Si nanowire growth with ultrahigh vacuum scanning tunneling microscopy

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Si nanowire growth with ultrahigh vacuum scanning tunneling microscopy

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Using a scanning tunneling microscope (STM), Si nanowires were grown by applying a voltage at a constant current between a Si substrate and a gold STM tip. Silicon atoms were deposited onto a gold tip by field evaporation. The field evaporation rate of silicon atoms was activated by heating the substrate. Silicon nanowire was grown on the gold tip at a substrate temperature of 700 °C. Nanowires could not be grown on a clean tungsten tip when using a gold-free Si substrate. The presence of gold atoms is important for the growth of silicon. Apparently, gold atoms deposited on the silicon substrate by field evaporation reduce the activation energy of field evaporation by attacking Si–Si bonds. © *1997 American Institute of Physics.* [S0003-6951(97)04214-9]

Scanning tunneling microscopes (STM) provide a new approach to nanostructuring techniques by taking advantage of a variety of tip-sample interactions. Fabrication techniques of nanoscale wires were developed for applications such as STM tips, quantum wires, quantum dots, and field emitters. Electron-beam-induced deposition (EBID) has been demonstrated as a new technique to fabricate a three-dimensional nanostructure on a surface.[1] EBID is caused by the dissociation of adsorbed molecules on the surface. However, the deposition contains impurities from the original precursor with this technique. Whisker growth is another technique of fabricating nanowires. For example, vapor liquid solid (VLS) growth has been used for fabricating Si whiskers.[2] Atoms were supplied from the gas phase in these techniques.

On the other hand, the field evaporation method is useful to extract atoms from a surface. Field evaporation is a phenomenon in which atoms are ionized and extracted from a surface by a high electric field.[3] Thermally activated field evaporation rate is given by an Arrhenius equation. On the other hand, it is reported that there is some probability of extracted atoms depositing on a tip.[4] If the temperatures of the apex of the tip and substrate are different, the field evaporation rate becomes higher on the high temperature side than on the low temperature side. For this reason, it is expected that nanostructuring is made possible by depositing atoms on the low temperature side owing to field evaporation.

Figure 1 shows the tendency of the activation energy Q versus melting point T_M. It is plotted in case of a singly charged ion at zero electric field about many materials. This graph shows that the activation energy decreases with decreasing melting point. Field evaporation occurs at the surface, while the melting points are a bulk property. Therefore, we cannot simply discuss the relation between the activation energies and the melting points. However, a method for decreasing the activation energy may be suggested. For example, the melting point of Si–Au alloy is lower than that of Si and Au, because Si–Au alloy can form eutectic as shown the phase diagram[5] in Fig. 2. Therefore, it is expected that the activation energy of the field evaporation decreases by depositing gold atoms on the silicon surface. We tried nanostructuring by depositing silicon atoms on a gold tip by field evaporation.

The ultrahigh vacuum scanning tunneling microscope (UHV-STM)(JOEL JAFM-4500XT) was operated in a base pressure of 2×10^{-10} Torr. Scanning electron microscopy (SEM) is mounted on the UHV-STM chamber to monitor a tip. The substrate that mounted on a holder is attached to a piezo actuator. This piezo actuator can be moved along the direction perpendicular to the substrate for up to 3 μm, and it is thermally insulated by ceramics, so thermal drift is reduced. Si(100) substrate (P doped n type 0.02 Ω cm) was heated by flowing direct current. Surface oxide was removed by heating the substrate at 1400 K for 30 s in UHV. The electrochemically etched gold tips or tungsten tips were used. The tips were cleaned by heating in UHV. The temperature of the substrate was monitored by a pyrometer.

For nanostructuring of silicon, positive substrate voltage was applied between the gold tip and the clean silicon substrate by heating the substrate at 700 °C, and then the tip was held at constant tunnel current for a few minutes. The applied sample voltage was 5 V and the tunneling current was 10 nA. The voltage was applied for a period of 15 min. The tip-sample distance was 6 Å under the above condition (5 V, 10 nA). The deposition on the gold tip could be monitored by *in situ* SEM.

