Morphological evolution of Ag nano-wires via thermal evaporation

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Recent progress in the synthesis and characterization of nano-materials has been driven by the need to understand the novel optical and electric properties of one-dimensional materials with a size in the range of a nanometer scale. Many research groups have focused their attention on the development of new nano-materials that have potential applications in the fabrication technology of new types of electronic and photonic devices with nano-size. Various nano-wires including Si-based, metal oxides, metal sulfides, nitrides and metal/oxide composite nano-wires have been successfully synthesized by non-lithography methods including the vapor-phase transport process, laser ablation, arc discharge, solution and a template-based method [1–10]. A large part of such works has been focused on semiconductor systems including both element and compound semiconductors such as Si, Ge, GaN, GaAs and MgO, ZnO, and also oxide systems with insulation nature such as SiO_2, GeO_2, Ge_2O_3, Cu_2O, SnO_2 and PbO [10–20]. These nano-wires may have different morphologies and diameters. A few studies on metals exist in the literature. Metal nano-wires exhibit a number of interesting properties: their electrical conductance is quantized, their shot-noise is suppressed by the Pauli principle, and they are remarkably strong and stable. The metal nano-wires are expected to be used as components in new technology devices, as the size of the future electronic devices will be down to nano-scale. Intensive study focused on the fabrication of the metal and metal oxide nano-wires has been conducted recently, which has resulted in the synthesis of some metal nano-wires such as Ag, Ni, Cu and alloy nano-wires, including Fe-Co and Fe-Ni-Co based on electroplating, template and reduction process [21–23]. The Cu nano-wires have been synthesized via thermal evaporation [24, 25], but at present, the growth mechanism of metal nano-wires has not been completely elucidated. Therefore, synthesis of metal nano-wires is of importance from both the technological and scientific point of view. In this letter we report the fabrication of Ag nano-wires with the configurations of Ag cores covered by a thin amorphous SiOx shell at the outer surface via thermal co-evaporation of AgO and SiO powders in an inert gas mixed with hydrogen atmosphere. We focus both on developing new metal nano-wires and also on revealing the growth mechanism of the metal nano-wires. We conclude that the formation of Ag nano-wires most probably occurs as the famous Vapor-Liquid-Solid (VLS) model [26, 27]. The mass transported from the vapor phase to the catalyst droplet is the critical parameter for controlling the growth of Ag cores with the thin SiO_x shells.

The raw materials of AgO and SiO powders were mixed according to a volume ratio of AgO:SiO=10:1. This mixture of source materials was placed in an alumina crucible and transported into a CVD chamber with a diameter of 300 mm. A 50 mm × 50 mm silicon chip ($\langle 100 \rangle$ p-type) was put above the crucible to serve as a deposition substrate. The distance between the crucible and Si substrate was about 50 mm. A mixture of Ar and H_2 gases with a ratio of 9:1 was allowed to enter the chamber when vacuum in the chamber reached 10^{-3} Pa. The pressure was kept at 200 Torr and then the system was closed by cutting off the inert gas and sealing the vacuum system. The temperature of the substrate was first held at ∼1100 °C and then reduced to 900 °C for the deposition. In order to reveal information on the initial stage of the nano-wires growth, a very short deposition time (∼30 s) was used, and then the heater was turned off to let the chamber quickly cool to room temperature.

The substrate was pale white in appearance after deposition of the source materials, and was examined using a XL-1500 scanning electron microscope equipped with a field emission gun (FEG) and an energy dispersive X-ray spectrometer (EDS). The microstructures of the depositions were characterized using Tecnai-20 TEMFEG equipped with an EDS.

