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Alternative vapor–liquid–solid process in Au-assisted growth of silica nanowires

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ABSTRACT

We report the growth process of silica nanowires (NWs) grown by using a thick Au film as a catalyst, and suggest an alternative vapor–liquid–solid mechanism for NW growth. The silica NWs were grown by high-temperature annealing of silicon substrates coated with an Au film measuring either 20 nm or 60 nm thick in a N_2 atmosphere. A number of Au particles were observed inside the NWs, unlike NWs grown a single Au particle at their top. The results are attributed to the push-up growth of NWs by the continuous formation of silicon oxide on the top and/or side surfaces rather than underneath of the eutectic liquid Au–Si alloy suggested in the conventional vapor–liquid–solid process.

The metal-assisted growth technique is widely employed for fabricating one-dimensional (1-D) nanostructures, such as nanowires (NWs). Using this method, NW growth has typically been understood on the basis of a conventional vapor–liquid–solid (VLS) process that was first proposed by Wagner and Ellis [1], but the detailed growth mechanism, which is of particular relevance to the present study, still remains controversial.

In the conventional VLS mechanism [1–11], the precursor materials of NWs are absorbed into a liquid-metal particle formed on a substrate, which is then supersaturated and subsequently results in the solid material for NWs at the interface between the liquid-metal particle and the substrate. The continued formation of the solid material at the interface between the liquid-metal particle and solid material leads to the growth of a NW, lifting the liquid-metal particle, which rides atop the growing NW. In this process, two distinct features emerged: the liquid state of the metal particle during NW growth and the presence of the metal particle at the top of the NWs after growth. However, it has also been shown that this growth mechanism is contradictory to the results reported by many researchers. That is, many studies in the literatures have reported the absence of a particle at the top of NW [12–16] and that 1-D nanostructures may result from the solid phase of the metal particle during growth instead of the liquid phase [6–9]. These findings lead to growth mechanisms alternative to those of conventional VLS processes, such as the vapor–solid–solid (VSS)/vapor–solid (VS) process [17–20].

In this work, we present an alternative VLS process based on silica NWs grown using a thick Au film as the catalyst. NW growth was achieved by depositing Au films measuring 20 nm and 60 nm thick on Si substrates and annealing the resulting structures at 1100 °C for 1 h in a high-purity N_2 purging ambient. The silica NWs were observed to have a number of Au particles inside their structure. The results are attributed to the push-up growth of the silica NWs from lump-like liquid Au–Si alloy.

In this study, nanowires were produced by thermally annealing Si substrates coated with thick Au films. Commercially prepared (100)-oriented p-type Si substrates (0.4–0.9 Ω cm) were coated with 20-nm and 60-nm layers of Au by thermal evaporation deposition. Prior to Au coating, the native oxide layer on the substrates was etched using a hydrofluoric acid (HF) solution diluted with deionized water. For NW growth, the Au coated Si substrates were then annealed at 1100 °C for 1 h in a quartz-tube furnace under N_2 gas flowing at a rate of 50 mL/min. The N_2 gas was dried prior to entering the furnace by passing it through a laboratory drying canister filled with anhydrous $CaSO_4$. Samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) using a Hitachi S-4800 ultra-high resolution SEM microscope and a Jeol JEM-2100F Schottky field emission TEM microscope with an energy dispersive X-ray (EDX) spectrometer, respectively.

Fig. 1 shows SEM images of Si substrates coated with 20-nm (a) and 60-nm (b) layers of Au after thermally annealing at 1100 °C for 1 h. Both samples are clearly shown to have grown long nanowires (NWs) of various diameters ranging from ~20 nm to ~80 nm, similar to the results reported in the literature. However, the present results clearly show a feature different from those previously reported. As can be observed in the SEM images, the NWs show a number of white dots inside their structure. This feature was also observed in both samples grown using Au films of

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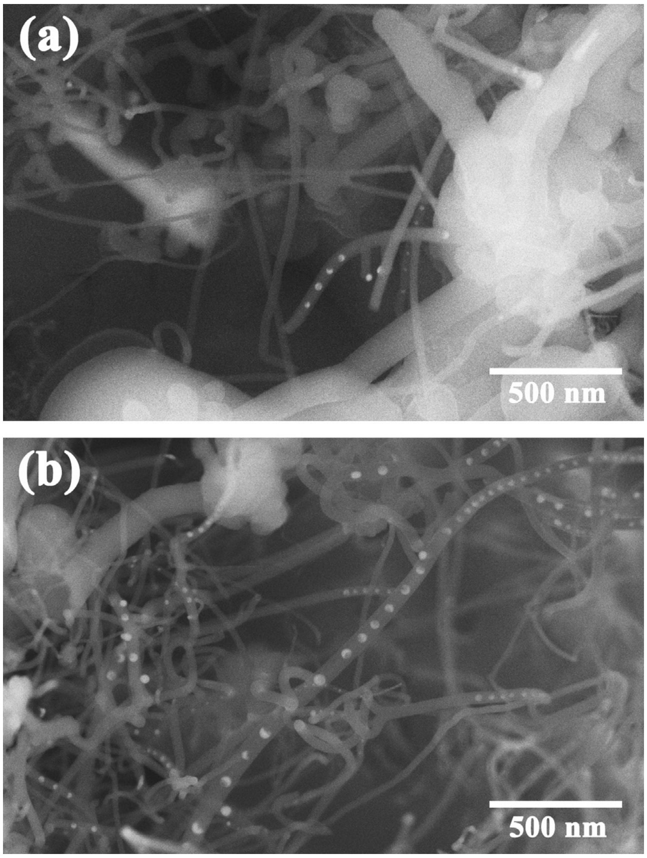

Fig. 1. SEM images of Si substrates coated with Au film of (a) 20 nm, (b) 60 nm thick after annealing at 1100 °C for 1 h. Note that numerous dots are inside the nanowires.

different thicknesses. The present results clearly differ from those expected for the conventional VLS and VSS/VS mechanisms, in which one dot is usually observed at the top of NW.