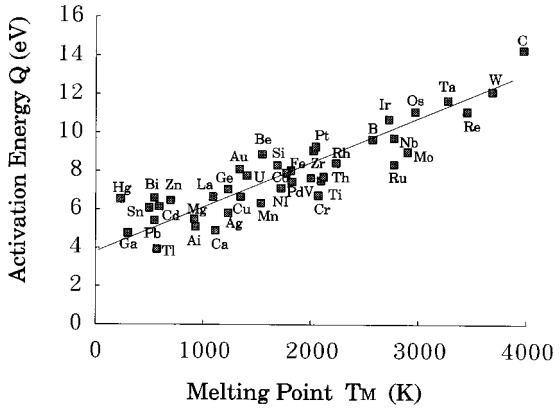

FIG. 1. The relation of activation energy vs melting point. It is plotted in the case of a singly charged ion at zero electric field about many materials. This graph shows that the activation energy decreases with decreasing melting point.

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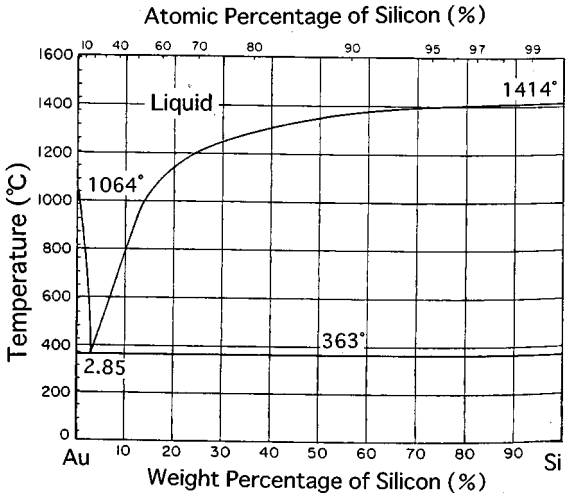

FIG. 2. The phase diagram of silicon-gold alloy (see Ref. 5).

Figure 3 is a transmission electron microscope (200 kV TEM HITACHI HF-2000) image of the deposition. The image shows that the deposition has a wirelike structure. The diameter and length of the wire were approximately 20–150 nm and 3 μm, respectively. Usually, the diameter of the deposition becomes narrower as the growth continues. Features of the deposition, length, diameter, and shape were different in each experiment. Still more, it was difficult to measure the growth rate instantaneously, because the piezo actuator was slightly drifted owing to thermal conduction from heating the substrate to the piezo actuator during the above procedure.

Figure 4 shows a dark SEM image of the wire. Bright spots were found on the wire surface in Fig. 4. Energy-dispersive x-ray analysis (EDX) revealed the composition of the grown materials. At the bright spot, gold was 15 at. % and silicon was 85 at. %. At another point, gold was only 2% and silicon was detected 98%. Electron diffraction patterns obtained at 200 keV show diamond structure. The lattice constant is almost consistent with that of bulk silicon. It is found that the wire consists of silicon, and gold precipitated on the wire surface. Figure 5 shows a magnified TEM image of the wire at point 3 of Fig. 3. This image shows that the wire is crystalline.

