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Reductive Growth of Nanosized Ligated Metal Clusters on Silicon Nanowires

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The reductive growth of metal clusters on silicon nanowires (SiNWs) is reported. The HF-etched SiNWs were found to reduce ligated Au–Ag clusters of single size, shape, composition, and structure. In the process, the surfaces of the SiNWs were reoxidized. The reductive cluster growth on the SiNW surface was followed by high-resolution transmission electron microscopy (HRTEM). The reduced metal clusters grew to different sizes in the nanometer regime (1–7 nm in diameter) on the SiNW surfaces. At sizes greater than approximately 7 nm, they tend to separate from the SiNW surfaces. Further growth and/or agglomeration of these colloidal particles to sizes greater than roughly 25 nm in diameter eventually causes the particles to precipitate from solution. Two interesting phenomena, the "sinking cluster" and the "cluster fusion" processes, were observed under TEM.

I. Introduction

Nanotechnology is a culmination of many facets of developments in the nanorealm, including nanofabrication, nanomachineries, quantum devices, molecular machines, molecular computers, and so forth. The first steps toward building such nanodevices are the synthesis and characterization of nanomaterials and the study of their chemical and physical properties. In this regard, the nanosized polyicosahedral mixed-metal clusters[1,2] of well-defined sizes and shapes synthesized and characterized by one of us (the UIC group) may potentially serve as building blocks for such nanodevices. The metal frameworks of these nanosized Au–Ag clusters can be described as vertex-sharing polyicosahedra. We refer to these high-nuclearity mixed-metal clusters as "clusters of clusters". This "cluster of clusters" growth pathway follows a well-defined growth sequence, from a single icosahedron with 13 atoms ($s_1(13)$) to an icosahedron of 13 icosahedra with 127 atoms ($s_{13}(127)$). The early members of the vertex-sharing polyicosahedral mixed-metal clusters are portrayed in Scheme 1. These ligand-protected nanosized metal particles are of interest in that they exhibit quantum-size effects with properties highly dependent upon the size, shape, structure, and composition of the metal core. We now wish to combine these nanoclusters, which may be considered as zero-dimensional "nanodots," with one-dimensional "nanowires". It is believed that the fabrication of such metallic nanodots on, for example, semiconducting nanowires will eventually lead to new and novel composite materials of importance in nanotechnology.

Because silicon is of great technological importance in microelectronics and considerable advances have been made recently on the fabrication, characterization, and properties of semiconducting silicon nanowires (SiNWs) in the nanosize

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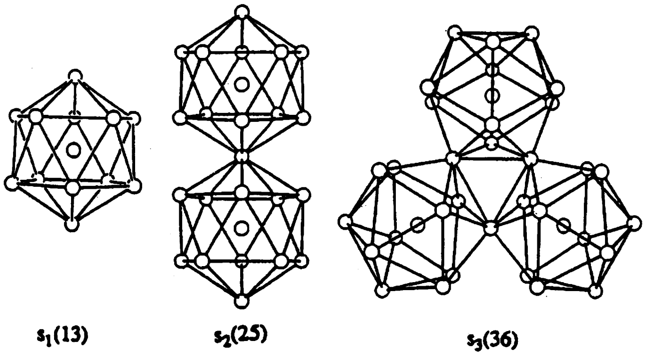
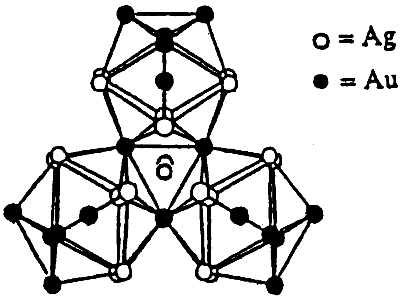
Scheme 1



regime,[3−17] we decided to utilize SiNWs as our one-dimensional semiconducting nanowires. We note that SiNWs in the nanosize regime exhibit quantum confinement effects and are expected to play a vital role both as interconnection and functional components in future nanosized electronic and optical devices.[3−18] Such expectation is fuelled, in particular, by the recent discovery of luminescence from porous silicon (PS), a spongelike silicon comprising an interconnecting network of crystalline silicon nanowires with pillars and nodules of nanometer sizes.[19] The PS luminescence is exciting in that bulk Si, an indirect band gap material, is not expected to luminescence in the visible region. Also, getting silicon nanostructures to emit light has enormous technological implications.[20]

