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Arrangement of Catalyst Islands at Surface Atomic Steps toward Position Control of Nanowires

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1. Introduction

Semiconductor nanowires are attracting intense attention as building blocks of future nanoscale electronic and optoelectronic devices [1]. To pursue their application, we have to produce nanowires with controlled size, structure, and position. This is critically related to the control of the metal catalyst used in nanowire formation based on the vapor-liquid-solid mechanism. Gold is one of the most widely used metal catalysts, and there have been some attempts at controlling Au in this role [2].

In this paper, we present another approach to controlling the size and position of Au islands. In this approach, surface atomic steps are used as templates for island formation. The islands act as catalysts for the fabrication of vertical nanowires aligned in one dimension. This method does not involve any "top-down" lithographic techniques; it is a pure "bottom-up" self-assembly method. Self-assembly has potential advantages of low cost, large scale, high quality, and so on, but there still remain lots of problems to be solved, especially in the controllability of the size and position of nanostructures. We hope that our approach will greatly contribute to establishing self-assembled nano-device fabrication methods.

2. Experimental

We monitored Au island formation on Si(111) surfaces *in-situ* in real time using a commercial low-energy electron microscopy (LEEM) system (Elmitec LEEM III) [3]. Chemically cleaned Si(111) samples were introduced into the UHV through a load lock. The samples were annealed by *e*-beam bombardment and cleaned by flashing at 1200°C. Au was deposited from a W filament, and the typical deposition rate was $2\text{-}3\times10^{-3}$ monolayers (ML) per second.

Nanowire growth was carried out in a low-pressure (76 Torr) horizontal metalorganic vapor phase epitaxy (MOVPE) reactor [4]. Trimethyl-gallium (TMGa) was the group III source, and PH_3 was the group V source. The carrier gas was palladium-diffused H_2, and the flow rate was 6.0 *l*/min. The flow rate of TMGa was 1×10^{-5} mol/min and the V/III ratio was 46.

3. Results and discussion

To obtain Au islands arranged at atomic steps, we deposited Au on Si(111) in two stages; at high (~700°C) and then low (~400°C) temperatures. During the Au deposition on a clean 7×7 surface, the surface structure changes from 7×7 to 5×2 and to √3×√3. These surface structures have different surface Si atom densities. Therefore, during the transformation, the step shape may become rough or two-dimensional islands may even form. Therefore, we first deposit Au at relatively high temperatures around 700°C in order to obtain regular straight step arrays on the √3×√3 surface.

In the second stage, Au was deposited on the √3×√3 surface at around 400°C. During the deposition, the surface structure changes from √3×√3 to 6×6, which corresponds to the Au coverage of 0.96 ML [5]. Three-dimensional (3D) islands simultaneously form at the steps a short time after the completion of the 6×6 structure. The island density steeply increases as the deposition temperature decreases, but the islands finally nucleate even on the terraces. The temperature control is critical in obtaining a high density of islands only at the steps.

Figure 1 shows a LEEM image obtained during Au deposition at 420°C. Single-layer steps run vertically with the average spacing of 400 nm. All the 3D islands are lined up along the steps. Additionally, because the islands nucleate within a narrow coverage window, they have a narrow size distribution, and their sizes can be precisely

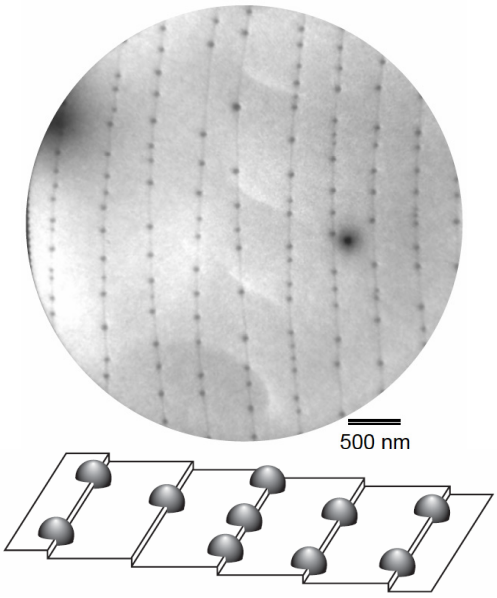

FIG. 1. LEEM image of Si(111) during Au deposition at 420°C and a schematic illustration of the surface. The electron energy for imaging was 2.7 eV. The large dark spot on the right side is a defect in the microchannel plate.

controlled by the growth time. We obtained a 9% relative deviation in island height on one sample using *ex-situ* atomic force microscopy (AFM) measurements. This value is comparable to that of the colloidal Au particles used for the diameter selective synthesis of nanowires [6].

