Silicon Nanowires Wrapped with Au Film

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In an attempt to provide ohmic contacts to silicon nanowires (SiNWs), SiNWs wrapped with Au film have been fabricated. Au particles were deposited on the as-grown SiNWs and followed by electron beam annealing under transmission electron microscopy (TEM). The high-resolution TEM (HRTEM) study showed the transformation of the Au particles into crystalline Au film. The uniformity of Au film was dependent upon the size and the separation of the Au particles.

Introduction

Silicon nanowires (SiNWs) are drawing much attention in recent years due to their potential applications in interconnection and basic components for future mesoscopic electronic and optoelectronic devices [1]. For this reason, the electrical conductivity of SiNWs and patterning of electrical contacts to SiNWs are major issues. Although SiNWs can be mass-produced,[2−3] it is hard to increase the electrical conductivity of SiNWs during the growth process. A number of strategies to provide ohmic contacts to SiNWs have been developed, including deposition of Ag particles on SiNWs by chemical methods,[4] or formation of metal silicide layers on SiNWs.[5] In this paper, we report a simple and effective technique to fabricate a metal thin film on the surface of SiNWs, thereby providing a good electrical contact to SiNWs.

Experimental Section

SiNWs were prepared by thermal decomposition of pure SiO powder (Aldrich, 325 mesh, 99.9%) at 1320 °C [2,3] in an evacuated alumina tube. The carrier gas consisted of 95% Ar and 5% H_2 with a flow rate of 50 SCCM and a total pressure of 500 Torr. The dark brown and spongelike SiNWs were obtained on the inside wall of the alumina tube. Two types of SiNWs were used. The first type is the as-grown SiNWs of 20−50 nm in diameter, covered with an oxide layer; the second type is the SiNWs without the oxide layer, which were removed by HF (5% aqueous solution) treatment. In both cases, the SiNWs were dispersed onto "holey" carbon TEM grids followed by double-sided deposition of Au nanoparticles by argon-ion sputtering at room temperature in a pressure of 1×10^{-2} Torr. The nanostructure of the samples was then characterized by transmission electron microscope (TEM), with a high-resolution transmission electron microscope (HREM) (Philips CM200 at 200 kV). For annealing in TEM, SiNWs were exposed to a convergent 200 kV electron beam of 32 nm in spot size and about 100−150 μA in emission current for 10−30 s.

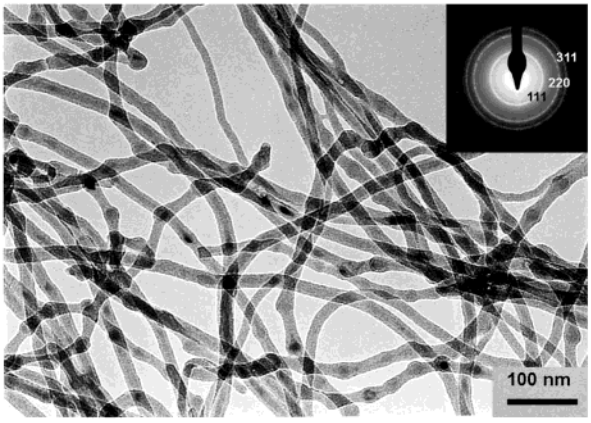

Figure 1. The as-grown SiNWs are randomly oriented nanosized crystalline silicon wires with an average diameter of 20 nm and more than 10 μm in length.

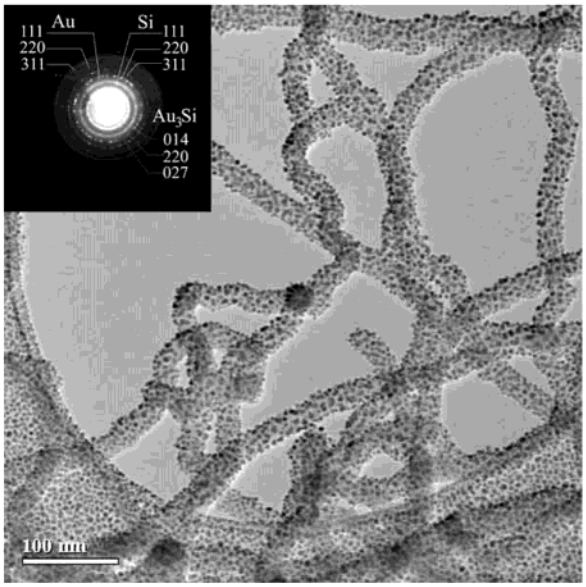

Figure 2. The SiNWs coated with Au nanoparticles. The SAED taken from this area reveals the crystalline structure of Si, Au, and Au_3Si.