Many successful synthetic strategies have now been developed to obtain bulk quantities of SiNWs, using both gas phase and condensed phase techniques.[3−7] A number of properties such as the morphology, structure, photoluminescence, electron field emission, thermal and electronic conductivities, and surface chemical properties of SiNWs have been studied.[8−15] Recently, we (the COSDAF group) reported the study of the reaction of SiNWs with a number of metal ions such as silver and copper in solution to produce metal nanoclusters.[15] It was found that the HF-etched SiNW surface is hydrogen passivated and can readily reduce silver and copper ions to metal nanostructures at room temperature with concomitant reoxidation of the SiNW surface.

Scheme 2



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The purpose of this paper is to study the heterogeneous reaction, if any, of ligated metal clusters of a single size, shape, composition, and structure with silicon nanowires after HF treatment which effectively removes the oxide layer. As we shall see in this paper, the heterogeneous reduction causes a progressive growth of the metallic particles, in a way similar to the homogeneous reductive cluster growth observed in solution.[1,2] In the latter case, progressive reductive condensation of the metal clusters caused by chemical reducing agent [R] is a spontaneous but stepwise agglomeration process of smaller cluster building blocks (in this case, icosahedral cluster units) as follows (cf. Scheme 1):

$$M^+ \xrightarrow{[R]} s_1(13) \xrightarrow{[R]} s_2(25) \xrightarrow{[R]} s_3(36) \xrightarrow{[R]} s_4(46) \ldots$$

Here, M^+ denotes monocationic Au(I) or Ag(I) complexes, and [R] represents reducing agents such as $NaBH_4$. In this process, instead of adding one atom at a time, the cluster "grows" by adding one icosahedron at a time, giving rise to the vertex-sharing polyicosahedral growth sequence via spontaneous self-assembly.

We report herein the reductive cluster growth of a 38-metal atom cluster, $(Ph_3P)_{12}Au_{18}Ag_{20}Cl_{14}$ (**1**), depicted in Scheme 2, on the surface of the hydrogen-passivated SiNWs. Cluster **1** is a vertex-sharing triicosahedral cluster with 18 gold and 20 silver atoms, encapsulated within a ligand shell containing 12 Ph_3P ligands and 14 chloride ligands (not shown), as depicted. The metal core measures 1 × 1.5 × 1.5 nm^3 and has an oblate shape. The heterogeneous reaction was followed by high-resolution transmission electron microscopy (HRTEM).

II. Experimental Section

SiNWs were synthesized by thermal evaporation techniques as described previously.[7] The as-synthesized SiNWs are long (microns), free-standing wires with a diameter of several nanometers to tens of nanometers, depending on the preparation conditions, and are usually encapsulated by a silicon oxide layer (see Figure 1a,b). The as-prepared SiNWs are relatively inert because of the