The morphologies of the products at the substrate in the present closed system at different deposition times have been characterized by SEM and TEM. Fig. 1 is a SEM image showing the typical morphologies of the products deposited on the Si substrate at the initial stage of deposition. In this case the catalyst droplets with a diameter over 1 micron are very large with respect to the reported droplets on the tips of Cu nano-wires and PbO nano-belts. There are some nano-wires with the uniform diameter of ∼100 nm extruding directly from

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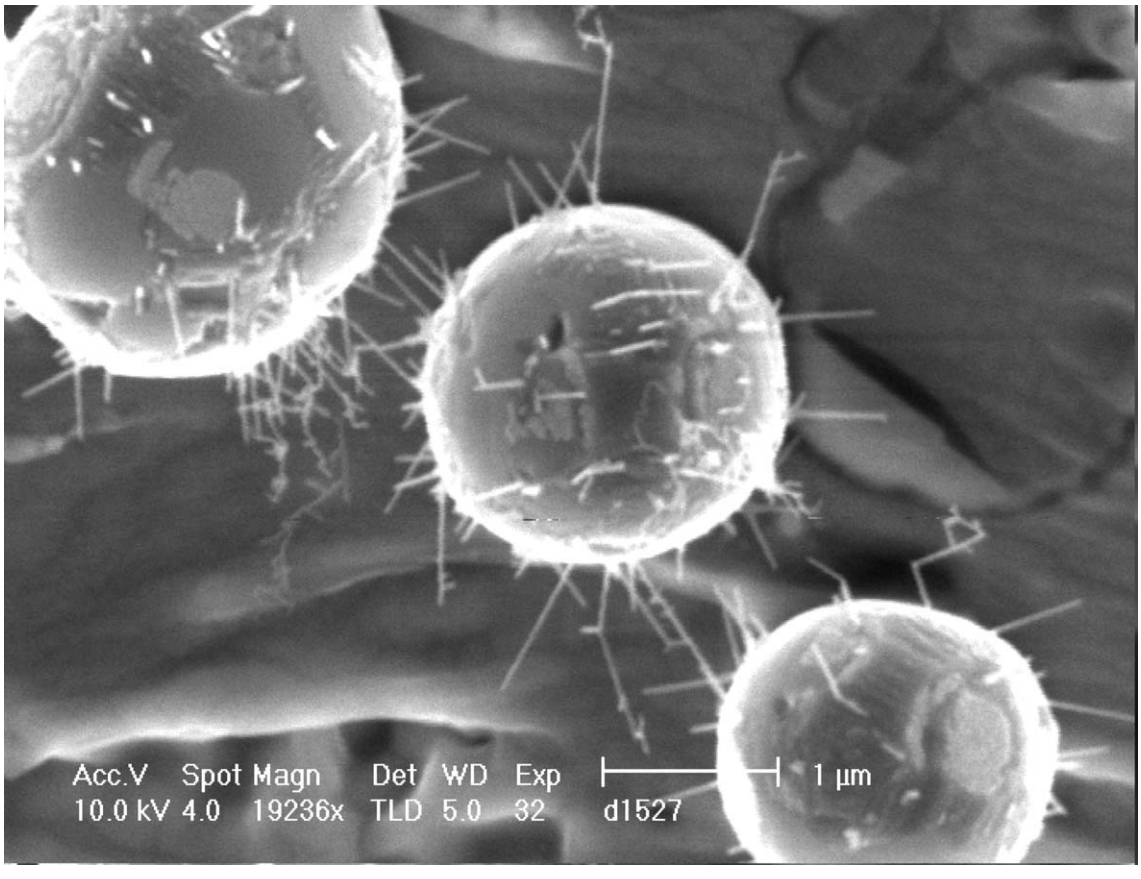

Figure 1 SEM micrograph showing the morphology of nano-wires extruding directly from the catalyst droplet, the nano-wires have the branch characteristic.

