Formation of Au nanoparticles on the surface of Si nanowire

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The evolution of Au nanoparticles on the sidewall surface of Si nanowires has been investigated by thermal treatments using high resolution transmission electron microscope and high angle annular dark field scanning transmission electron microscope. At first, the Si nanowire grown at 550 ^{o}C using Au catalyst by rapid thermal chemical vapor deposition and has been observed to be surrounded by Au nanoparticles with less than 5 nm in diameter and ~10^{12} cm^{-2} in density on the whole of Si nanowire surface. The Au nanoparticles on the Si nanowire are annealed at the temperature range of 700 – 900 ˚C for 20 min, performed ex situ to explore the size change of Au nanoparticles. From the high-magnification HAADF-STEM image, the Au nanoparticles on the surface are stably located in the substitutional sites. The size distribution represented Gaussian distribution with the average size of 4 nm, 6 nm, and 7 nm for 700, 800 and 900 ˚C. In addition, the distribution for high temperature above 900 ˚C is changed to a bimodal distribution. The activation energy by which make the small Au nanoparticles change to the larger nanoparticles is calculated. Surface diffusion rate of Au NPs on Si NW greatly slow down as compared with bulk substrate due to the substitutional diffusion mechanism.

Because of a large active surface area compared with a film, silicon nanowires (Si NWs) are promising candidates for key building blocks of applications in future nanoscale electronics, optical devices, and biosensors.[1] In this work, we demonstrated the evolution of the Au NPs on Si NW surface by the thermal treatments. The Si NW with a uniform and high density of Au NPs (< 5nm) has been grown at 550 ˚C by rapid thermal chemical vapor deposition (RTCVD). To study the control of Au NPs, the Si NWs was annealed in nitrogen ambient at various temperatures and the transition of Au NPs was investigated by means of high resolution transmission electron microscope (HR-TEM) and high angle annular dark field scanning transmission electron microscope (HAADF-STEM). The evolutions in transition of Au NPs size by thermal energy were explained through the activation energy calculated from Arrhenius plot of the particle diffusivity as a function of 1/T.

Figure 1 shows the HAADF-STEM and HR-TEM images of the Si-NW with the length of ~5 μm and the diameter of ~100 nm annealed at 700 ˚C using the standard annealing furnace. It was confirmed that there are the abundant NCs on the whole surface of the Si-NW in the previous work.[2] To explore the evolution of Au NPs on the surface of Si NW, we have carried out the *ex-situ* annealing at 700, 800, and 900 ˚C for 20 min at nitrogen ambient after removing growing Au tip by a Au etchant (see the HAADF-STEM image of Fig. 1(a)). An in-depth study taken from the magnified HAADF-STEM and HR-TEM images in the middle part *l* shows that while as-grown Si NW clearly has uniform coverage of Au NPs with a high number density on the whole surface of the Si NW, annealed Si NW exhibit a slight change with random size distribution of Au NPs (bright spot in HAADF-STEM of Fig. 1(b) and black one in HR-TEM of Fig. 1(c)) as a result of coalescence and Ostwald ripening during the high temperature annealing over growth temperature. The size distribution of Au NPs after annealing at 700 ˚C was 2 ~ 8 nm.

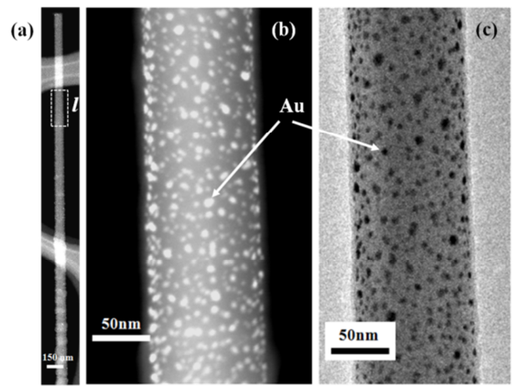

Fig.1 (a) HAADF-STEM image of Si-NW with the diameter of ~100 nm annealed at 700˚C using the standard furnace. (b) Magnified HAADF-STEM and (c) HR-TEM images of the Si-NW in the middle part *l* of (a). The bright spot in HAADF-STEM and black one show the Au NPs.

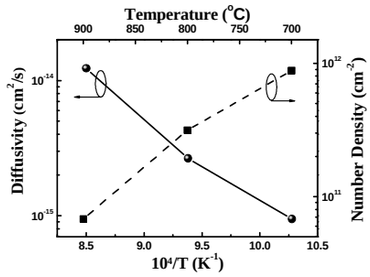

Fig. 2 Diffusivity and number density of Au NP with each annealing temperature exhibit an Arrhenius dependence on temperature.

Figure 2 shows the Au NP diffusivity and number density with the annealing temperature which exhibit an Arrhenius dependence on temperature. When the Au NPs on Si NW surface start to diffuse by means of the thermal activation energy, the activation energy is carried out from jump rate theory. The activation energy E_a and the diffusion-prefactor D_0 of Au NP was calculated by fitting the particle diffusivity data to an Arrhenius expression to be 1.31 ± 0.23 eV and 5.01 × 10^{-9} cm^2/s. Surface diffusion rate of Au NPs on Si NW greatly slow down as compared with bulk substrate due to the substitutional diffusion mechanism as well as unusual structure like the nanowire.

Therefore, it is supposed that the surface diffusion of Au NPs on Si NW surface may be affected by the substitutional diffusion mechanism, and the surface diffusion rate is greatly slower than it on bulk substrate.

[1] Gao X.P.A., Zheng G.F. & Lieber C.M., 2010. Nano Lett. **10**, 547(2010).
[2] G.S. Park., et al., Nano Lett. **12**, 2176(2012).

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