Metal Nanocrystals Grown by Vacuum Deposition on Aligned Carbon Nanotubes

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When the vacuum evaporation method was used to deposit metals, such as Au, Ag, or Cu, on a substrate covered with aligned carbon nanotubes which were fabricated by the microwave-plasma-enhanced chemical vapor deposition method, we found that nanoscale single crystals of the metals with well-defined facets were grown on the surfaces of the carbon nanotubes. Nanocrystals ranging from approximately 50 to 500 nm in diameter were obtained when the deposition time ranged from 1 to 60 min. Whiskerlike crystals with high aspect ratios could also be found frequently in these nanocrystals, which can be applied in field-emission display devices.

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1. Introduction

Nanostructured materials have attracted significant interest because of their unique properties which differ from those of the bulk materials. Nanoscale crystals of metals have also been found to exhibit some new structural, thermal, mechanical, electronic, and magnetic properties. Although much attention has been paid to controlling the crystal size, their shapes have seldom been controlled. Synthesis of nanocrystals with well-defined surfaces and shapes will be important to achieve many more useful functions and applications.

A variety of methods for producing nanocrystals have been reported, including physical and chemical approaches. For the physical vapor deposition methods, nanocrystals are usually formed based on the collisions of the vapor with inert gas which is partially introduced in the evaporation chamber. In the case of the so-called gas deposition method, which is a popular method for synthesizing large quantities of nanocrystals of metals, the inert gas pressure is higher than 10 Torr. Nanoparticles can also be formed by sputtering, or laser vaporization methods, in which inert gas of higher than 1 Torr is required. Because of the random gas collisions, most of the nanoparticles formed by these methods are round (or round-like) in shape, and multiply twinned or polycrystalline particles are dominant.

In this paper, we demonstrate that the conventional vacuum evaporation method can be used to produce aggregations of nano-sized single crystals of some metals with well-defined facets. The vacuum evaporation method is known as a convenient tool for depositing continuous thin films on a smooth substrate. It is known, however, that the films are grown from single-crystalline small islands by coalescence, and the small islands are grown from atoms and clusters which diffuse on the smooth substrate surface. We demonstrate that the growth of single crystals with well-defined facets can be enhanced, while the round particles formed due to diffusion and coalescence can be avoided by using a substrate with a highly irregular surface. We prepared such surfaces by applying the microwave-plasma-enhanced chemical vapor deposition (MW-PECVD) method to deposit well-aligned multiwalled carbon nanotubes on a smooth substrate. We also found that nanoscale thin metal whiskers can be grown with a suitably high density, and these can be applied in field-emission display devices.

2. Deposition and Morphology of Aligned Carbon Nanotubes

In order to achieve a highly irregular surface, we deposited carbon nanotubes on a smooth substrate. Although numerous methods have been developed for synthesizing carbon nanotubes, the direct growth of aligned carbon nanotubes on a substrate can only be established by chemical vapor deposition methods. In the present study, we used the MW-PECVD method, by which well-aligned multiwalled carbon nanotubes can be directly grown on a catalyst metal (Ni, Co, Fe) film or substrate with high density. The nanotubes grown by this method have an average diameter ranging from 50 to 100 nm and an average length ranging from 3 to 10 μm. The detailed experimental conditions are reported elsewhere.

Figure 1(a) shows a scanning electron microscopy (SEM) image of the typical morphology of the as-grown nanotubes, and Fig. 1(b) shows a transmission electron microscopy (TEM) image of the typical microstructure of the nanotubes. From Fig. 1(a), it is evident that most of the nanotubes are grow straight in the direction perpendicular to the substrate surface, and some of them are curled or bundled. From Fig. 1(b), it is evident that the structure of the thus-prepare nanotubes is different from that of nanotubes synthesized by the arc discharge method, we can always observe a “bamboolicke” structure and the top of each nanotube is capped with a catalyst metal particle. Because of these features, the outermost surface of each nanotube is not atomically smooth, but contains a large number of dislocations, steps, and graphite edges. The surface morphology of a thus-prepared substrate is desirable for our purpose, because we can obtain a nanoscale irregularity in both the parallel and perpendicular directions to the surface.
3. Deposition and Morphology of Metal Nanocrystals

Au, Ag, and Cu have been deposited on the carbon-nanotube substrates using the vacuum evaporation method. Here we primarily present the results for Au. The vacuum chamber was maintained at a pressure of $3 \times 10^{-3}$ Pa throughout the deposition process, and the substrates were kept at room temperature. The deposition rate was varied by controlling the heating temperature of the tungsten crucible.