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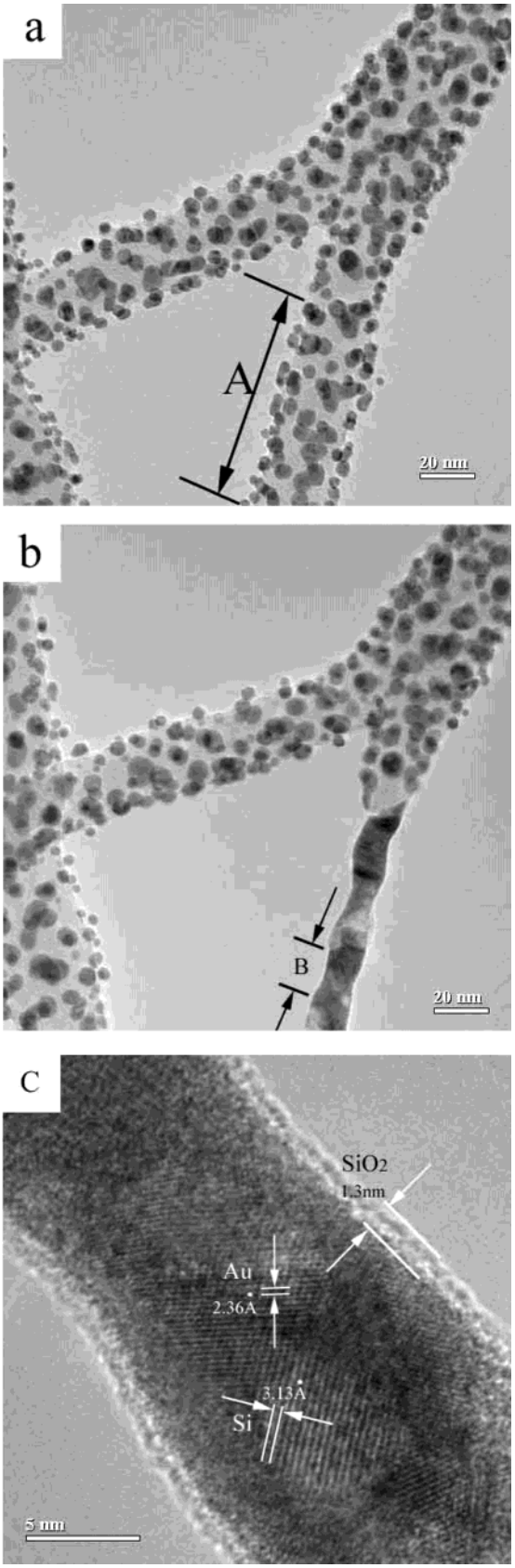

Figure 3. (a) The Au nanoparticles, with an average diameter of 5 nm, are randomly attached to the surface silicon oxide layer of the SiNWs. (b) The region marked "A" (in (a)) was annealed by the electron beam in the TEM. It can be seen that all Au particles in this region transformed into a metallic layer dramatically covering the surface of the SiNW. (c) Corresponding to region "B" in (b), a HREM image shows an Au film covering the SiNW, which is in turn covered by a SiO_2 layer of about 1 nm.