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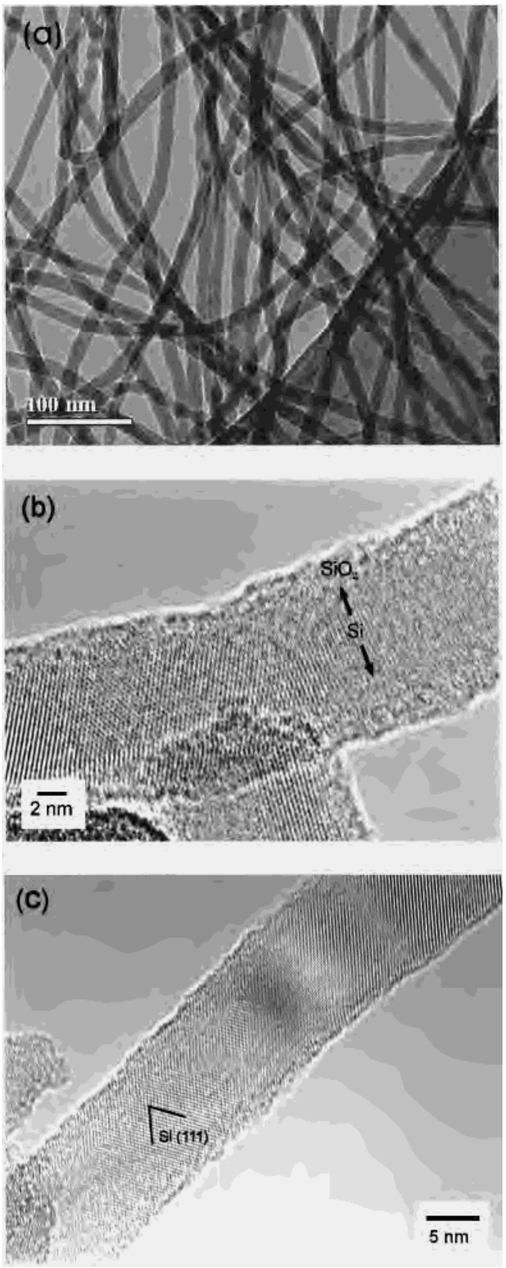


Figure 1. (a) TEM image of as-prepared SiNWs synthesized by thermal evaporation. (b) HRTEM image of a single SiNW covered with an oxide layer. (c) HRTEM image of a single SiNW after the removal of the oxide layer by treatment with 5% HF solution.

silicon oxide layer. The oxide layer was removed by immersing the as-prepared SiNWs in 5% hydrogen fluoride solution for 5 min. The HF-etched SiNWs were immersed in a dichloromethane solution containing cluster **1** for different time intervals. A few drops of the resulting solutions were put onto "holey" carbon TEM grids (this effectively quenched the reaction) and examined with high-resolution transmission electron microscope (HRTEM) (Philips CM200 FEG) operated at 200 keV.

III. Results and Discussion

As noted in the literature, the as-prepared SiNWs are known to have a relatively thick oxide layer (Figure 1b). Its presence has been associated with the preferred linear growth of the SiNWs. On the basis of HRTEM results (Figure 1c) and X-ray absorption fine structure (XAFS) results,[16] the morphology of SiNWs remains intact after removal of the surface oxide layer via controlled HF treatment. It has also been observed by STM[17] and FTIR[18] that the Si dangling bonds so created were passivated by hydrogen, forming $-SiH_x$ ($x = 1-3$) on the SiNW surfaces. The hydrogen passivated surface showed relatively good stability in air and common organic solvents.[18]

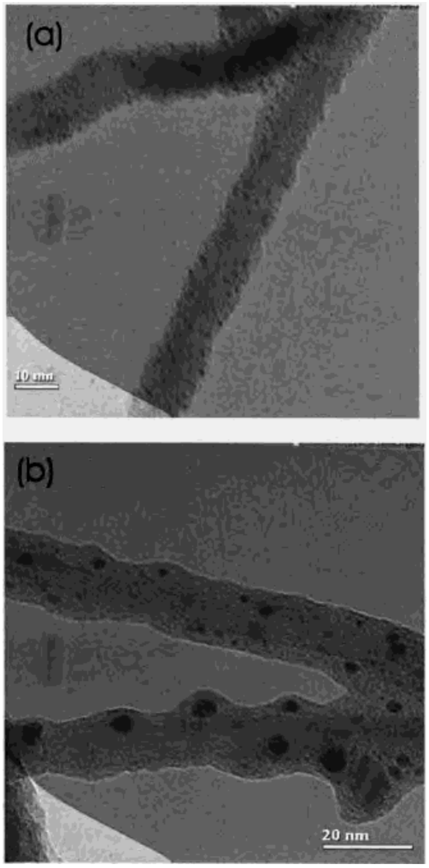


Figure 2. TEM image of reduced cluster **1** on silicon nanowires (a) at the beginning of the reaction and (b) after about 30 min of reaction.

