Formation and evolution of self-assembled crystalline Si nanorings on (001) Si mediated by Au nanodots


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(Received 2 May 2005; accepted 27 September 2005; published online 21 November 2005)

The growth of high-density Si nanorings has been achieved on ultrathin Au films on silicon substrate. Nanorings, which are gold-free and epitaxially grown on (001) Si, had a narrow distribution of height and diameter of 1.4±0.3 and 24.9±4.0 nm, with a density of 4.3×1010 cm−2. In situ ultrahigh-vacuum transmission electron microscopy revealed that the formation of nanorings involves a mechanism mediated by Au nanodots and evaporation of Au-Si eutectic liquid droplets at high temperature. The process promises to be an effective nanofabrication technique to produce high-density and uniform-sized nanorings. © 2005 American Institute of Physics. [DOI: 10.1063/1.2136219]

Nanorings, which are artificial nanoscale clusters that confine electrons in three dimensions, are attractive due to their unique physical properties of large, negative exciton permanent dipole moment, high oscillator strength for the ground-state band-to-band transition, possible tunable electronic states, and optical emission from a charged single nanoring. Nanorings of various materials have been fabricated, especially for III-V compound semiconductors based on the thermodynamic and kinetic growth models. However, the investigations on Si-based nanorings have been scarce.

Recently, Hobbs and co-workers have fabricated the amorphous Si (a-Si) nanorings by using Ar+ sputter redeposition in porous alumina templates. With the presence of Coulomb correlation, the so-called Aharonov-Bohm effect of excitons exists in a finite (but small) width of nanoring. When the width of the ring becomes large, the non-simply-connected geometry of nanorings is destroyed and in turn yields the suppression of the Aharonov-Bohm effect. Therefore, nanorings need to scale down to exhibit the size effects.

In the present study smaller, steeper, and higher density Si nanorings than those obtained previously were formed with the mediation of Au nanodots. In order to elucidate the detailed formation mechanism of nanorings, in situ ultrahigh-vacuum transmission electron microscopy (in situ UHV-TEM) and cross-sectional transmission electron microscopy (XTEM) have been conducted. Nanorings were epitaxially grown along the [001] direction on silicon. In situ UHV-TEM was applied to visualize the processes occurring at surfaces in real time and is therefore capable of providing detailed information about reaction mechanisms of nanostructures in a clean environment. Video imaging enables us to track the dynamical development of nanorings from Au-Si eutectic droplets, evaporated at high temperature. The formation mechanism for the nanorings has been found to involve a process mediated by Au nanodots by in situ UHV-TEM investigation.

Single-crystal, 3−5 Ω cm, phosphorous-doped (001) Si wafers were used in the present study. Si wafers were cleaned chemically by a standard Radio Corporation of America (RCA) cleaning process. A 2-nm-thick Au thin film was then deposited onto Si substrates at room temperature in an electron-beam evaporation system. The vacuum was better than 5×10−6 Torr during the deposition of ultrathin Au films. For the formation of Au nanodots, rapid thermal annealing (RTA) was employed in a high-purity N2 atmosphere at 400 °C for 30 s. Finally, the samples were placed into a tube furnace. After the tube had been evacuated for several hours to remove O2 from the system by a rotary pump to a pressure of 1×10−3 Torr, the samples were heated to 1050 °C at a rate of 5 °C/min and held at 1050 °C from 5 s to 2 h in an ambient with Ar+5% H2 flowing through the tube.

The morphology of the Si nanorings was examined by atomic force microscopy (AFM) (D3100, Digital Instruments) in tapping mode. Dynamical changes of nanorings have been investigated by in situ UHV-TEM. The in situ system is based on a JEOL 2000 V UHV-TEM (base pressure 3×10−10 Torr). Electron-transparent Si specimens were used as substrates for the growth. The specimens were cleaved from 200 μm thick (001) Si wafers and chemically etched to thin down the samples until a hole was developed at the center. They were then cleaned by degassing at 700 °C for 10 h and flashed at 1000 °C for 2 min under UHV so that the surfaces were atomically clean. After cleaning, the electron-transparent area was typically several microns across with no contamination. The depositions of ultrathin Au films on electron-transparent substrates were carried out in a UHV pretreatment chamber. The specimens were then transported into UHV-TEM without breaking the vacuum. The samples were heated from room temperature to 1050 °C in a specially designed heating holder inside the TEM for examination. For the energy dispersive spectrometer (EDS) analysis, the electron beam can be converged to as small as 1.5 nm in size. The XTEM micrographs were taken along the [110] zone axis of single-crystal Si.

