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ON THE STUDY OF SILICON NANO-WIRES SELF-ASSEMBLED AS PARTICLES

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Two different types of Silicon nano-wires (SiNWs) have been observed by scanning and transmission electron microscopy. One are of free standing SiNWs deposited uniformly on the surface of silicon substrates, and the other are self-assembled into special shaped particles. These SiNWs were synthesized by thermal evaporation of SiO amorphous powders without any metal catalysts in the temperature range of 900–1250°C. Growth history reveals that the self-assembled SiNWs are formed by original nucleation from the surface of amorphous SiO_x particle matrices through phase separation and silicon precipitation followed by further growth through oxide-assisted vapor-solid reactions. The above results provide a solid experimental support for the oxide-assisted growth model of SiNWs.

Keywords: Silicon, nano-wires, growth mechanism, microstructures
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Since the discovery of silicon nano-wires (SiNWs),[1–3] the relationship between the microstructure and the quantum size confinement, photoluminescence, Raman spectra[4–6] and some other physical properties[7] have been extensively studied. The typical structural characteristic of these SiNWs is a type of nanowires formed in the gas phase and deposited relatively uniformly on to cold-finger collectors or substrates in the furnace, by employing laser ablation or thermal evaporation methods. Recently, some experimental results of thermal evaporation synthesis have shown that SiNWs are rich in morphology in different temperature regions under the same synthesis condition. The variation of morphology not only exist in the diameter distribution from 10–100 nanometers, but also in the changes of shapes from octopus-like, chain-like, tadpole-like, to single wires with a constant diameter.[8–10] Since the size, shape and structure of SiNWs depend sensitively on the temperature, composition and other growth conditions, there are still some open questions concerning the growth mechanism of SiNWs with different morphologies.

To investigate the variation of morphology, growth history and related mechanism of SiNWs, we have carried out a systematic study. In our experiment, silicon substrate wafers as collectors were arranged within the furnace in the temperature region ranging from 600–1350°C. The thermal evaporation condition for SiNWs synthesis is the same as reported previously,[10] but with a different wire growth time of 10 minutes. By microstructure study with scanning electron microscopy (SEM) and transmission electron microscopy (TEM), we found a new type of SiNWs self-assembled as clusters and/or particles with specific shapes at different temperature zones. Our results show that the formation of the SiNWs is closely related to the amorphous SiO_x particles deposited on the surface of substrate-collectors. The growth and self-assembling process of SiNWs on the surface of SiO_x particles strongly supports the oxide-assisted growth model of SiNWs with various morphologies.[11]

Figure 1(a) shows a typical SEM image of SiNWs deposited on the Si substrate at a temperature around 1000°C. A noticeable feature of this image is that there is a layer of SiNWs and an abundant of different sized particles deposited on to the substrate. The deposited layer consists of free standing SiNWs formed in the gas phase deposited on to the surface of the collector substrate and are shown in Fig.1(b) with a higher magnification as those studied extensively by TEM before. It is interesting to note that

those SiNWs are aligned along some favorite directions (denoted as white arrows) and normally connected to different sized particles showing a brighter contrast in the SEM images. A close investigation of the particles show that there are also some SiNWs wrapped onto the surface of particles as evidenced in Fig.1(c) with a higher magnification, which are more curved compared with those deposited directly on the collector substrate. The composition of the particles was confirmed by an X-ray energy disperse spectrometer (XEDS) to be SiO_x, with x close to 1. Our experiments have shown that where there is such a SiO_x particle, there are some curved SiNWs wrapped onto it. These SEM images reveal a close relationship between the SiNWs and SiO_x particles of any visible size. We have found also that the Si substrate plays only the role as a collector for SiNWs deposition having no other relationship with SiNWs.