The dots were characterized by using energy dispersive X-ray (EDX) spectroscopy and transmission electron microscopy (TEM) measurements, as presented in Fig. 2. Fig. 2(a) shows a TEM image of a NW with dots inside of it and a line-scanning EDX spectrum (inset) of Au measured along the solid line drawn in the image. The peaks in the spectrum are shown to coincide well with the locations of the dots, supporting the premise that the dot is composed of Au. Fig. 2(b) presents a high-magnification TEM image of a dot inside a NW and the corresponding fast Fourier transform (FFT) pattern (inset). A regular lattice structure is clearly shown in the image,

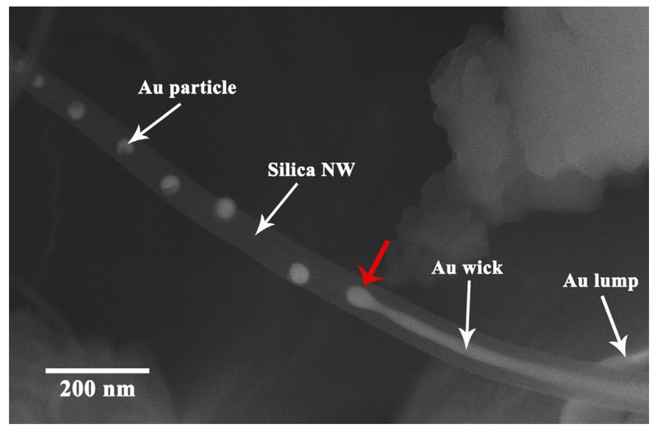

Fig. 3. SEM image of a NW attached to a lump-like Au structure on a Si substrate. In addition to Au particles, it is shown that there is a wick-like Au structure extended from the Au lump. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

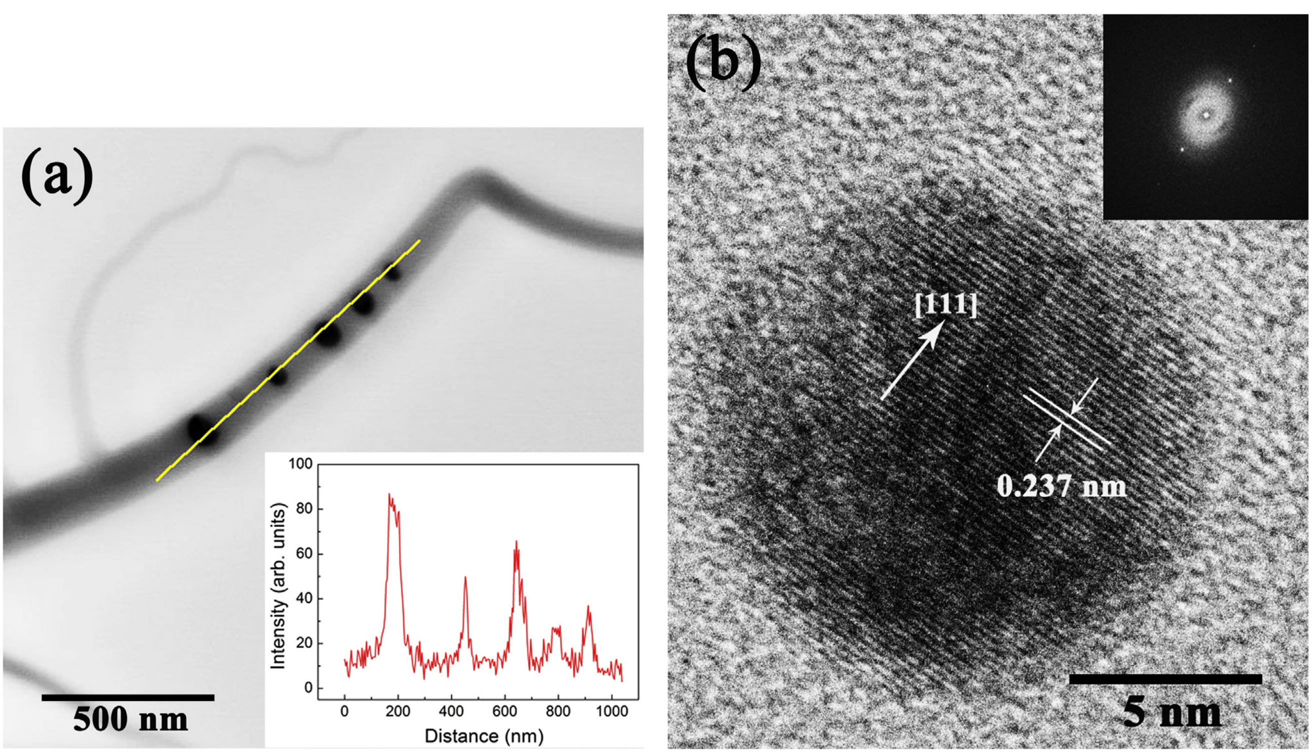

Fig. 2. (a) TEM image of NW containing Au particles and line scanning EDX spectrum of Au along the line shown in the image and (b) high-magnification TEM image of an Au particle and the corresponding FFT pattern (inset). The inter-planar spacing is 0.237 nm.