So far we have mentioned nothing about the structure of the islands, but the Au-Si binary phase diagram, which displays a eutectic point with a eutectic temperature of 363°C and 18.6 atom % Si [7], indicates that the 3D islands should be Au-Si alloy droplets at the growth temperature. To confirm this, we interrupted the Au deposition to reduce the number of islands, and then restarted the deposition. Figures 2(a) and 2(b) show LEEM images before and during the redeposition. These images clearly show that islands move with trails left behind. *Ex-situ* AFM images, as shown in Fig. 2(c), clarify that the trails are trenches 20-30 nm wide and a single layer deep. Si atoms are incorporated into the 3D islands during the Au deposition. Considering their mobility, we conclude that the 3D islands are Au-Si alloy droplets. Real-time LEEM observations also showed that the islands move on terraces at almost constant velocities, but when they approach the upper-side steps, they quickly move to the steps. The atomic steps provide stable positions for Au-Si alloy islands, which helps them to arrange at the steps.

After the Au-Si alloy island formation, the samples were removed from UHV to air, and were introduced into the MOVPE reactor without any special treatments. Before the TMGa and PH_3 supply, the samples were annealed to around 500°C in H_2 ambiant. First, TMGa and PH_3 gasses were co-supplied for 5 seconds, then the TMGa supply was stopped and the temperature was decreased to around 470°C. Finally, the TMGa gas was supplied for one minute.

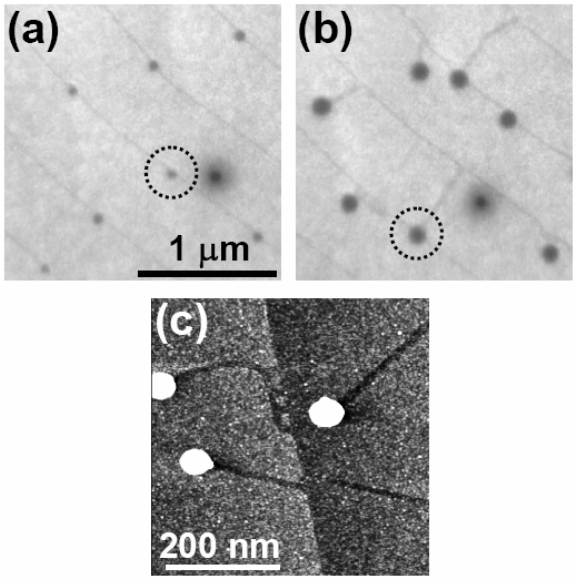

FIG. 2. (a)-(b) LEEM images of Si(111) before and during Au deposition at 420°C. The nominal coverages of Au were (a) ~1.03 and (b) ~1.43 ML. The same island is indicated by the dotted circle. (c) *Ex-situ* AFM image of Si(111) after deposition of ~1.65 ML of Au.

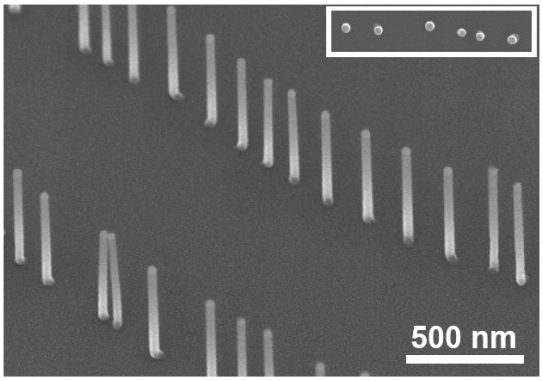

FIG. 3. An SEM image of GaP nanowires viewed from the direction inclined 38° from the surface normal. Inset shows the top view.

Figure 3 shows a scanning electron microscopy (SEM) image of vertical nanowires self-arranged in lines with the length of several micrometers. We confirmed that these are GaP wires using cross-sectional transmission electron microscopy, energy-dispersive X-ray spectroscopy, and photoluminescence. One-dimensional alignment of the wires proves that the Au-Si alloy islands arranged at the steps can be used as catalysts for nanowire formation. On this sample, about 80% of wires were vertically and orderly grown. The SEM images also show that the wires have fairly constant length and diameter. By evaluating several ten typical wires, the length and diameter at the middle of the wire were found to be 612±17 nm, 34±5 nm, respectively.

4. Conclusions

We showed that the position and size of Au-Si alloy islands can be controlled by using atomic steps on Si(111) as templates for island formation. One-dimensional alignment of vertical GaP nanowires was achieved using these islands as catalysts. Intentional doping and heterostructure formation as well as the optimization of the growth conditions are our next targets. Gold is also widely used to attach functional molecules. The Au-Si alloy islands could be used to integrate various functions, which are unavailable from Si, on Si substrate.

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