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Growth of carbon nanotubes on cobalt disilicide precipitates by chemical vapor deposition

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We have successfully grown carbon nanotubes on cobalt-implanted silicon with various doses. The morphology of such tubes has been examined by scanning electron microscopy, transmission electron microscopy, and Raman scattering. On contrary to the commonly used transition-metal nanoparticle catalysts, nanometer-sized $CoSi_2$ precipitates produced in the as-implanted substrates are believed to act as nucleation centers for the formation of carbon nanotubes. © *1998 American Institute of Physics.* [S0003-6951(98)03625-0]

Since its observation in 1991,[1] the carbon nanotube (CNT) has been widely investigated both for its novel electronic properties and application potentials.[2–5] Ideally, a nanotube consists of concentric cylindrical shells of graphitic sheets, which can be viewed as rolling up the graphitic layer into a tubule. The nanotube can be a metallic conductor or semiconductor, which is uniquely determined by a pair of integer indices (n,m).[6] Both theoretical predictions[7] and experimental results[8] show that it is possible for a tube to show different conducting properties at different parts. Thus, nanodevices based on a tube can be realized. Nowadays, large quantity carbon nanotubes can be systhesized by arc discharge, laser ablation, and chemical vapor deposition (CVD).[6] Among them, the latter method is a cheaper way, and the reaction process can be easily controlled. Moreover, the required deposition temperature by CVD is relatively low, the commonly used reaction temperature is around 700 °C. Using the CVD method, carbon nanotubes (CNTs) have been prepared by decomposition of hydrocarbon on various substrates containing transition-metal nanoparticles[9] or through decomposing the metal complex which contains both metal and carbon.[10] We report here a catalyst or nucleation center other than a transition-metal catalyst for the systhesis of carbon nanotubes by CVD, i.e., cobalt disilicide formed in Co-implanted silicon. To our knowledge, there is yet no report on carbon nanotube production based on such substrates. On the other hand, growth of CNTs on silicon is particularly useful for future integration of CNTs-based nanodevices since silicon is the headstone of the modern semiconductor industry.

The Co implantation was performed with a metal vapor vacuum arc ion source into (100) or (111) n-type silicon wafers with resistivity of 10–20 Ω cm at an extraction voltage of 30 kV to a dose of 2×10^{17} cm^{-2}. The substrate temperature during implantation was kept lower than 200 °C. Details of the implantation process and characterization of the as-implanted and postannealing samples can be found in the literature.[11] Previous transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) studies have revealed that two types of $CoSi_2$ precipitates are formed in Co-implanted silicon, which are denoted as A type and B type. Generally, no purely Co particles were found in the implanted samples.[11] These precipitates distribute from the sample surface down to about 200 nm in the bulk. The density of the precipitates shows a Gaussian distribution, which is correlated with the Co depth profile. It is expected that only the surface precipitates (part of the precipitate is above the silicon surface) can act as the nucleation centers for the growth of carbon nanotubes. The size of the precipitates above the surface is nearly the same as that of the precipitate itself,[11] and the size of the precipitates increases with the implantation dose, e.g., 15 nm for a sample implanted with a dose of 1×10^{17} cm^{-2}. The as-implanted samples have been investigated by conducting atomic force microscopy, i.e., simultaneously monitoring the surface morphology and current image. The position of the surface precipitates and their distribution can be obtained from the current image.[12]

The implantation doses used are 1×10^{15}, 5×10^{15}, 1×10^{16}, 5×10^{16}, 1×10^{17}, and 2×10^{17} cm^{-2}, the corresponding $CoSi_2$ size ranges from several nanometers to 15 nm for the as-implanted samples. These samples were put into a quartz boat, then transferred to a stainless-steel chamber for reduction and growth. Reduction was performed at 500 °C with pressure about 150 Torr, a mixture of hydrogen and nitrogen was used with flux rates 10 and 50 cc/min, respectively. 10% acetylene in N_2 with a total flowing rate of 110 cc/min was introduced for the growth at 650 °C in 150 Torr. The growth process continues from 2 to 5 h, and the reduction time is about 1 h. To compare, some samples were directly sent to the growth chamber without reduction.