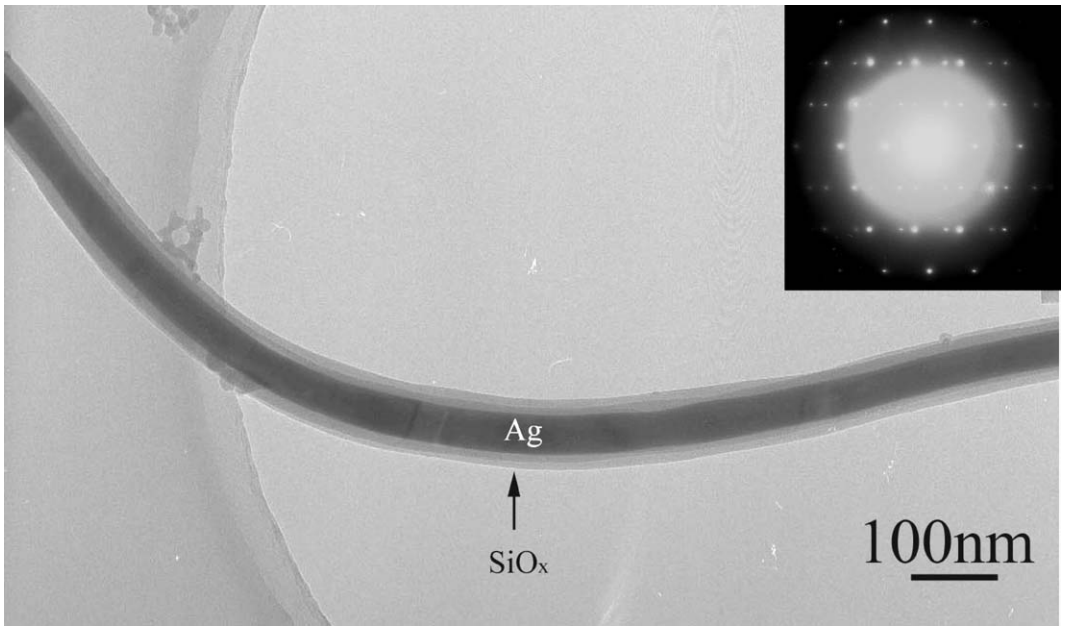

Figure 2 TEM bright field image showing the microstructure of the nano-wires, the wire consists of the SiO_x outer shell and Ag core confirmed by the inserted electron diffraction pattern. The band-like structure in the core results from multi twinning on the (111) plane.

the surface of the catalyst droplet, but the density is rather low. The length of these nano-wires is in a range from hundred nanometers to 1 micron. A characteristic of these nano-wires in Fig. 1 is multi-branching. Usually, the nano-wires synthesized by thermal evaporation have a catalyst droplet on the tip of each nano-wire. The reported diameter of the droplet is slightly larger than that of the nano-wires. The catalyst droplets shown in Fig. 1 are much larger than the reported ones. Thus, many nano-wires extrude out of the same droplet instead of the droplet on the tip of a single nano-wire. The composition of the nano-wires and catalyst droplet were analyzed by EDS and the results are shown in Fig. 3. Both the nano-wires and the droplets are highly dominated by Ag and Si.

The microstructural details of the nano-wires characterized by TEM are shown in Fig. 2. The wire consists of a uniform core in dark contrast to a bright outer shell.

The determined diameter of the core is ∼80 nm and the thickness of the sheath is about 15 nm as shown in Fig. 2. This image shows the encapsulated silver present as continuous and uniform nano-wires inside the SiO_x sheath. The band-like structure with the different contrast in the core portion suggests the polycrystalline nature. The selected area electron diffraction pattern taken at the core is inserted at the right top corner. Because this pattern can only be indexed based on the lattice parameter of Ag ($a = 0.409$ nm), the structure of the core is confirmed to coincide with the silver. The extra reflections resulting from the twinning on the (111) plane are also present in the diffraction pattern. Thus, the band-like microstructure may correspond to the multi-twinning on the {111} planes. Careful analysis shows that the longitude direction of the wire is perpendicular to the habit planes of the twinning, i.e., the growth direction of Ag nano-wire is parallel to the normal of the habit planes of the twinning. Usually, the [111] direction is a favorable growth direction for Si nano-wires and whiskers grown via VLS technique [26, 27]. Since Ag and Si all have the face-centered cubic lattice, the coincidence of their growth directions is predictable. In order to confirm the configuration of the nano-wires, a large angle tilt around the longitude direction (the [111] direction) of the nano-wire was made, using double tilt goniometer stage. Their morphologies and diameters were obviously unchanged when rotating through about $\pm 30^\circ$. Thus, it is believed that the wires have a cylindrical shape with a nearly uniform diameter.