The TEM images of the products from the reaction of the HF-etched SiNWs with a solution containing cluster **1** are shown in Figure 2. It was found that the original clusters (**1**) were reduced to clusters of larger sizes by the SiNWs within minutes. Concomitantly, surface Si atoms were reoxidized to silicon oxide. This surface oxidation process was quenched when a few drops of the resulting solution containing the suspended SiNWs were withdrawn and placed onto a TEM grid at different time intervals. (No further oxidation of the SiNW surfaces was observed even if the TEM samples were stored in air for hours.) On the basis of the time sequence of the HRTEM images, the following general observations can be made. At the beginning, the metal clusters were chemisorbed (anchored) to the SiNW surface (Figure 2a). As the reaction progressed, the anchored metal clusters were reduced by the SiH_x (where $x = 1-3$) and/or Si atoms on the SiNW surfaces and grew to form larger clusters on the SiNW surface. After about 30 min, metal clusters of different sizes, ranging from 1 to 7 nm in diameter, were observed on the SiNW surface (Figure 2b). In solution, larger metal clusters of 7−25 nm in diameter,

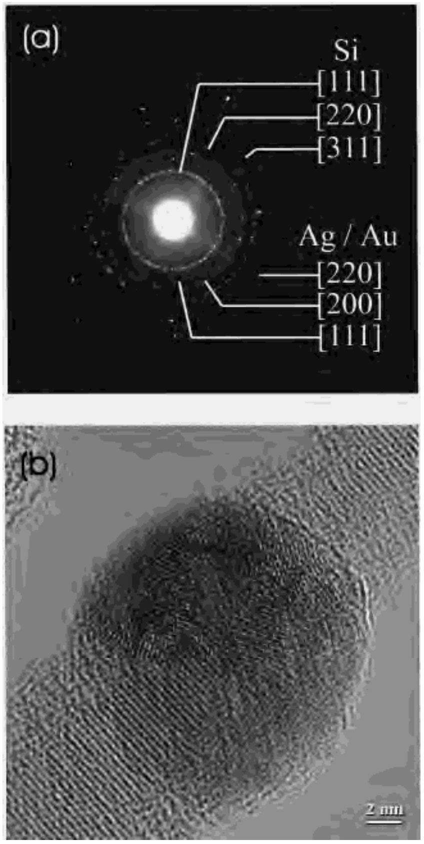
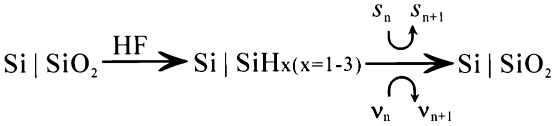


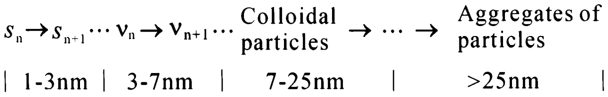
Figure 3. (a) Selected area electron diffraction (SAED) pattern of an area approximately 180 nm in diameter which contains metal particles ranging from 5 to 15 nm in diameter, showing the face-centered cubic (fcc) structure of the metal clusters, in addition to the expected diamond structure of the underlying SiNWs. (b) HRTEM image of a composite multifaceted metal particle. Triangular and square faces of the individual polyhedral metal clusters can clearly be seen.

as indicated by TEM (not shown), were obtained. Metal particles of sizes greater than about 5 nm in diameter are bulklike with the face-centered cubic structure (fcc), as indicated by the "selected area electron diffraction" (SAED) pattern taken under TEM shown in Figure 3a. This SAED pattern was taken for an area of about 180 nm in diameter, which contained metal particles ranging from 5 to 15 nm in diameter on SiNWs. Many of these particles exhibit well-defined facets, suggesting high-frequency polyhedral structures of I_h or O_h symmetry or multiply twinned particles (MTP), as observed by the HRTEM. The most commonly observed MTPs are the icosahedral and the decahedral MTPs.[21−25] Many of these particles exhibit twin planes, stacking faults, truncations, missing atoms, lattice distortions, and so forth, or combinations thereof. One such Au−Ag particle is shown in Figure 3b. This particle, roughly 6 nm in diameter, appears to be a multiply twinned particle with several faceted crystal faces. Triangular and square faces can clearly be seen on the surface of individual polyhedra.