Nanotubes from samples implanted with doses ranging from 1×10^{15} to 2×10^{17} cm^{-2} have been examined by scanning electron microscopy (SEM) (Hitachi, S-4200). As can be seen with the naked eye, the mirror-like silicon surface was covered with a black layer after several hours growth. Under SEM, these black layers were the nanotubes with a diameter around 15 nm, no significant difference of

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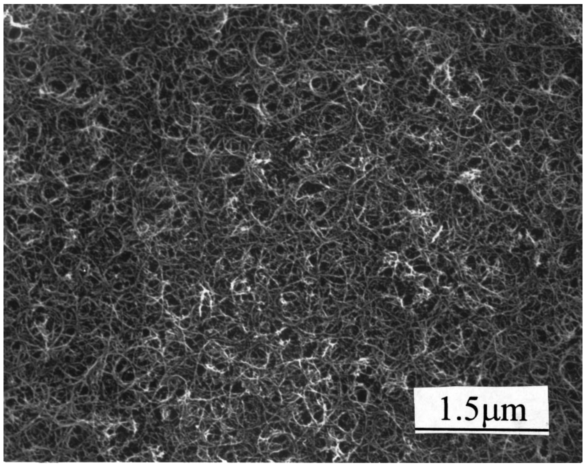

FIG. 1. Low-magnification SEM image of the carbon nanotubes grown for 3 h, reduced for 1 h on cobalt-implanted silicon with a dose of $5\times10^{15}\ \mathrm{cm}^{-2}$.

the nanotube diameter was found for the samples implanted with different doses. Figure 1 is the low magnification SEM picture for the samples with a Co dose of $5\times10^{15}\ \mathrm{cm}^{-2}$ grown for 3 h with 1 h reduction. The nanotubes are uniformly sprayed over the substrates and tend to form a tangled structure. The yield of the nanotubes increases slowly with the implantation dose. CNTs grown on the sample for 2 h with a dose of $5\times10^{16}\ \mathrm{cm}^{-2}$ are depicted in Figs. 2(a) and 2(b). It can be seen that the purity of the CNTs is quite high, no amorphous carbon and graphitic debris were found. The tubes tend to aggregate which is similar to that from the sample with a dose of $5\times10^{15}\ \mathrm{cm}^{-2}$. Since $CoSi_2$ precipitates are resistant to oxidation,[12] we have grown CNTs without prereduction. In Fig. 3, we present the SEM results of a sample grown for 3 h without the reduction process, the Co implantation dose is $5\times10^{16}\ \mathrm{cm}^{-2}$. The nanotube yield is as high as that with reduction. However, the quality is not as good as that with prereduction. The average nanotube diameter is also about 15 nm, but it has a broader distribution. This can be considered as the following. Besides deoxidation, the precipitates coarsen during reduction, the coarsening and coalescence effect is expected to be reduced at deposition time. Therefore, the grown tubes' diameter will show a more uniform distribution. Generally, the coarsening and coalescence effect accompanied the growth. The movement and aggregation of the precipitates led to the coarsening and clustering of the tubes. This process continued to the end of the deposition, but it is stronger at the beginning of the growth, especially for the sample without the reduction process. Hence, CNTs grown with no prereduction are easy to cluster and will show a nonuniform distribution of the tube size.

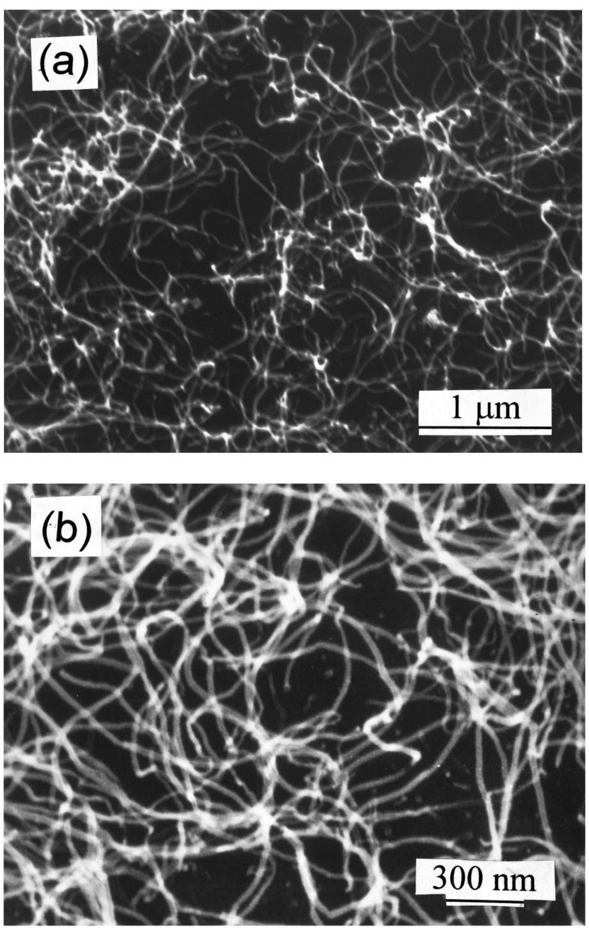

FIG. 2. Low-magnification (a) and high-magnification (b) SEM image of the carbon nanotubes grown for 2 h, reduced for 1 h on cobalt-implanted silicon with a dose of $5\times10^{16}\ \mathrm{cm}^{-2}$.