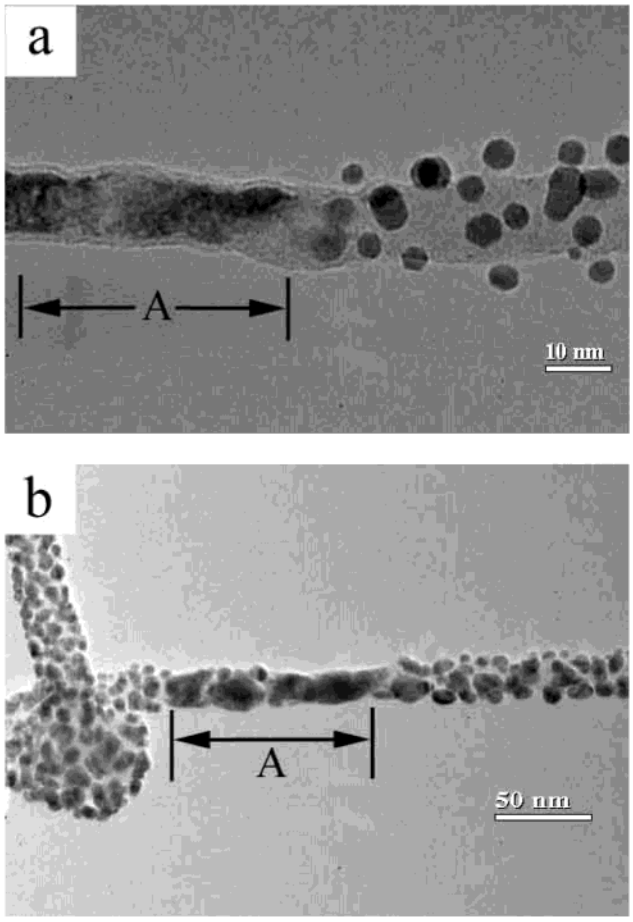

Figure 4. (a) and (b) show SiNWs coated with Au nanoparticles in 10 s and 20 s, respectively.

Results and Discussion

As shown in Figure 1, the as-grown SiNWs were randomly oriented nanosized crystalline silicon wires with an average diameter of 20 nm and more than 10 μm in length. The surface of the SiNWs was an oxide layer, probably SiO_2, of 20 nm in thickness, as previously reported.[6] A selected area electron diffraction (SAED) pattern taken from this area reveals the crystalline structure of Si (see inset). Figure 2 shows the SiNWs coated with Au nanoparticles. The SAED taken from this area reveals the crystalline structure of Si, Au, and gold silicide. Due to the similar *d* spacing of the three phases of gold silicides (Au_3Si, Au_5Si, and Au_7Si), it is difficult to identify the phase of the gold silicide in the SAED. As Chang et al.[7] reported the formation of Au_3Si by argon-ion sputtering of gold onto Si, it is likely that the gold silicide in our case is also Au_3Si.

In Figure 3a, the Au nanoparticles, with an average diameter of 5 nm, were randomly attached to the surface silicon oxide layer of the SiNWs. Most, if not all, of the Au particles were crystalline with distinct facets. Some of the Au nanoparticles, however, aggregated to form larger fused clusters. The region marked "A" was annealed by the electron beam in the TEM. It is remarkable that all Au particles in this region were transformed into a metallic layer covering the surface of the SiNW as depicted in Figure 3b. The diameter of the annealed region was reduced about 50% in comparison with the original oxide-covered SiNWs. Corresponding to region "B" in Figure 3b, a HREM image shows an Au film covering the SiNW which is in turn covered by a SiO_2 layer of about 1 nm, as shown in Figure 3c. From the lattice parameter (*d* spacing), Au and bared (uncovered) Si can be found in Figure 3c.