Scheme 3



Scheme 4



Electron diffraction patterns of metal particles of sizes less than 5 nm were difficult to obtain because they tend to be mobile, palpitating, or changing shape. They also have a tendency to fuse with other metal nanoclusters (vide infra) or to disintegrate under intense electron beam irradiation. As the metal clusters grew to larger particle sizes (approximately 7−25 nm in diameter), they tended to separate from the SiNW surfaces. And finally, after a few hours, aggregates of these colloidal particles were formed and precipitated from the solution. As a result, the color of the solution turned from a dark cherry red color at the beginning to light red in about 30 min, and eventually to almost colorless after 1 h.

A plausible mechanism for the heterogeneous reductive cluster growth of the Au−Ag cluster **1** on the surfaces of SiNWs is shown in Scheme 3. Here, the vertical lines represent schematically the interface between the crystalline silicon lattice of the core and the amorphous silicon dioxide layer on the surface of the SiNWs. Etching the SiNWs with a dilute HF solution removes the oxide layer. The HF-etched SiNW surface is hydrogen passivated and can reduce an s_n cluster to an s_{n+1} cluster, or a ν_n cluster to a ν_{n+1} cluster. In the process, the SiNW surface is reoxidized. The ranges of the particle size of the proposed heterogeneous reductive cluster growth are shown in Scheme 4. We believe that, on the SiNW surfaces, particles with sizes of 1−3 nm follow the "cluster of clusters" growth pathway, resulting in the vertex-sharing polyicosahedral structures, s_n, portrayed in Scheme 1 (only the early members are depicted). In the size regime of 3−7 nm, the clusters grow via the so-called "layer-by-layer" mechanism, giving rise to the high-frequency polyhedral clusters, ν_n. These ν_n clusters may adopt either icosahedral or octahedral symmetries. It is believed that smaller clusters (say, ν_3−ν_8 of 3−5 nm in size) tend to adopt icosahedral symmetry (mostly truncated ν_n icosahedra) whereas larger clusters (say, ν_9−ν_{12} of 5−7 nm in size) tend to adopt octahedral symmetry (mostly truncated ν_n octahedra). In the intermediate regime, the structures can fluctuate between I_h or O_h symmetries, especially under intense electron beam irradiation.[23−26] Indeed, such transformation between different morphologies (often occurring on the scale of seconds or fractions of a second), a phenomenon referred to as quasi-melting,[25] has been observed for Au or Ag particles of 3−5 nm in diameter.[23−26] It should be emphasized that these "idealized" structures are chosen here to illustrate the reductive growth of the metal clusters on the surfaces of

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SiNWs. In reality, polyhedral truncations, missing atom columns or crystal faces, and lattice defects and/or distortions can occur, giving rise to more or less irregular particle shapes. Furthermore, formation of twin planes, stacking faults, or reentrant notches can lead to multiply twinned particles (MTP).[23,24] As the clusters grow further to larger sizes, forming colloidal particles of approximately 7−25 nm in diameter on the SiNW surfaces, they have the tendency to separate from the SiNW surface. And finally, further growth and/or aggregates of these colloidal particles lead to the formation of even larger particles, which eventually precipitate from the solution.