EDS was used to determine the composition of the wires. Fig. 3a is a spectrum obtained at the core portion. The elements detected in this spectrum are Ag, Si and O, respectively, but Ag highly dominates the constitution of the core. The quantitative analysis of the core composition was not made since there is a thin layer of silicon oxide at the surface, the silicon content in the core could be predicted to be less than 20 at.% according to the Ag-Si phase diagram [28]. This result is consistent with the selected area electron diffraction pattern. Thus, the silver should be a major constitution of the core of the nano-wires. Fig. 3b also depicts a similar result obtained from the catalyst droplet shown in Fig. 1. The composite nano-wires with a cable-like structure of Ag nano-wires covered by a thin layer of the amorphous SiO_x are prepared. The volume ratio of the core and the outer shell was calculated to be 4:1. This value deviates significantly from the ratio of AgO:SiO = 10:1 in the source mixture.

In order to understand the microstrucutral evolution of the Ag/SiO_x nano-wires in the different stages of the deposition process, long deposition times were also used. Fig. 4 is a SEM image showing the typical nano-wires obtained as the deposition is performed at 900 °C for 1 h. Compared to the initial stage of growth (Fig. 1) the density of the nano-wires increases considerably and the catalyst droplet is covered by the nano-wires. The length of the nano-wires is over ten microns. The measured diameter of the nano-wires in Fig. 4 is over a hundred nanometers. The major characteristic of the nano-wires is their curling, which results in the jungle-

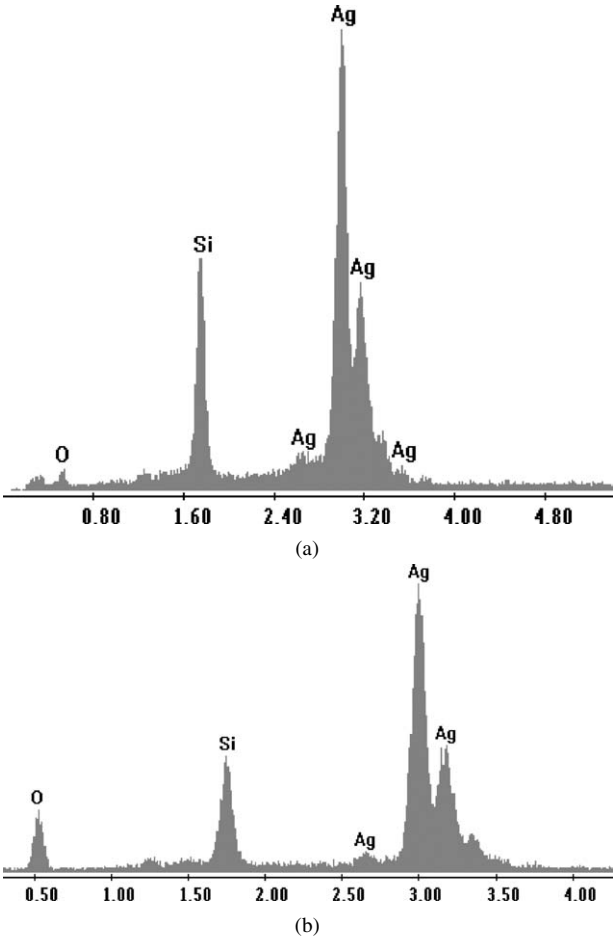

Figure 3 EDX spectra obtained from the nano-wires (a) and the droplet (b) in Fig. 1 showing their composition, the spectra are highly dominated by Ag and Si.

like morphology of the nano-wires over the catalyst droplet. After the SiO_x sheath is derived by putting the nano-wires into the H_2F dilute liquid, the electric measurement of the nano-wires is made by a four point method. The result shows the linear I-V relation [29].

Evidence from the SEM and TEM observations on the microstructures of the nano-wires confirms that the nano-wires were initiated from the catalyst droplet. The observed growth characteristics of the nano-wires in this study are probably coincidential with the VLS model originally proposed by Wager and Ellis for the growth of silicon whiskers [26, 27], in which the central idea concerns the existence of a catalyst droplet of a different composition than the growth phase. The catalyst has a high adsorption rate for vapor precursors and can be supersaturated with the growth phase, leading to one-dimensional precipitation of the excessive precursor species and nano-wires growth. The nano-wires extruded directly from the Ag-Si alloy droplet, indicating that these droplets have a similar function as the catalyst droplet with an eutectic composition to some extent. Although the conventional VLS mechanism requires a catalyst droplet of a different composition than does the growth phase, there have been some reported examples on catalyst functions of Cu and Pb tips for Cu nano-wires and PbO nano-belt growths [18, 19, 24, 25]. However, a different model, oxide-assisted formation

