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COMMUNICATIONS

Assembly of Metallic Carbon Nanodots Aligned on a Vicinal Si(111)-7×7 Surface

Jiajun Mao, Xiang Yang Kong,* Dan Wang, and Zhiqiang Zou

School of Materials Science and Engineering and Center for Physical and Chemical Analysis, Shanghai Jiao Tong University, Shanghai, 200030, P. R. China

Received November 23, 2006; E-mail: xykong@sjtu.edu.cn

Self-assembly of nanostructures with ordered arrangement on the step edges of a vicinal silicon surface has attracted substantial attention[1] and has been demonstrated in several systems, including Au atomic chains, Si atomic wires, periodic clusters, and SiC nanodots arrays.[2] These nanostructures grown using templates of sharp silicon step edges with uniform and controllable size are of potential applications in single-electron transistors, ultra-high-density storage media, and bionanosensors.[3] In this Communication, we report that pure carbon deposited on a vicinal Si(111)-7×7 surface can assemble into a nanodot array along the sharp step edges with a size ranging from 5 to 30 nm. These nanodots perform a metallic transport on the p-type silicon.

We carried out the assembly of carbon nanodots on vicinal silicon surfaces in an ultra-high-vacuum (UHV) apparatus with a base pressure of 10^{-10} Torr. The p-type Si(111) substrates with resistivity of ~0.01 Ωcm were used for deposition. The vicinal silicon (111) surface with sharp and parallel step edges was first reported by the Himpsel group.[4] We prepared the substrate by flashing at 1260 °C for 10 s. We quenched it to 800 °C in a few seconds to skip the coexisting phase between the 1 × 1 and the 7 × 7 reconstructions around 860 °C. Then, the substrate was annealed at 800 °C for 10 h with dc current in the direction parallel to the step edge to produce the straight-step array. A pure graphite rod (purity 99.99%) was used as the source of electron-beam evaporation, the deposition rate was controlled at ~0.04 monolayer (ML)/min (1 ML = 7.8×10^{14} atoms/cm^2), and the substrate temperature was held around 600 °C. The original silicon(111) reconstruction surface and carbon deposited surfaces were observed by Omicron scanning tunneling microscopy (STM) in the UHV apparatus at constant current mode at sample biases between −2 and 2 V and a tunneling current of 0.20−0.25 nA. All STM images were recorded at room temperature. The carbon deposited sample was examined by ultraviolet (UV) micro-Raman to identify bonding structures of carbon nanodots on the silicon surface. Raman spectra were taken by a Renishaw microprobe RM1000B with a 514-nm Ar ion laser at a laser power of 1−2 mW, with light polarized linearly along the step-edge direction.

Figure 1a shows the STM image of the Si(111) surface after carbon deposition for 1 h around 600 °C. It can be seen that the carbon atoms accumulate and aggregate into nanodots aligned on the sharp and parallel step edges of the vicinal silicon surface. The nanodots have a size ranging from 5 to 30 nm and a height ranging from 0.8 to 3.5 nm and the density is ~200 μm^{-2}. The formation of the three-dimensional (3D) nanodots is stimulated by the mismatch between C and Si lattice constants (Volmer−Weber growth mode).[5] From the 3D topographic images shown in Figure 1c, we see that the nanodots exhibit a pyramid-like morphology and clear facets, which means that the nanodots are crystallized. With the increase of deposition time, for example 90 min, the density of carbon nanodots increases rapidly to ~300 μm^{-2}. They have a tendency to align along certain directions in the terraces of the Si(111)-7×7 surface, but the size of nanodots remains almost the same as does the pyramid-like morphology with clear facets (Figure 1d). Around the pyramid-like carbon nanodot, there are little defects and vacancies in the Si(111)-7×7 surface, indicating that no local Si atoms have been extracted out to incorporate into the nanodots (see Supporting Information).

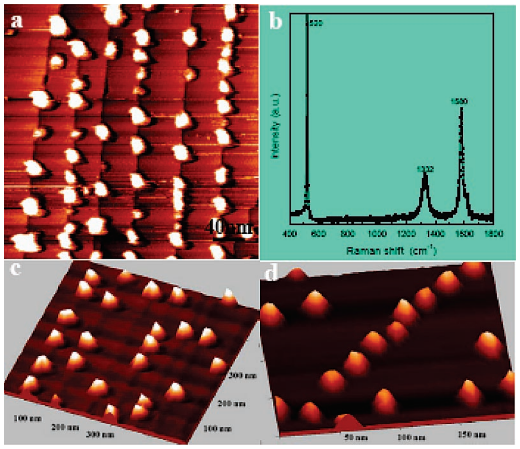

Figure 1. (a) STM image of carbon nanodots aligned on the sharp step edges of a vicinal Si(111)-7×7 surface. (b) Typical UV micro-Raman spectrum recorded from a carbon-deposited silicon surface. Panels c and d are the 3D topographic images of pyramid-like carbon nanodots aligned on the step edges and on the terrace of the silicon surface, respectively.

Raman spectroscopy is effective for identifying bonding structures of carbon-based materials.[6] Figure 1b shows the typical Raman spectrum taken from the carbon deposited Si(111) surface with the density of ~300 μm^{-2}. It is very clear that two significant Raman peaks at 1332 and 1580 cm^{-1} originate from the carbon nanodots, and the reference peak at 520 cm^{-1} originates from the pure silicon substrate. In general, the prominent Raman peaks of graphite and diamond at the ambient conditions are identified at 1581 and 1332 cm^{-1}, respectively. Here, we do not find any other obvious peaks from other materials, such as silicon carbide. It is possible that the SiC phase is minor in our case and could not be detected by Raman spectroscopy. We also find that the spectrum is fairly sharp and does not show any other diffuse band between 1140 and 1450 cm^{-1}. This indicates that the nanodots are in the crystalline state on the Si(111)-7×7 surface and are free of amorphous carbon.