As shown in Figure 2b, for metal clusters that remained on the SiNWs, some were attached to the outside surfaces while others were partially or completely submersed in the oxide layer of SiNWs. This can be rationalized as follows. In the process of reduction and growth of clusters on the HF-etched SiNW surfaces, some of the phosphine and/or chloride ligands on the metal cluster were lost. At the same time, silicon oxides were reformed on the SiNW surfaces. As a result, some of these clusters were partially or completely surrounded by the oxide anions of the silicon dioxide layer, thereby appearing to be partially or completely submersed in the oxide layer. In this regard, the oxides serve as the replacement ligands, stabilizing the metal clusters on the SiNW surfaces.

Two interesting phenomena, the “sinking cluster” and the “cluster fusion” processes, were observed during the TEM observation of the reaction products. It was found that some metal clusters attached to the SiNW surface were sinking into the amorphous oxide layer under TEM observation. This observation may be likened to a cluster “sinking” in a “sea” of oxide layer. Two snapshots of the entire process are depicted in Figure 4. In the beginning of the TEM probe, the cluster of approximately 2 nm in diameter (indicated by an arrow in Figure 4a) on the surface kept throbbing under the intense electron beam of TEM (while barely attached to the SiNW). Eventually, the cluster began to sink beneath the surface of the oxide layer. (Note: In many other instances, the cluster may eventually separate, often abruptly, from the surface of the SiNWs. For smaller clusters, they may disintegrate altogether.) And, after about 1 min, the cluster was completely submersed in the oxide layer (Figure 4b). A similar phenomenon was also observed by Marks et al., [21,22] when the same type of ligated Au−Ag clusters were deposited on magnesium oxide and examined by the TEM.[22] We believe that, in both cases (referring to refs 21 and 22 on one hand and the present work on the other), the ligands may play a role in the cluster “sinking” process. In other words, under intense electron beam irradiation, some of the phosphine and/or chloride ligands on the cluster were lost, and the cluster became coordinatively unsaturated and, hence, was unstable. The oxide ions in the silicon oxide layer became the replacement ligands, thereby stabilizing the cluster. Phenomenologically, the metal cluster “sank” into the oxide layer; some were completely submersed, while others only partially. Obviously, the anchoring and the engulfing of the metal clusters on the surfaces of the SiNWs depend critically on the interaction between the metal cluster surfaces and the substrate and, hence, are intimately related to processes such as adhesion and wetting.[23] It should also be mentioned that we found no evidence of cluster “floating,” though it has been predicted theoretically.[22] (Here, we make a distinction between the gradual “floating” process, which is the reverse of the “sinking” process, and the sudden “departure” phenomenon discussed earlier which often occurred after the cluster had been throbbing or pulsating violently for a few seconds.)

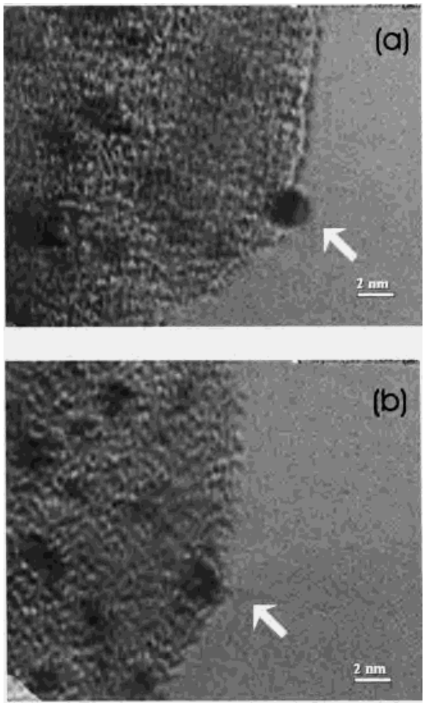

Figure 4. TEM image of “sinking cluster” process (a) in the beginning of the TEM observation and (b) after 1 min of TEM observation.