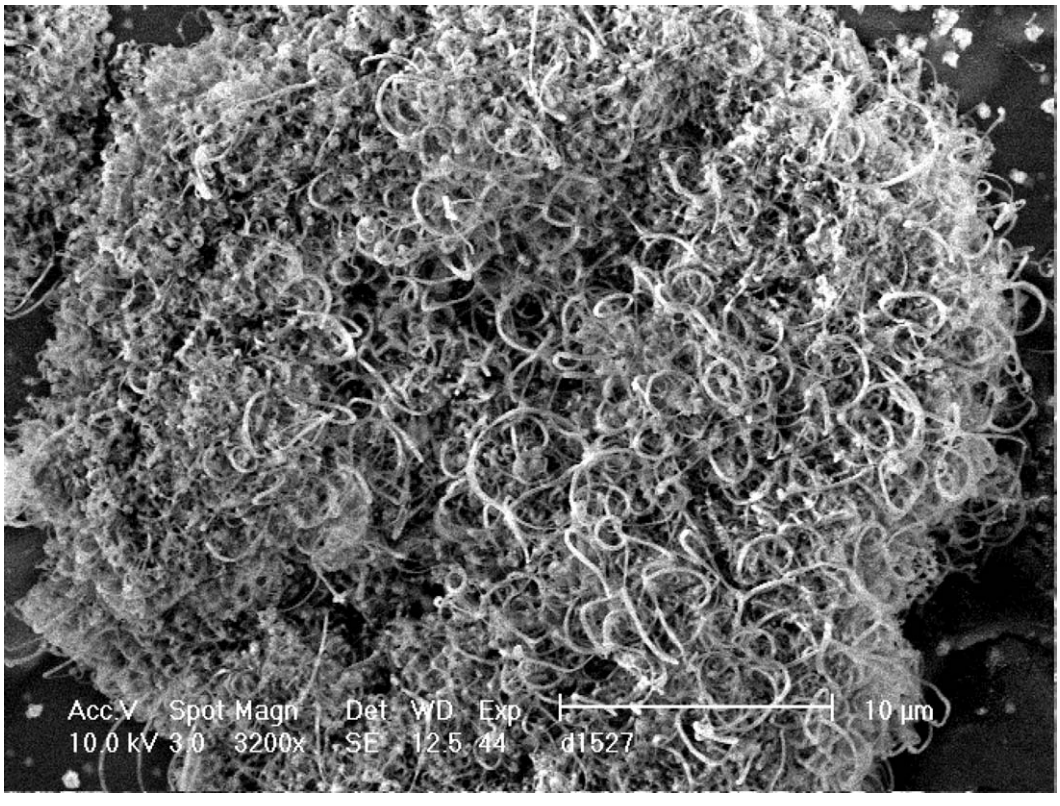

Figure 4 SEM image showing the nano-wires obtained after the deposition lasted for one hour at 900 °C, the length of the nano-wires increased significantly with respect to those nano-wires at the initial stage.

mechanism, different from the classic VLS mechanism was also proposed and was supported by the fact that the silicon oxide outer layers play the catalytic effect and retard the one dimensional growth [30, 31]. Once the silica species accumulates on the substrate, the newly formed molecular silica tends to diffuse toward such areas. Due to different bonding energy, SiO_x is preferable for the formation of an amorphous silicon oxide sheath, which could result in the phase separation of Ag and silicon oxide. The formed solid SiO_x component can retard the lateral growth of the nano-wires along one direction, to result in the structure consisting of the Ag wires surrounded by the SiO_x sheath.

In summary the Ag/SiO_x composite nano-wires with the cable-like structure, i.e., Ag core covered by an amorphous SiO_x shell, have newly been synthesized by thermal evaporation of AgO and SiO powder mixtures with a ratio of 10:1. Evidence from the microstructural characterization of the nano-wires by SEM and TEM strongly suggest that the growth mechanism of the nano-wires may coincide with the VLS model. The density and length of the Ag/SiO_x may alternate depending on the deposition time. Long time deposition may result in highly densified nano-wires.

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