Au nanodots, 12 nm in average size, were formed on Si substrate in the samples annealed at 400 °C for 30 s. After annealing at 1050 °C, surface morphologies were observed to change drastically. A typical AFM image reveals the formation of a high density of ring-shaped nanostructures in a sample after annealing for 2 h, as shown in Fig. 1(a). EDS
measurements revealed that the surface is free from Au. The density of nanorings was determined to be about $4.3 \times 10^{10}$ cm$^{-2}$. In addition, nanorings have a narrow distribution of height and diameter of $1.4 \pm 0.3$ and $24.9 \pm 4.0$ nm, respectively. In comparison, the size distribution and density of α-Si nanorings fabricated using Ar$^+$ sputter redeposition of material in a porous alumina mask were 50 nm in inner diameter, 10–15 nm in wall thickness, and had heights ranging from 50 to 200 nm and $1.4 \times 10^{10}$ cm$^{-2}$, respectively. As a result, smaller- and higher-density crystalline nanorings were formed with the mediation of Au nanodots.

To find the role played by the Au nanodots in forming nanorings, the samples were annealed at 1050 °C for 5 s. From the examination of a sample near the boundary between the regions with and without the presence of Au nanodots, it is clear that the formation of nanorings is mediated by Au nanodots. Distinct nanoring structures with residual and shrunk Au nanodots were observed in the region with Au nanodots, as shown in the right region of Fig. 1(b). In contrast, in the neighboring region without Au nanodots, smooth surface features remained, as shown in the left region of Fig. 1(b). Figure 1(c) further highlights the surroundings of the remaining Au nanodots on the samples. The role played by the Au nanodots was further clarified by the atomic images of XTEM samples annealed at 1050 °C for 5 s. Figure 2 shows the burrowing of Au nanodots into the silicon substrate. The Au nanodot was observed to be surrounded by the Si nanoring, as seen in the inset of Fig. 2. The atomic image reveals that the Si nanoring is grown epitaxially on [001] Si.

The evolution of the formation of nanorings was elucidated by in situ UHV-TEM observations. Images captured from the video were acquired for the same region so that the dynamic development of nanorings from Au-Si eutectic droplets was observed, as shown in Fig. 3. The liquid Au-Si alloy droplets are expected to form on the surface of Si substrate at a temperature above the eutectic temperature of the Au-Si (363 °C). After the sample was flashed at 1000 °C for cleaning in a pretreatment chamber, the Au islands were formed, as shown in Fig. 3(a). The Au-Si liquid droplets underwent a growth-coarsening process and change in shape during the observation, as seen in Figs. 3(b)–3(f), indicating a change in surface tension resulting from the variation in composition. Lower density of droplets was observed after prolonged annealing. Most of the Au-Si droplets remained and did not migrate away after prolonged annealing at such a high temperature. In contrast, Au-Si droplets were seen to migrate over several micrometers upon cooling from 900 °C in a previous in situ scanning electron microscopy (SEM) study. It is remarkable that most Au-Si droplets faded away suddenly instead of coalescing with one of their neighbors in 2 min at 1050 °C under UHV. The disappearance of Au nanodots was rather abrupt instead of gradual with time. It suggested that the diffusion of Au atoms into Si should not be
the dominant cause of disappearance of Au nanodots. Owing to the lack of experimental data on vapor pressure of Au-Si eutectic alloy at 1050 °C (near the Au melting point: 1063 °C), the vapor pressure of Au-Si eutectic alloy is deduced from the vapor pressures of the Au and Si by linear interpolation herein. The Clausius–Clapeyron equation, applicable to both liquid/gas or solid/gas equilibrium curves, is used to determine to vapor pressure with annealing temperature,11

$$\ln \frac{P_2}{P_1} = -\frac{H_{\text{evap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right),$$

