Selective nucleation and growth of carbon nanotubes at the $CoSi_2/Si$ interface

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A patterned $CoSi_2/Si$ substrate was used for the catalytic growth of carbon nanostructures and nanotubes in the temperature range of 750–800 °C, using acetylene/N_2 as a reaction mixture flowing through a quartz tube at ambient pressure. Selective nucleation confined to the $CoSi_2/Si$ interface region was achieved. Scanning electron microscopy and transmission electron microscopy were used to investigate the grown nanostructures. © *2000 American Institute of Physics.*
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Carbon nanotubes (CNTs) discovered by Iijima[1] at the beginning of this decade have remarkable electronic and mechanical properties.[2] Indeed, scanning tunneling spectroscopy (STS) measurements confirmed the theoretical predictions regarding the electronic structure of single-wall carbon nanotubes (SWNTs).[3,4] More recently, several groups produced nanometric field-effect transistors (FET) from SWNTs,[5,6] and from deformed multiple-wall carbon nanotubes (MWCNTs).[6] The procedure used to manufacture these nanometric electronic devices consisted of predeposition of gold electrodes on a SiO_2 substrate over which a few droplets of a suspension obtained by ultrasonicating a CNT containing material in some organic solvent were deposited.[5,6] After the evaporation of the solvent, a random arrangement of CNTs lays over the gold contacts. CNTs bridging two or more contacts were used to demonstrate FET-like operation.[5,6] However, the large contact resistance arising not only from technological issues but also from the differences of the basic properties of the CNTs and Au,[7] may seriously question whether the manufacturing of nanodevices via this route will be used in practical applications. Another possible application which seems to turn into industrial devices is the use of carbon nanotubes as electron emitters.[8–11]

While the growth mechanisms of the CNTs still remain unclear, different production techniques have been established. Among these techniques, a few have been optimized for the synthesis of SWNTs,[12,13] which are made of one single rolled sheet of graphene. These methods yield good quality SWNTs for scientific purposes but their up-scaling to industrial size is not straightforward. CNTs synthesized by catalytic thermal decomposition of acetylene by Co, or other supported transition-metal nanoparticles[14] is more likely to be the industrial route. Recently, the synthesis of SWNTs by a volatile catalyst-based procedure was reported.[15]

To manufacture devices from carbon nanostructures, two distinct ways may be developed: (i) to produce large amounts of nanostructures by a suitable procedure, then to purify and to size select the as-grown material, after which, by some technique like self-assembly, to deposit in a controlled way the selected nanostructures to the desired location; and (ii) to grow the carbon nanostructures directly at the desired location. The second approach may have several advantages: it eliminates time-consuming and costly procedures, like purifying, size selection, etc., and the not quite straightforward manipulation of a large number of nanostructures in a reasonably short time. An additional advantage of the second approach could be the fact that the contact between the CNT and the conducting pad is much less ill defined than compared with the first case.

Several attempts have been made to control the nucleation and growth site of CNTs. Co thin films evaporated onto quartz were patterned by laser ablation. Placing the patterned substrate in a two-zone oven and using Ar as the carrier gas to carry the decomposition product of 2-amino-4,6dichloro-s-triazine, the growth of parallel oriented CNTs was observed at the ablated edges.[16] A mixture of $Fe(NO_3)_3 \cdot 9H_2O$, MoO_2, and alumina was deposited through a mask onto Si, and the patterned substrates prepared in this way were placed in a furnace heated to 1000 °C, and methane was used as the carbon source. The growth of carbon nanotubes was observed all over the pattern.[17] Recently, plasma-enhanced hot-filament chemical-vapor deposition of well-oriented carbon nanotubes by using thin films of Ni on glass as catalytic substrates was reported.[18] None of these procedures seems to be easily compatible with standard microelectronic technologies. The only procedure reported up to now

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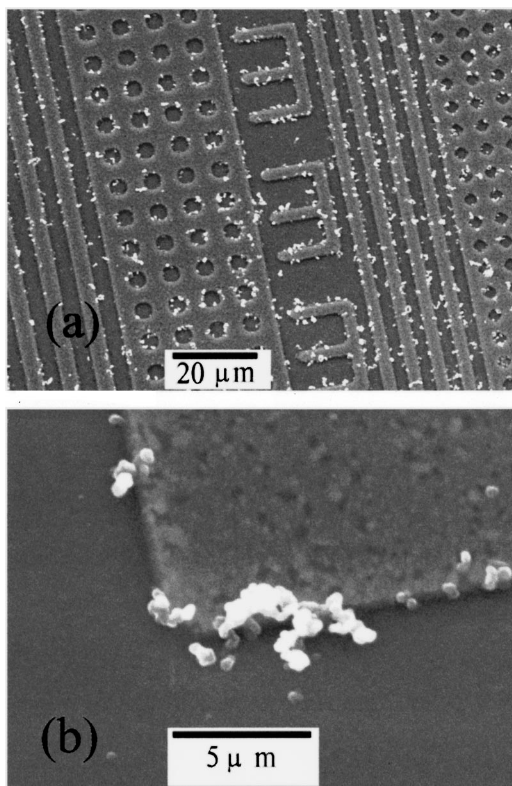

FIG. 1. SEM image of the patterned $CoSi_2/Si$ after the catalytic growth of carbon nanostructures at 750 °C. (a) Large-scale image; note that nucleation occurred and growth started only where the $CoSi_2/Si$ interface was exposed by etching; (b) detail of (a) showing the interface region and carbon nanostructures with typical diameters in the 500 nm range.