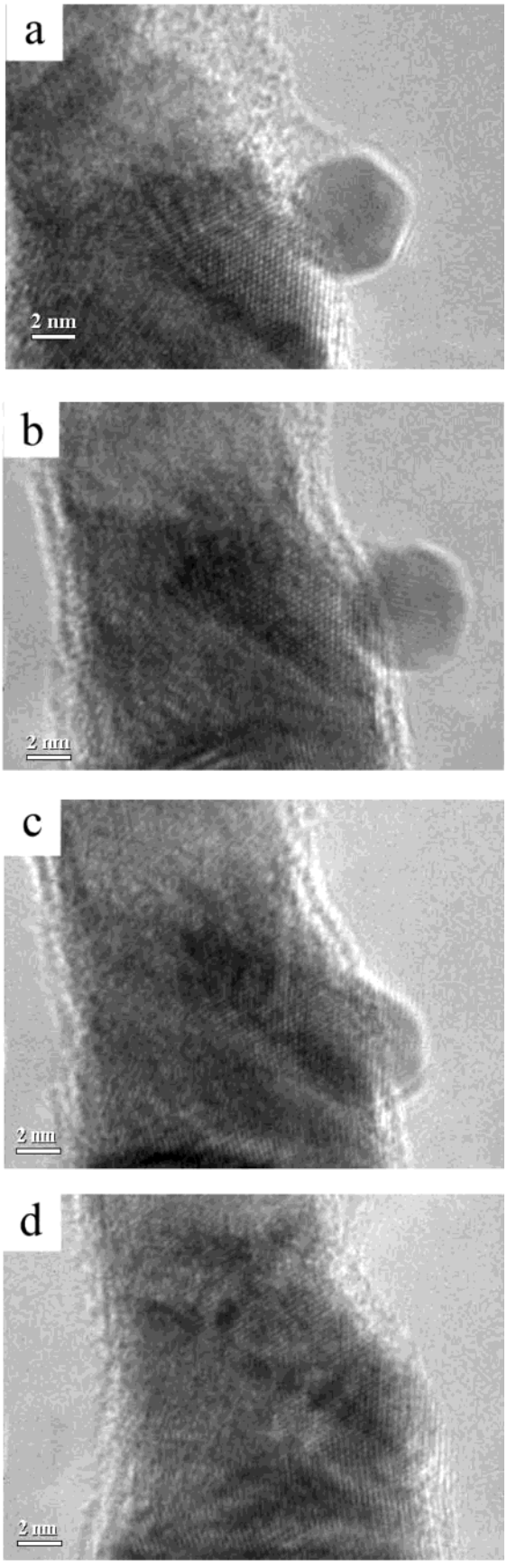

Figure 5. (a) A polyhedral Au nanoparticle, about 5 nm in diameter, was attached to the surface of a SiNW. (b) The attached SiO_2 ligand began to disappear, and the Au nanoparticle started to sink into the SiO_2 layer of SiNW. (c) Half of the Au nanoparticle merged with the existing Au film layer. (d) The entire Au nanoparticle disappeared and integrated with the existing Au film layer.

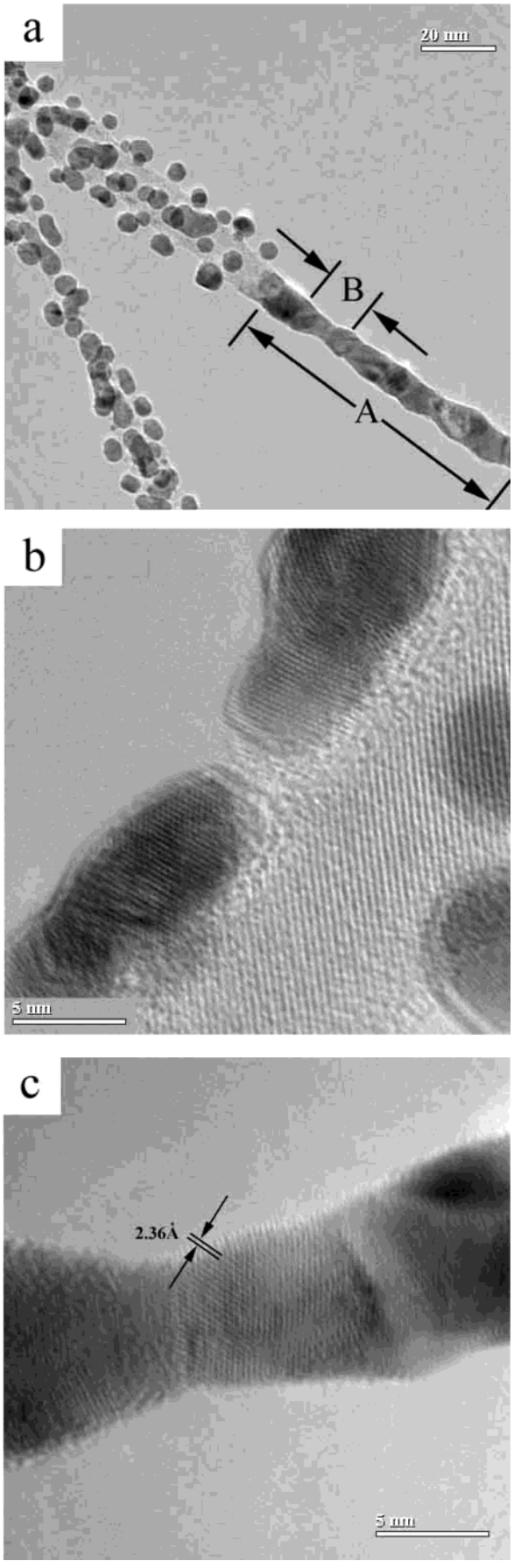

Figure 6. (a) A SiNW coated with Au nanoparticles (5 s evaporation time) with the electron beam annealed the region marked "A". (b) HREM image of the Au nanoparticles attached to the Si core. (c) HREM image of the region marked "B" in (a).