A typical SEM image of the Au film deposited on a carbon-nanotube substrate is shown in Fig. 2. It is evident that nanocrystalline particles with uniform crystal size and well-defined facets were formed on the carbon-nanotube substrate. We have confirmed that only a continuous film was formed on a smooth glass substrate under the same deposition conditions. The deposition rate was 1.5 nm/s, and the deposition time was 20 minutes. The film thickness was 1.8 μm, and the average size of the crystals was 350 nm.

We found that the average crystal size depends on both the deposition rate and time. When the deposition rate is in a low range, below 10 nm/s for example, the average crystal size is mainly proportional to the deposition time. When the deposition rate is in a high range, the average size is almost independent of the deposition time, but inversely proportional to the deposition rate. We confirmed that a continuous film was always formed on a smooth glass surface for each case. Figure 3 shows a TEM image of the Au nanocrystals with an average size of 35 nm. The deposition rate (1.5 nm/s) was the same as that in the case of Fig. 2, but the deposition time was as short as 2 minutes.

As is evident in Fig. 2(b), we could frequently observe some whiskerlike crystals or their seed crystals among the nanocrystals. By increasing both the deposition rate and time, we could obtain more whiskers, as shown in Fig. 4. The thickness of these whiskers ranged from 10 to 200 nm, and their lengths ranged up to 700 nm. Figure 5 shows a TEM image of one of these whiskers, for which a twinned structure can
be observed. By electron diffraction study of the whisker, we found that the whisker axis is parallel to the (110) direction and the surfaces are surrounded by stable (111) and (100) planes. The structure is similar to that of the nanowires formed by electron beam etching of Au thin films.39

Ag and Cu, as well as Au, have also been investigated, and similar morphologies have been observed.

4. Crystal Growth Discussion

The irregularity of the substrate surface may play a key role to ensure the stable growth of the single crystals with well-defined facets even at high density. It is known that when atoms are deposited on a smooth surface, most of them will diffuse on the surface and collide with each other to form clusters and then crystalline islands due to coalescence. In the case in which the metal (e.g. Au, Ag, or Cu) does not wet the substrate (e.g. graphite), single-crystalline islands with well-defined facets can be formed. When the islands reach a high density however, they will easily coalesce into round, bridge-like or filmlike shapes without well-defined facets. This is because the islands are not firmly attracted to the smooth substrate and they can easily change their positions and lose their facets during the coalescence process. If a highly irregular surface is used however, most of the clusters will firmly nucleate at these irregular points, and thus large polyhedron single crystals with well-defined facets can stably grow without coalescence even if they are close to each other. Since the (110)

Fig. 3 TEM image of smaller Au nanocrystals deposited on carbon nanotubes under conditions of a low deposition rate and a short deposition time.

Fig. 4 SEM image showing the whiskers appeared among the deposited nanocrystals when a longer deposition time is applied.

Fig. 5 TEM image of a long Au whisker.
planes of face-centered cubic metals have a growth speed that is more rapid than that of the (111) and (100) planes, whiskers can also be formed under coalescence-free conditions.

5. Summary

We have demonstrated that nanoscale single crystals of metals with well-defined facets can be formed by the vacuum evaporation method using a highly irregular substrate instead of a smooth substrate. Such irregular surfaces have been achieved by depositing aligned carbon nanotubes on a smooth substrate using the MW-PECVD method. The crystal size can be controlled easily by the deposition time. Nanocrystals ranging from approximately 50 to 500 nm in diameter were obtained when the deposition time ranged from 1 to 60 min.

Whiskers have also been obtained by this method. If the density of the whiskers can be further increased and controlled, the whisker-containing substrate can possibly be used as a field-emission display device, in which the whiskers will act as electron emitters.

REFERENCES