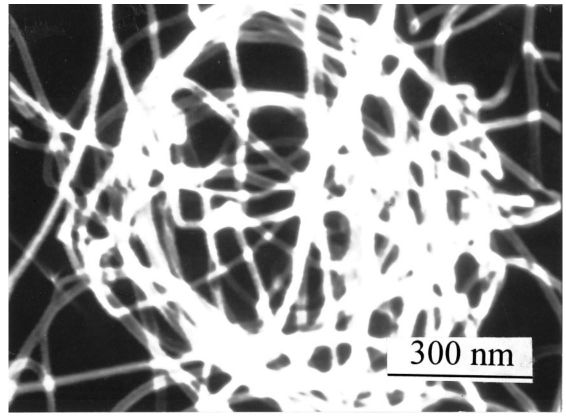

FIG. 3. SEM image of carbon nanotubes from a sample grown for 3 h without the reduction process. The Co implantation dose is $5\times10^{16}\ \mathrm{cm}^{-2}$.

The specimens for TEM (H-9000, NAR) analysis were prepared by dissolving the deposit in ethanol. After ultrasonic treatment, a drop of the liquid was then sprayed to a holey carbon copper grid. Well-defined graphitic fringes were observed from the HRTEM images of the tubes grown with the reduction process (not shown). The outer periphery of the tube was coated by a layer of amorphous carbon, which is the ordinary phenomenon observed in the tubes produced by the catalyst thermal decomposition method, where a relatively low temperature (about 700 °C) was used during reaction. A typical HRTEM image of the tube grown without prereduction is shown in Fig. 4, and graphitic fringes can be seen too. However, the direction of the veins was tilted with respect to the axis of the tube. This may be due to the coarsening and coalescence effect during CNT growth as mentioned above. Microarea Raman scattering spectrum of a typical sample deposited with the reduction process is displayed in Fig. 5. The experiment was conducted in a Renishaw equipment. The spectrum of the deposit shows two

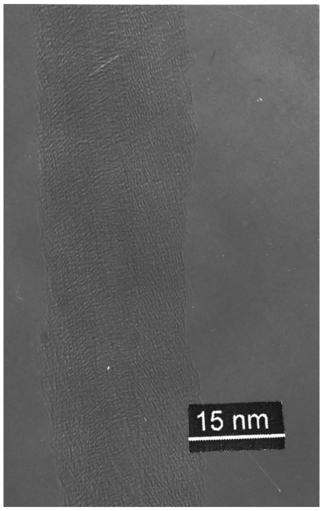

FIG. 4. High-resolution TEM image of a carbon nanotube from the sample deposited without the reduction process.

clear peaks at 1324 and 1587 cm^{-1}. The relative intensity of the two peaks and the narrower half width of them indicate a good degree of sp^2 to sp^3 bonding.[6]

In summary, carbon nanotubes with high quality have been obtained on cobalt-implanted silicon by thermal decomposition of hydrocarbon. This indicates that $CoSi_2$ precipitates embedded in a silicon matrix are a good catalyst for the production of carbon nanotubes. For the point of view of application, the growth of nanotubes on $CoSi_2$ embedded in silicon is particularly useful since $CoSi_2$ is a suitable candidate for wide applications in microelectronic devices such as contact materials, gate electrodes, and interconnects. It is interesting to resolve the nanotubes grown from each type of the precipitate since the A type is coherent while the B type is semicoherent. This can be studied by TEM cross-section investigation, and such work is under progress in our laboratory.

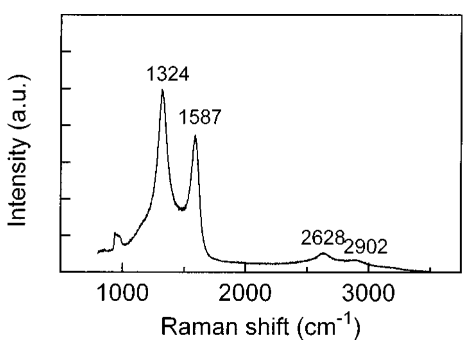

FIG. 5. Raman scattering of the carbon nanotubes grown on a sample with the reduction process, the implantation dose is 5×10^{15} cm^{-2}.

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