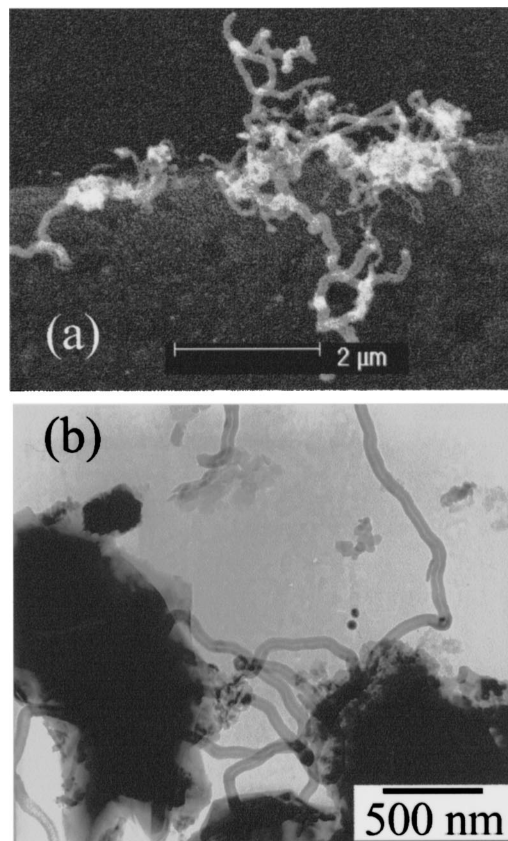

FIG. 2. Carbon nanotubes grown at 800 °C. (a) SEM image of the $CoSi_2/Si$ interface and tubular nanostructures with typical diameters in the 50 nm region; (b) TEM image of carbon nanotubes separated from the substrate by ultrasonication in toluene. Note the lighter (hollow) central channel. The presence of dust particles in the image (spongy black material), is a consequence of not carrying out the experiments in a clean room environment.

for *in situ* CNT growth, under conditions compatible with microelectronic technology, is the work of Mao *et al.*[19] They used a continuous $CoSi_2$ layer produced by high-dose ion implantation into Si. Except the work reported in Ref. 17, the other procedures yielded multiwall carbon nanotubes. In this letter, we report on $CoSi_2$ patterns prepared on Si by a succession of steps common in microelectronic technology, and used in catalytic growth experiments in a similar experimental setup as that reported in Ref. 14. Our aim was to achieve the selective nucleation and growth of carbon nanostructures and of nanotubes selectively at the $CoSi_2/Si$ interface.

A 50-nm-thick Co film was evaporated from an e-beam heated target onto Si substrates followed by *in situ* annealing at 800 °C for 20 min, to produce a $CoSi_2$ film. The patterning of the $CoSi_2$ film was achieved by standard photolithographic techniques followed by ion etching. After the removal of the photoresist, a step height of 160 nm was measured from the top of the $CoSi_2$ layer to the Si substrate exposed by etching. In this way, the $Si/CoSi_2$ interface is ''revealed'' over the Si surface. The patterned substrates were placed in a quartz-tube reactor in a flow of N_2 inside a preheated oven at 750 °C. After the temperature of the substrates equilibrated with the furnace, acetylene was introduced in the carrier gas flowing through the quartz tube. The flow rates were 300 cm^3 N_2/min, respectively, 40 cm^3 C_2H_2/min. The reaction time was 60 min.

After the reaction was completed, the substrates were examined by scanning electron microscopy (SEM). The grown carbon nanostructures were separated from the substrate by ultrasonication in toluene for transmission electron microscopy (TEM) examination. The suspension was dried onto TEM grids covered by amorphous carbon. As shown in Fig. 1(a), the selective nucleation of carbon nanostructures was achieved. The growth started only in the regions where the $Si/CoSi_2$ was revealed by etching, nucleation was observed neither on the Si, nor on the $CoSi_2$ surfaces. A further observation is that nucleation was more frequent at straight edges as compared with the round features having negative curvature. The detail in Fig. 1(b) shows that the average size of the grown nanostructures is in the range of 500 nm.

The increase of the reaction temperature by 50 °C favors the formation of tubular structures, like the ones shown in Fig. 2(a). In Fig. 2(b), TEM images are shown for similar structures where one can clearly observe the hollow core. This offers a possible tool to tune the type of grown structures by changing the reaction conditions and eventually the gas mixture, too. In the present experiment, we used only two reaction temperatures separated by 50 °C, however, the long tubular furnace used to carry out the growth allows an accurate temperature control within 1 °C. A more detailed exploration of the temperature range of 700–800 °C could reveal intermediate structures. In order to control the tube diameter and chirality, which determine the electronic structure of the carbon nanotubes, further investigations are needed. The direction in which the tubes grow may be influenced by applying an electric field during the growth,[20] or by investigating the nucleation and growth of carbon nanotubes

on different crystalline planes of the silicide/Si interface. Many silicides,[21–23] including $CoSi_2$,[24,25] can be grown epitaxially on Si. Knowing the wafer orientation, one can choose the orientation of the interface with respect to the Si crystal.

In summary, carbon nanostructures were selectively grown at the $Si/CoSi_2$ interface without nucleation occurring on Si or $CoSi_2$. The growth procedure is technologically simple and compatible with standard semiconductor technologies. The characteristics of the grown nanostructures can be modified in a convenient way by slight modifications of the reaction conditions. This may offer the possibility for growing tailored nanostructures.

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