where $H_{\text{evap}}$ is enthalpy of vaporization (J/mol), $R$ is the gas constant and equal to 8.3145 (J/mol K), $T$ is temperature in K, and $P$ is vapor pressure in Torr. The enthalpies of vaporization boiling points of Au and Si at 760 Torr are 330 kJ/mol and 2856 °C and 359 kJ/mol and 2900 °C, respectively. Therefore, the vapor pressures of Au and Si are calculated to be $2.3 \times 10^{-5}$ and $4.1 \times 10^{-6}$ Torr at 1050 °C, respectively. It can be inferred that the evaporation of Au-Si alloy is severe inside the UHV chamber with a pressure of $3 \times 10^{-10}$ Torr at 1050 °C during the in situ investigation. The observation is consistent with the EDS measurement that no Au peaks were detected in XTEM and plane-view TEM samples of nanorings after annealing. Although it is possible that the evaporation rate of Au is different in the UHV environment inside the UHV-TEM and gas ambient in the tube furnace, the morphology of nanoring structures remaining the same indicates that the same formation mechanism is operating. As a result, it is concluded that the Au nanoparticles evaporated and left behind a nanoring structure at 1050 °C.

As seen in Fig. 1(b), the size distribution of Au nanodots is rather large. On the other hand, the nanorings have a narrow size distribution. It is likely that the ripening process during the annealing, prior to the nanoring formation, causes a narrowing of dot size distribution. Indeed, it is seen in Fig. 3(b) that the size distribution of Au nanodots has narrowed down to 21.1±3.1 nm after annealing at 1050 °C for 14 s. In addition, if the Au nanodots are too small in size, it may evaporate without leaving a trace of nanorings as demonstrated in a previous work.12

From the SEM, in situ TEM, and XTEM observations, a clear picture emerges for the formation of Si nanorings, different from previous suggestions for SiGe nanorings. Upon high-temperature annealing, diffusing Si atoms migrated rapidly toward the liquid Au-Si droplets. As the Au-Si droplets became supersaturated, precipitation of Si atoms occurred at the Au-Si/Si boundaries. The precipitation promoted protrusions of Si surrounding those of Au-Si droplets to form ringlike nanostructures. At the same time, the evaporation of eutectic Au-Si droplets at the centers of nanorings progressed. The Au-Si eutectic droplets shrank further and eventually disappeared. As a result, Si nanorings, free from the Au atoms, were formed. The scenario is consistent with the finding of a previous study that the surface-migrating Si atoms were incorporated into Au nanodots resulting in the formation of eutectic Au-Si droplets, and then precipitated at the interface of eutectic Au-Si droplets. Precipitated Si atoms grew into epitaxial Si nanorings on the underlying substrate at high temperature.13

A previous work showed that self-assembled Si$_{0.3}$Ge$_{0.7}$ nanorings can be fabricated on Si$_{0.3}$Ge$_{0.7}$/Si substrates with a similar procedure.7 A parallel study also revealed that high-density, small-size Si$_{0.3}$Ge$_{0.7}$ nanorings can be produced on Si$_{0.3}$Ge$_{0.7}$/Si substrates by applying the same practice.14 The present work further demonstrates the creation of Si nanorings with the mediation of Au nanodots on silicon. The combined achievements indicate that the nanorings with a wide range of Si-Ge compositions can be readily fabricated with a simple process. In contrast, the nanorings formed in Si-capped Ge quantum dots on (001) Si are varied in composition, which depends on the preceding condition, and difficult to control.15 The availability of Si-Ge nanorings with a wide range of concentrations promises to serve as a useful platform for the fundamental understanding of nanorings. The result may open up the possibility for practical applications.

In summary, high-density, small-size epitaxial Si nanorings have been grown on ultrathin Au films on silicon substrate. The formation of Si nanorings was found to be mediated by the Au nanodots. The evolution of nanorings was further clarified by in situ UHV-TEM, SEM, and XTEM observations. Upon high-temperature annealing, Si atoms were rapidly incorporated into the Au nanodots to form Au-Si alloy droplets. Once the Au-Si droplets became supersaturated with Si atoms, the precipitation of Si atoms occurred at the Au-Si/Si interface and resulted in the formation of ring-shaped Si nanostructures. In the meantime, the severe evaporation of the Au-Si alloy droplets, which resulted from high vapor pressure at high temperature, led to the shrinkage and eventual disappearance of Au-Si droplets. Finally, the nanorings free from Au were formed.

The research is supported by the Republic of China National Science Council Grant No. NSC 92-2112-M-029-011 and Ministry of Education Grant No. 91-E-FA04-1-4.