bias and the deposition distance for the energy of adatoms, Co films of fcc, hcp and amorphous phases can be successfully produced as in Fig. 1.

No apparent damage is observed at all positive biases. Instead, isolated islands form at positive substrate biases under these deposition conditions. When a more positive bias is applied, the size distribution of the cobalt nanoparticles becomes narrower, the island density being about $1\times10^{13}$ cm$^{-2}$. The size ranges from 5 to 30 nm while the shape of the islands becomes more spherical and the aspect ratio (height/diameter) is in the range of 0.1-0.2. Most of the nanoparticles are still single crystals in either fcc or hcp phase as shown in Fig. 2. However they bear no crystallographical relationships with the substrate or with each other.

2. Co nanoparticles and films by UHV-IBS

Since the Co surface energy is larger than Si, Co islands immediately form upon deposition, following the V-W growth mode. Moreover, the deposition rate and the ion energy can be independently controlled, thus the island density can be varied over 10 times at about $10^9$ ~ $10^{10}$ cm$^{-2}$ as shown in Fig.3. The islands are coarsened to form a continuous film of high degree of crystalline. All nanoparticles and films consist of fcc phase when synthesized by UHV-IBS. After demonstrating our ability of preparing cobalt catalysts with various microstructures, we are in great position to investigate the detailed CNT growth mechanism by looking at the effects of catalysts from

3. Co phase effect on CNT structure

Fig. 3. AFM images of fcc Co nanoparticles grown by UHV-IBS with island density of (a) $2\times10^9$ cm$^{-2}$ (b) $3\times10^8$ cm$^{-2}$ and (c) TEM image of a fcc Co film.

3. Co phase effect on CNT structure

Fig. 4. TEM images showing (a) carbon nanofibers from hcp Co catalysts and (b, c) hollow carbon nanotubes with and without Co on the tip.

4. Thickness and crystallinity of fcc Co film on CNT yield

Fig.5 shows the CNT morphology obtained from fcc Co catalysts with various thicknesses from just Co nanoparticles to a Co film of 300nm. All the samples have been etched by H$_2$ for 5 minutes prior to CNT growth. Although the growth conditions for CNT may not be optimized yet. But the differences in CNT are significant in terms of the yield and morphology. Both too thin and too thick catalyst layers seem to be difficult to produce long and intertwining networks.

Fig. 5. SEM images showing carbon nanotubes from fcc Co catalysts of various thickness (a) Co nanoparticle (b) 50nm (c) 300nm.

Under the same growth condition, only a Co film of around 50 nm has a high yield of CNT. However, the products in these three samples are the same including both hollow carbon nanotubes and nanofibers and the
average diameter of the nanowires is similar. From the fact that Co is almost found to be located on the tops of the nanotubes with few on the bottoms, we argue that the tip growth is easier than root growth. This also indicates that the better adhesion between Co and Si substrates from MS might account for the poor chemical reactivity of bare Co nanoparticles. However, most CNT grown from MS-grown Co is defective as shown in Fig.6, where two very defective CNTs are jointed by a C onion (cluster) rather than a Co catalyst. The cause is unknown but very complicated growth morphology is presented. Elemental mapping in energy-filtered TEM is extremely useful to distinguish the element distribution as shown in this case.

Fig. 6. TEM images showing two carbon nanotubes jointed where (a) bright field and elemental maps for (b) C and (c) Co

Given 50nm in thickness and fcc phase are optimal parameters for Co as catalysts for CNT growth, we can then compare the CNT grown from the Co catalyst layers synthesized by MS, MBE and UHV-IBS, as shown in Fig.7 where the Co thickness is 25 nm. We have shown and discussed the microstructure of the Co films grown by MS and UHV-IBS. In terms of the degree of the crystallinity, MBE-grown Co and UHV-IBS-grown Co are better than MS-grown Co due to its slower deposition rate and free of ion bombardment, which is shown in Fig.3c. Co is grown at room temperatures for MS, UHC-IBS and at 150ºC for MBE, thus the resulting average grain size is about the same around 20nm. However, the MS-grown Co has the most areas for grain boundaries. While most nanowires grown from MS-grown Co are curved and short and defective, they are longer, courser and more straight from the other two. The CNT density is highest and the catalysts are well dispersed upon CNT growth from the UHV-IBS grown Co. There results have illustrated that although presumably the chemistry should be almost the same between these three cases, however, the Co structure variations could affect CNT growth a lot. This probably indicates that not only surface diffusion but also bulk diffusion is also important in the CNT growth mechanism.

4. TEM simulations of CNT

The variety of nanodevices based on CNT has motivated this filed and the large range of possible properties is associated with many possible microstructures available in CNT. Due to the complexity, the precise control of selective CNT growth is difficult and reliability issue occurs. In addition, the detailed growth mechanism behind is a key but also difficult question. All these await a better understanding of CNT microstructure including helicity, type of CNT, chemistry and all possible defects, which demands a better characterization. Since the microstructure is complex, a TEM simulation from an ideal model helps understanding the correlation between diffraction experiment and real atomic structures. Fig. 8 shows our preliminary results. The ideal atomistic models are built first as in the top row of the figure. Through dynamical scattering theory, a multislice calculation is employed to simulate the diffractions patterns which are shown in the bottom two rows for single- and three-walled CNT with indices from (10,0), (10,5) to (10,10). The symmetry of the atomic arrangement in the CNT is reflected in the patterns. In principle, if the electron beam is perpendicular to the tubular nanowire, the relative positions of two (10-10) diffraction spots would be enough to derive the helicity and the type of the CNT. When more walls associated with the CNT, the diffractions patterns include all fundamental spots and the repeated unit from the arrangement of the walls, which becomes much stronger and makes the spot more sharp. If any additional spot or any spot missing, which then suggests some defects either destroy some symmetry or create new symmetry. The numbers of walls is better examined in imaging mode, which has also been simulated (not shown). More work is undertaken to be able to distinguish the defect type and the atomic structure for multi-walled CNT between “Russian doll” and “Swiss cake” models.

Fig. 8. Simulated diffraction patterns from single-wall and three-walled CNTs with the atomic structures of various types of CNTs including (10,0), (10,5) and (10,10) from left to right.