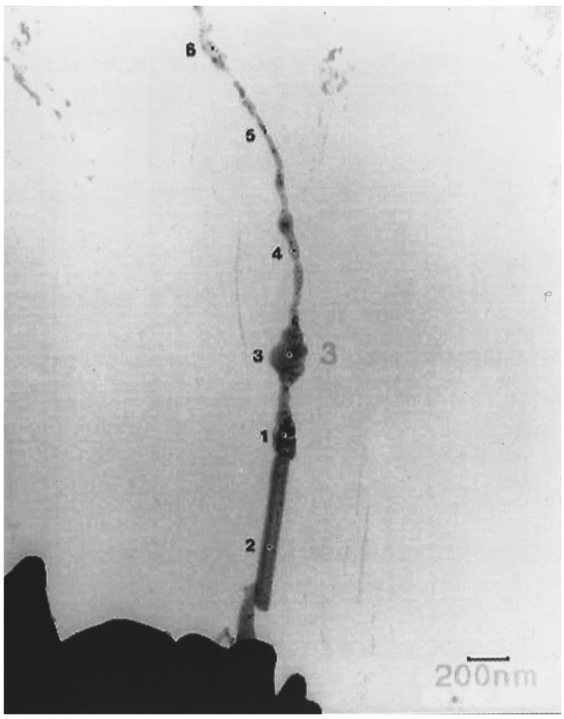

FIG. 3. TEM image of silicon nanowire grown on a gold tip. The diameter and length of the wire were approximately 20–150 nm and 3 μm, respectively. The applied sample voltage was 5 V and the tunneling current was 10 nA for 15 min. Substrate was heated about 700 °C.

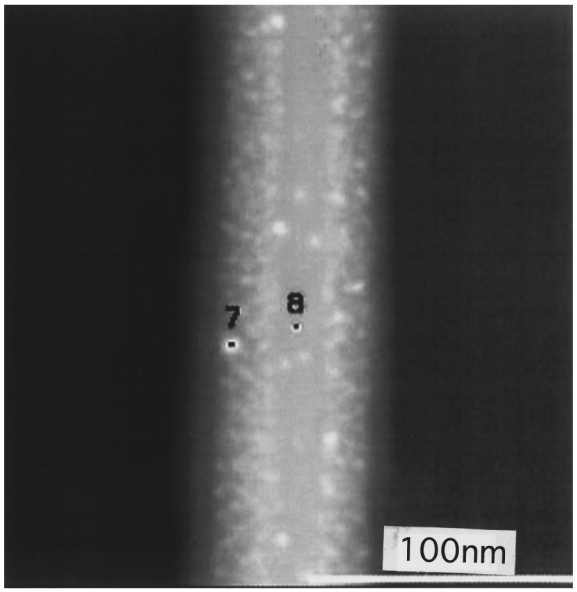

FIG. 4. Dark SEM image of nanowire. Bright spots are analyzed to be gold by EDX.

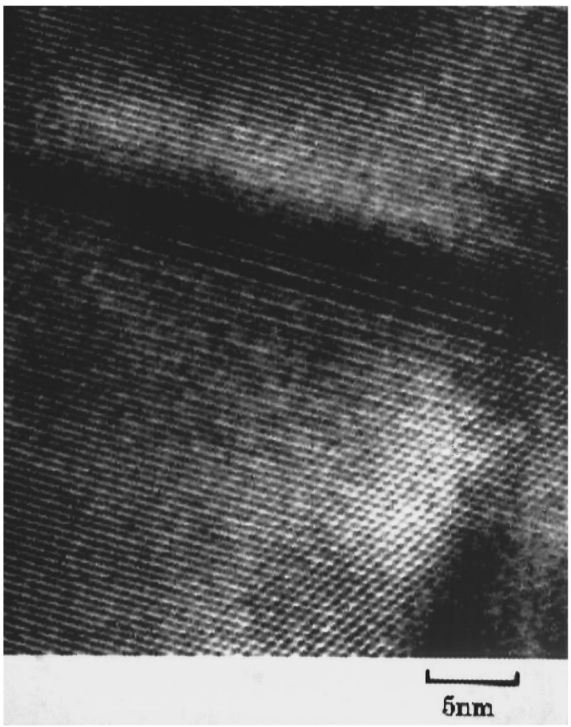

FIG. 5. Magnified TEM image of wire at point 3 in Fig. 2.