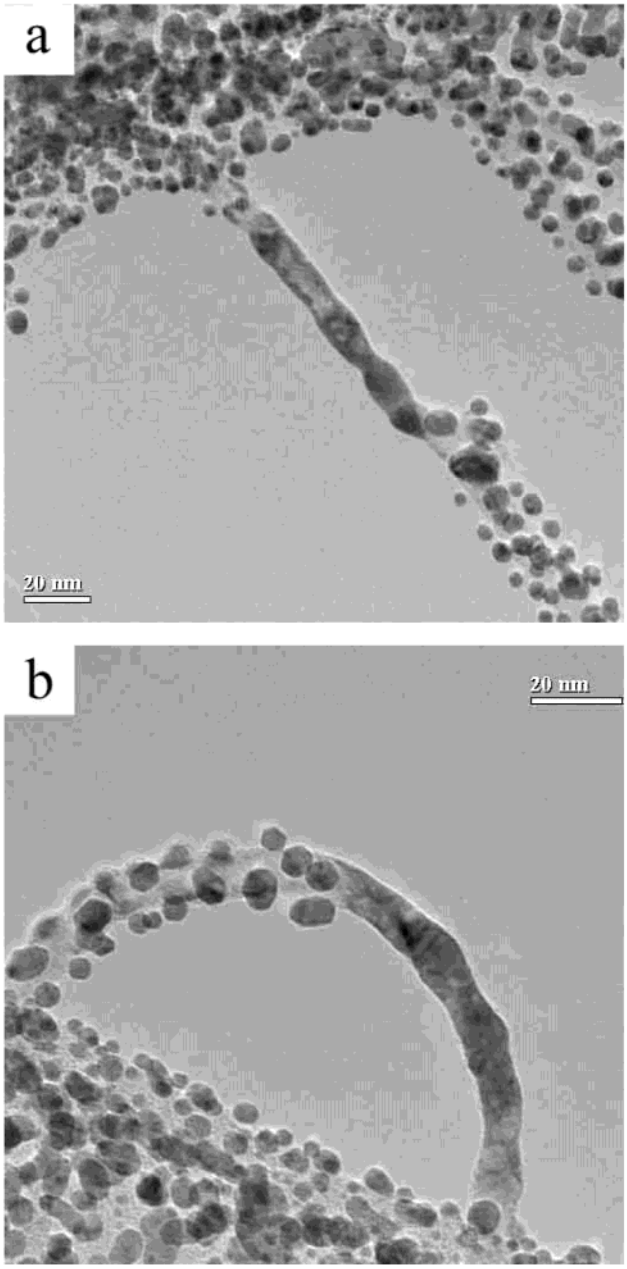

Figure 7. (a) and (b) show SiNWs coated with Au particles in 10 s and 20 s, respectively.

Figure 4, parts a and b, show the SiNW coated with Au nanoparticles by 10 s and 20 s deposition, respectively. The majority of Au nanoparticles changed shapes from symmetrical faceted nanocrystals to less symmetrical clusters. As the deposition time increased, the Au nanoparticles became densely distributed on the surface of the SiNWs and formed fused clusters as portrayed in Figure 4b. Au films were also formed after the regions marked "A" in these two figures were annealed by the electron beam of the TEM. Similar to the previous sample, the Au films in these two samples were also covered by a SiO_2 layer. However, the layers were rougher and more discontinuous as the deposition time increased.

Figure 5 shows the Au film formation process of a single SiNW when exposed under the constant converging electron beam of TEM. In Figure 5a, a polyhedral Au nanoparticle, about 5 nm in diameter, was attached to the surface of a SiNW. Part of this Au nanoparticle was covered by SiO_2 (serving as ligands). In Figure 5b, the attached SiO_2 ligand began to disappear, and

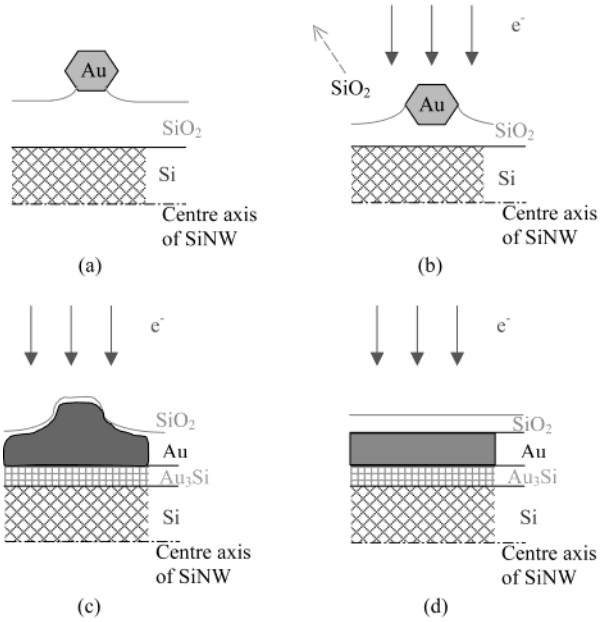

Figure 8. The mechanism of the Au film formation by annealing under the converging electron beam of TEM.