Another interesting phenomenon observed here is the “fusion” or “aggregation” of metal clusters. Figure 5 shows the TEM images of two of these aggregation processes. It can be seen that clusters A and B moved across the oxide layer by approximately 13 and 5 nm to fuse with clusters C and D to form two larger clusters. Though not indicated in Figure 5, other smaller clusters continue to move (some by more than 10 nm) to fuse with cluster C. These movements correspond to a diffusivity of about 1 nm^2 sec^{-1} or 10^{-14} cm^2 sec^{-1}, as it took the clusters roughly 2 min to travel a distance of about 10 nm. Under TEM observation, the dynamics of cluster growth via this aggregation process is rather interesting. The ability of these clusters to move by a distance more than 10 times its size is quite amazing, especially given the fact that some of the merging clusters were completely submersed in the silicon oxide layer. The driving force of the migration of nanoparticles on the substrate surface under TEM observation has been well discussed.[23−27] The electron beam induced effects[23−27] as well as Ostwald ripening[28] (growth of large clusters as a result

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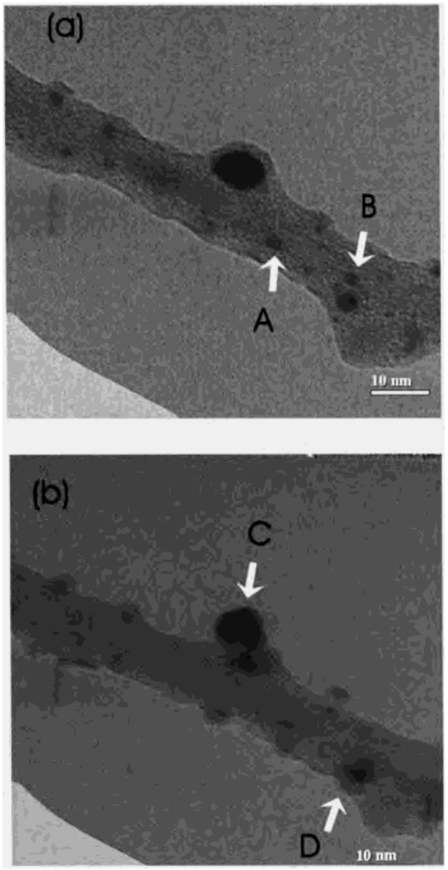

Figure 5. TEM image of "cluster fusion" process (a) in the beginning of the TEM observation and (b) after the fusion of the clusters.

of dissolution of smaller ones) or coagulation processes had been invoked to explain the phenomenon. Because the rates of both the sinking and the aggregation processes appear to increase with increasing electron fluxes, we believe that electron irradiation, rather than thermal effects, provides the driving force for these processes. (Of course, the softening of the silicon oxide layer as a result of heating by the electron beam also facilitates these processes.)

Work is in progress to shed new light on the dynamics and physics of these phenomena as well as the growth and chemistry of these metal clusters on the SiNW surfaces.

IV. Conclusion

The reductive growth of ligated metal clusters on the silicon nanowires is described. The HF-etched SiNW is a moderate reducing agent. It can be used to reduce Au−Ag clusters such as **1** of a single size, shape, composition, and structure. Reductive cluster growth on the SiNW surface was followed by TEM. The SiNW surface was found to be reoxidized in the process. The reduced metal clusters grew to nanoparticles of different sizes on the SiNW surfaces. Some large clusters separated from the SiNW surface, yet larger ones eventually precipitated from the solution. Two interesting phenomena, the "sinking cluster" and "cluster fusion" processes, on the SiNW surfaces, observed under TEM, were also discussed. It is apparent that the capability of TEM to focus on a single metal nanoparticle and to follow its movement, in real time, on a single silicon nanowire allows the study of the dynamics of many important surface processes in the nanorealm.

Acknowledgment. We would like to dedicate this paper to the memory of Anna Tang Lee. Financial support from the Research Grants Council of Hong Kong (CityU 1063/01P) and the National Science Foundation (to B.K.T.) are gratefully acknowledged. B.K.T. would like to express his most sincere gratitude for the kind hospitality S.T.L. and his colleagues at COSDAF extended to him during his visit to the center in the summer of 2001.

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