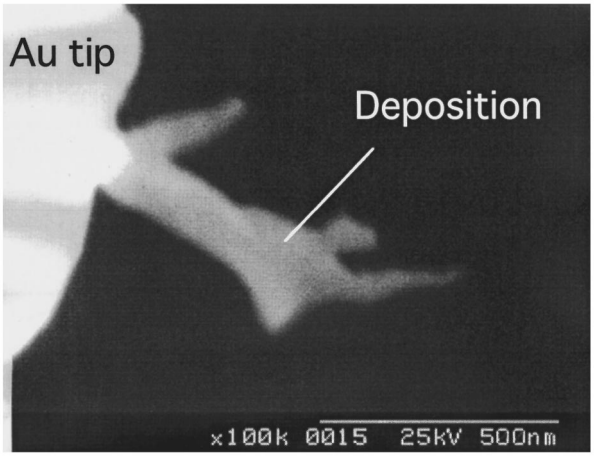

FIG. 6. SEM image of silicon nanowire. The wire is occasionally split as the growth continues.

Usually, the deposition forms a wire. However, a wire is occasionally split as the growth continues (Fig. 6).

When a gold film (3000 Å thick) formed Si(100) substrate and a tungsten tip were used, Si nanowire was grown by applying a voltage of 5 V between the tip and the substrate. The tunneling current was kept at 10 nA for 15 min, and the substrate was heated at 700 °C. The deposition was not observed with the tungsten tip and a gold-free silicon substrate.

Growth of Si wire is a result of atom transfer from a substrate to a tip. There are some possibilities of atoms transferring as following the two mechanisms: (1) mechanical contact between the tip and the substrate and (2) field evaporation. We could not observe any traces on the substrate and any changes on the tip except for the deposition. Still more similar experiments as described earlier was performed by applying a bias of 0 V at 0.1 nA to check possibility of mechanical contact. Consequently, deposition was not observed on the tip apex by the SEM. Thus, we considered that the wire was not grown by mechanical contact.

Next, we discuss the possibility of structuring the nanowire by field evaporation. In experiment, the maximum growth rate was 6.0 nm/s, and the maximum diameter of the wire was 150 nm. The deposition rate was 2.1×10^{7} (atoms/s). It was reported that the threshold field for desorption is about 1 V/Å in Si atoms,[3] and 0.4 V/Å in Au atoms[6] at room temperature. In our experiment, electric field is about 1 V/Å. However, it is not explained that many silicon atoms were deposited by field evaporation, even if the substrate was heated. We consider that the gold atoms reduce the activation energy of field evaporation, because Au atoms diffuse into the bulk and attack Si–Si bonds. Field-evaporated atoms were deposited and migrated on the tip surface. Field evaporated atoms have enough energy to be crystallized, because the wire was crystallized. It suggests that the activation energy for desorption be very low. Above a temperature of 800 °C, deposition cannot be observed, however, it is assumed that Au atoms diffused into the bulk completely. The mechanism of nanowire growth may be similar to that of whisker growth given vapor–liquid–solid (VLS).[2] The VLS growth can be distinguished into four main steps: (1) mass transport in a gas phase; (2) chemical reaction vapor–liquid interface; (3) diffusion in the liquid phase; and (4) incorporation of material in a crystal lattice. However, we could not recognize Au–Si liquid phase at the apex of wire. It is desirable to make a close experiment into growth mechanism.

Au atoms were field evaporated from the gold tip and deposited on the Si substrate at the beginning of the nanowire growth. We consider that the activation energy decreased, because Au atoms formed eutectic with Si. Au atoms play an important role for the nanowire growth.

In summary, Si nanowire was grown on the apex of the tip with UHV-STM. Si atoms are transferred from silicon substrate to the tip by field evaporation. The field evaporation was induced by applying constant voltage between the tip and the substrate at constant tunnel current. The substrate heating thermally activates the field evaporation rate on the substrate surface, which leads to deposit of Si atoms on the tip apex. In this procedure, field evaporation of Si atoms is supposed to be enhanced by forming Au–Si eutectic on the substrate.

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