the Au nanoparticle started to sink into the SiO_2 layer of SiNW. In Figure 5c, half of the Au nanoparticle merged with the existing Au film layer. In Figure 5d, the entire Au nanoparticle disappeared and integrated with the existing Au film layer. In the process (Figure 5b−d), the Au nanocrystal reoriented itself to match the lattice orientation of the existing Au film layer.

In the second part of this study, SiNWs with the oxide layer removed (by HF treatment) were coated with Au nanoparticles. The Au deposition times were 5, 10, and 20 s. Figure 6a shows a SiNW coated with Au nanoparticles (5 s deposition) with the electron beam annealed region marked "A". The diameter of the annealed part was only reduced by less than 15% of the original diameter. Figure 6b shows a HREM image of the Au nanoparticles attached to the Si core. Some of the Au nanoparticles fused together under the electron beam of TEM. Figure 6c shows a HREM image of the region marked "B" in Figure 6a. Figure 7, parts a and b, show SiNWs coated with Au particles in 10 s and 20 s, respectively. As in the previous cases, the densities of Au nanoparticles increased with the deposition time and the Au nanoparticles aggregated to form fused clusters.

The mechanism of the Au film formation by annealing under the converging electron beam of TEM is shown in Figure 8. The Au nanoparticles were deposited on the SiO_2 layer of the SiNWs as shown in Figure 8a. In Figure 8b, as this area was exposed to the converging electron beam of TEM, some of the SiO_2 were "blown away" by the intense electron beam; some were reduced to silicon by the negatively charged electrons. This explains why the diameter of the SiNWs with oxide layer was reduced by more than 50%. The SiO_2 layer that remained was softened and wetted the attached Au nanoparticles. The surface tension provided a driving force that drew the Au nanoparticles into the oxide layer. We call this a "sinking cluster" phenomenon. In the process, some of the Au nanoparticles aggregated to form larger (fused) clusters, some reacted with Si to form silicides, possibly Au_3Si, at the interface, as shown in Figure 8c. And the Au nanoparticle started to rearrange the lattice orientation at the same time. As annealing proceeds as depicted in Figure 8d, Au nanoparticles rearranged to form a continuous Au film covering the Si or Au_3Si layer. Eventually, the SiNW was covered with an Au_3Si layer, followed by an Au layer, and a thin outermost SiO_2 layer. Other "sinking

clusters" could fuse with the existing Au film, giving rise to further growth of the film. In such a process, it was observed that sinking Au nanoparticles often reorient themselves to match the lattice of the existing Au films.

The mechanism for the Au film formation for both as-prepared and HF-treated SiNWs is probably the same, as depicted in Figure 8, except in the latter case, there is no or little oxide layer to impede Au diffusion into and interaction with the Si core of SiNWs. In both cases, the SiNWs were eventually covered with a thin layer (a few monolayers) of Au_3Si, followed by an Au film, while the as-prepared SiNWs sample was also covered with a thin layer of SiO_2.

The size and density of the Au particles appear to affect the quality of the resulting Au film covering the SiNWs. However, under similar annealing conditions, the quality of the Au film formed on the as-prepared and HF-treated SiNWs are similar in terms of crystallinity, uniformity, and composition.

It should be noted that the annealing time for Au film formation was different for SiNWs of different sizes and shape. Furthermore, the annealing time was also dependent upon the density and size of the Au nanoparticles (both of which increased with deposition time).

Conclusion

In summary, SiNWs covered with Au film have been fabricated. The formation of this type of SiNWs wrapped with a continuous Au film is expected to lead to improved electrical conductivity of SiNWs and provide selective electrical contacts to SiNWs. The size of Au particles and their separation (density) greatly affect the uniformity of the resulting Au film on SiNWs. This technique can be extended to different metals (work in progress).

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