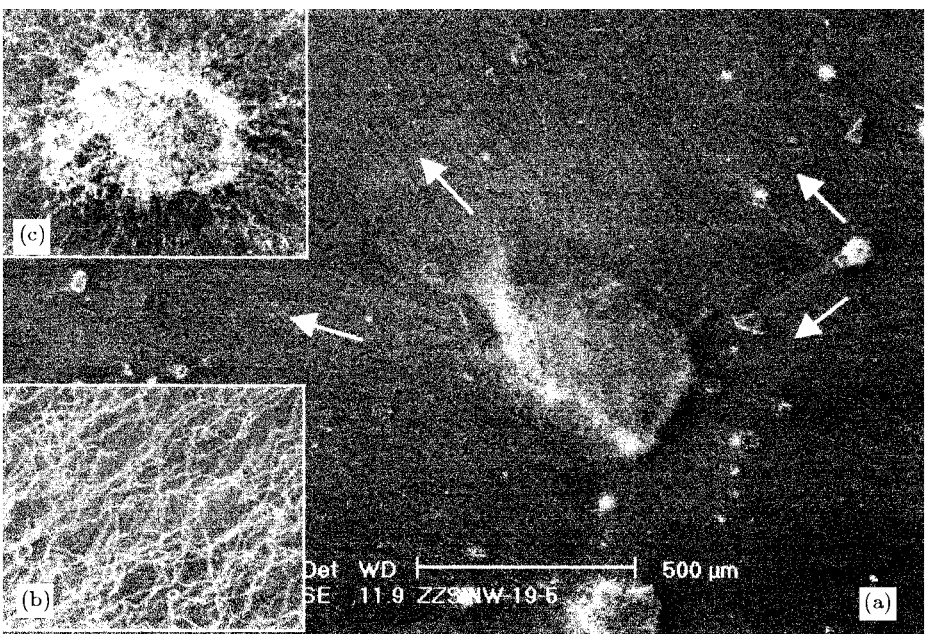


Fig.1. SEM images of SiNWs deposited on to a Si-substrate in the temperature range around 1000°C. SiNWs (magnified in (b)) deposited on the silicon substrate are aligned along some preferred directions (marked by arrows) and connected to some particles (a). Note the more curved SiNWs wrapped onto the surface of a particle connected by other SiNWs grown along radial directions with respect to the particle (c).

At a temperature of about 1180°C, particles with a special "Mushroom" shape are observed deposited on the surface of the collector substrate, as shown in Fig.2. A SEM image at higher magnification, as the up-right inset, shows that the particles have a cone shaped hairy surface and the top surface of the cone is rather rough. The bottom left inset of Fig.2 is the SEM image of the mushroom-shaped particles at still higher magnification, which shows clearly that the surface is full of self-assembled SiNWs of 30–40 nm in diameter. SiNWs at the top surface of the "mushroom" particles are of rather small diameter. Figure 3 shows SiNWs connected to a mushroom-shaped particle and another of it. The string-like SiNWs connecting two particles can be understood as follows: the heavily curved SiNWs have grown directly and self-assembled on the surface of particles. The separation of a piece of the particle forces the connecting wires to become more straight and aligned in parallel.

Figure 4(a) is a low-magnification SEM image of SiNWs deposited on the surface of the Si substrate collector at a temperature of about 1250°C. A characteristic feature of this image is that there are some "bottle-like" shaped particles, with a size of about $0.2\times\ 0.5\ mm^2$. In the vicinity of this type of particles, there are also other small particles with irregular shapes. Higher-magnification images show that all of the particle surfaces are self-assembled fully with SiNWs as shown in Fig.4(b). A careful examination at higher magnification (Fig.4 (c)) shows this type of SiNWs is with sub-branches terminated by a Si bulb at the tip, which is different from those SiNWs re-

ported before.[5,6] The average diameter of the main-branches of the SiNWs is in the range of 40–60 nm and their sub-branch SiNWs is of 30–40 nm. The bulb on the tip of the sub-branches is less than 100 nm in diameter (Fig.4(d)). It is noticed that the sub-branch SiNWs are thin and normally curved at the region close to their connecting points with the main-branch of SiNWs and its diameter increases gradually to form the bulb at its tip. HREM results reveal that the main- and sub-branches are SiNWs covered with a SiO_2 outer layer of a few nm in thickness. HREM (Fig.4 (e)) and electron diffraction results also show that the bulbs have a silicon structure and an amorphous SiO_2 outer layer.