The growth parameters play a critical role in the formation of the ordered carbon nanodot array on the Si(111)-7×7 substrate. If the deposition temperature is lower than 500 °C, the carbon atoms are difficult to nucleate along the step edge and aggregate into nanodots because of relative low mobility. On the contrary, the higher deposition temperature (normally above750 °C) makes the landing carbon atoms energetically reacted with Si atoms on the surface and aggregated into large islands. The step edges are etched

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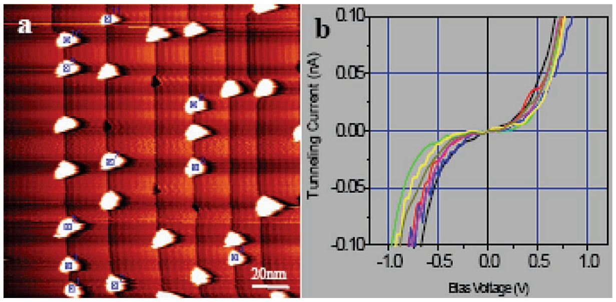

Figure 2. STM image (a) and corresponding scanning tunneling spectra (STS) (b) of carbon nanodots aligned on the step edges of a vicinal Si(111)-7×7 surface, showing metallic transport behavior.

into irregular kinks.[7] In our case, the deposition temperature is selected at about 600 °C. The reaction between the deposited carbon atoms and surface silicon atoms has been prohibited around the nucleation sites, and the step edges remain straight. The sharp step edges easily capture the deposited carbon atoms and promote an alignment growth along the step edges. The size distribution of nanodots ranging from 5 to 30 nm corresponds to the thermodynamic fluctuation during growth.

For the transport performance of carbon nanodots aligned on the step edge of a p-type silicon surface, we systematically recorded the scanning tunneling spectra (STS) from individual nanodots. Figure 2 shows the STM image of carbon nanodots aligned on the step edges of the Si(111)-7×7 surface as well as the measured STS on top of the nanodots marked in the left panel. It is clear that the I−V curves recorded from individual nanodots exhibit a nonzero slope even close to $V = 0$, indicating the metallic character of nanodots. It is known that 3C−SiC is a semiconductor with a band gap of ~2.4 eV, and diamond exhibits a wide band gap of 5.5 eV. On the basis of the Raman spectra as well as STM images, the nanodots are not SiC but likely to be a pure carbon-based material with a mixture of sp3 and sp2 carbon bonds and show the pyramid-like configuration with clear facets. It is assumed that the ideal structure of the nanodots is a nanodiamond with fullerene-like surface reconstruction or a bucky diamond cluster.[8] It should be noted that the surface reconstruction of nanodiamond in an ultra-high-vacuum environment with a fullerene-like surface gives rise to the surface conduction. Thus, the carbon nanodots we addressed here exhibit the properties of this structure, showing the facet configuration as well as metallic transport behavior. The carbon nanodots array can be used to immobilize DNA or protein structures and thus has a potential application in the field of nanobiotechnology.[9]

Interestingly, after flash heating the silicon substrate by using a dc current along the step edge direction at ~900 °C for 20 min, we find that most carbon nanodots deposited on the silicon surface were erased from the step edges, as shown in Figure 3. The step edges become clean and the terrace still preserves a fairly good 7 × 7 reconstruction, as shown by the inset of Figure 3b. It is believed that the electromigration of surface atoms occurred during the flash heating. The electromigration can not only ascend the kinks and lead to the straight step[10] but also drive the carbon nanodots migrating out along the step edges. Work is underway to induce the evolution of nanostructures or create novel nanostructures by the manipulation of electromigration.

In summary, we report the assembly of carbon nanodots aligned on the step edge of a Si(111)-7×7 reconstruction surface. The reactions between carbon atoms and surface silicon atoms have been retarded because of the relatively low-deposition temperature in an ultra-high-vacuum system. The UV micro-Raman spectra clearly indicate that the nanodots dominantly are a carbon-based nanostructure rather than silicon carbide. STS measurements show that the carbon nanodots exhibit a metallic behavior. The carbon nanodots could be erased from the step edges, while keeping a fairly good 7 × 7 reconstruction surface. The self-assembled and well-aligned pyramid-like carbon nanodots on Si substrates would be of potential applications for single electron transistors or bio-nanosensors.

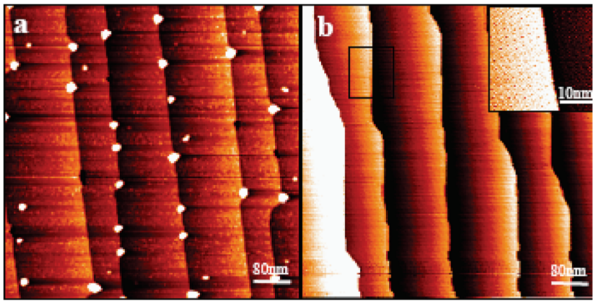

Figure 3. (a) STM image of carbon nanodots aligned on the step edges of Si(111)-7×7 (growth conditions: deposition time, 30 min; substrate temperature, 600 °C). (b) After flashing at 900 °C for 20 min, carbon nanodots are erased from the step edges. The inset shows the well-ordered 7 × 7 reconstruction surface and the sharp step edge.

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Supporting Information Available: STM images, STS spectra, Raman spectra for carbon nanodots deposited on a vicinal silicon(111) surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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