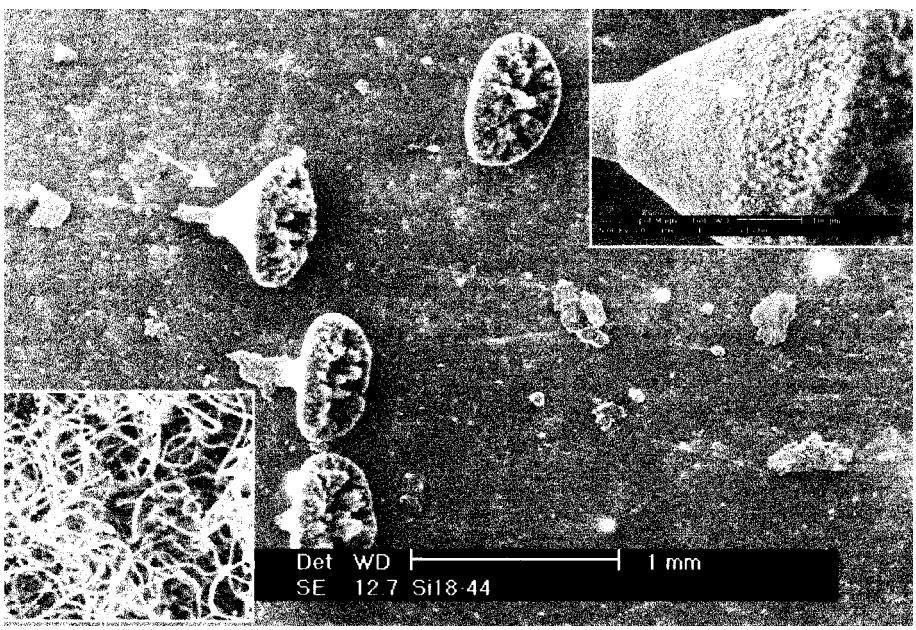


Fig.2. Curved SiNWs of 30–40 nm in diameter grown on SiO_x particles with self-assembled "mushroom"-shape at a temperature of 1180°C, these particles have a smooth cone surface (up–right inset) covered fully by SiNWs, as evidenced by a higher magnification image (bottom-left inset).

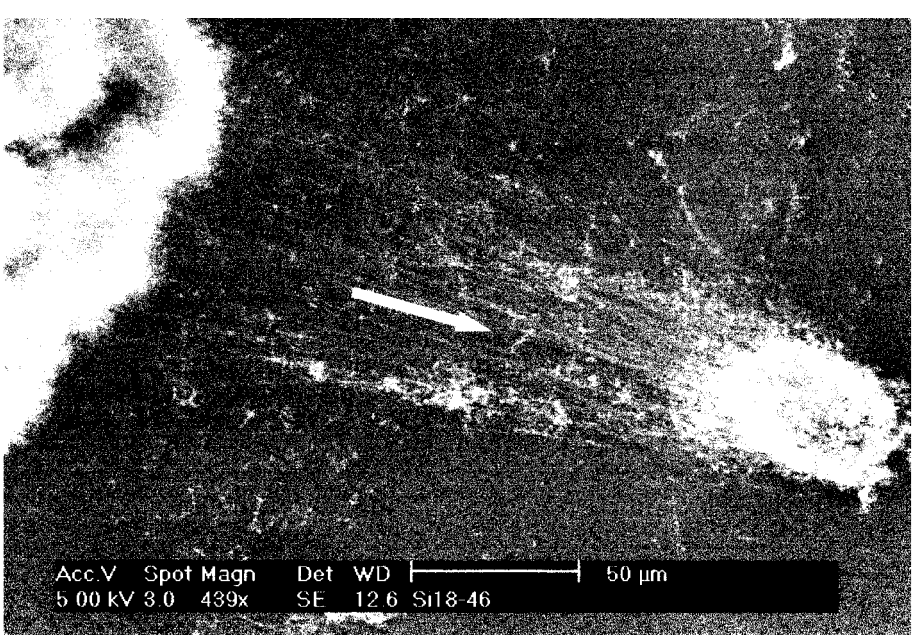


Fig.3. Separation of a piece of the "Mushroom" shaped particle introducing a brand of orientated relative straight SiNWs.

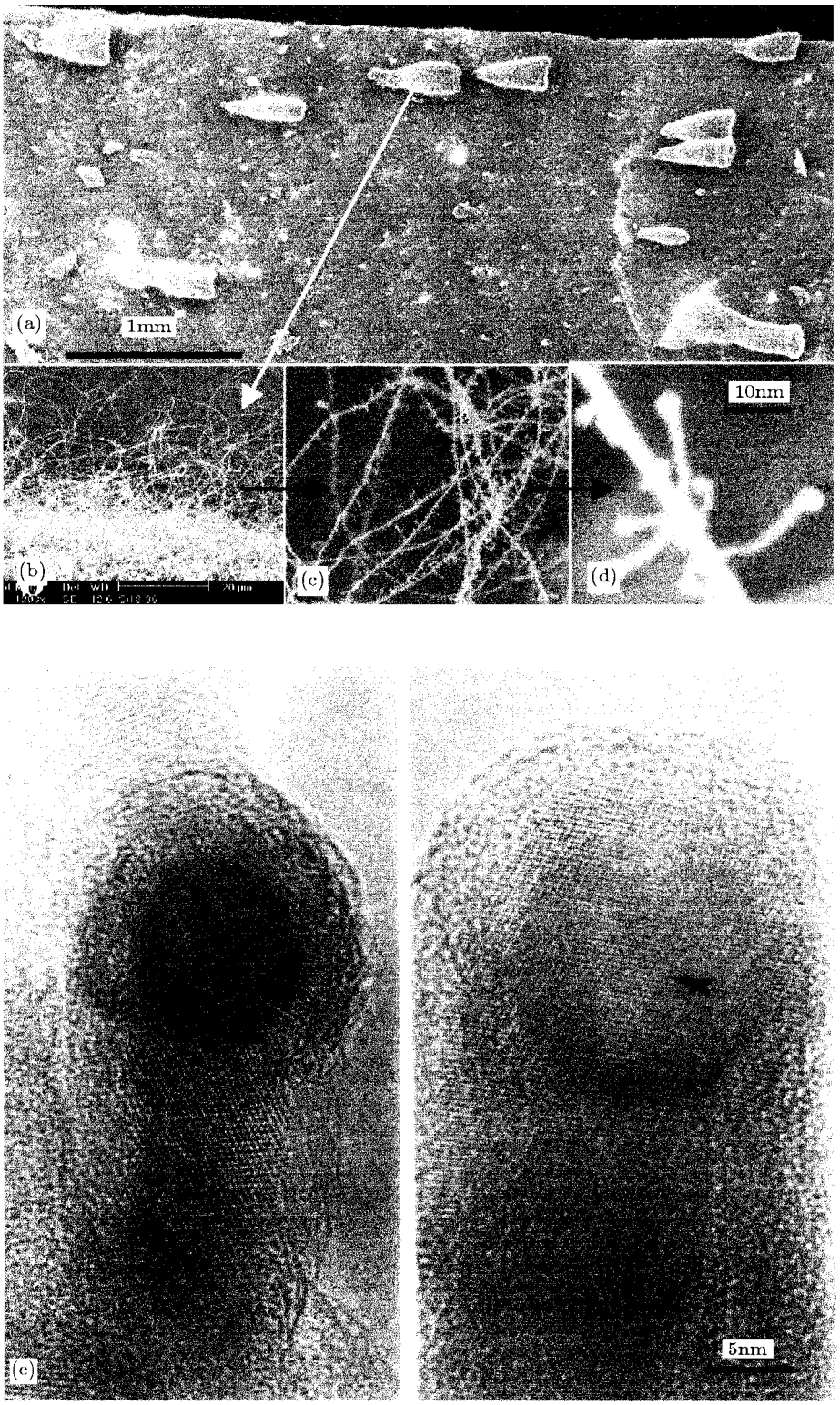


Fig.4. SiNWs grown self-assembly on surface of SiO particles with a "bottle-like" shape (a), these SiNWs are with a characteristic of sub-branch (b, c) and the main branch of SiNWs are of 40–60 nm in diameter and the silicon bulbs are found as termination of the sub-branch of SiNWs with diameters of 30–40 nm (d). HREM images show that these SiNWs with sub-branches terminated by bulbs are all with silicon structure and the bulbs are normally with micro-twins (e).

Above experimental results show that the morphology of SiNWs is sensitive to the growth temperature and composition, rendering the determination of the growth mechanism for SiNWs wrapped on particles more difficult.

Based on different synthesis methods, three models of SiNWs growth have been proposed. One is the vapor-liquid-solid (VLS) model,[1] in which metal catalysts (Ni or Fe) play the central role as a liquid droplet, which attracts vapor phase silicon atoms and/or silicon oxide clusters. When the Ni(Fe)Si_2 droplet has attracted sufficient silicon atoms from the gas phase, a supersaturating stage can be reached, resulting in the precipitation of silicon nano-wires from the droplet. Actually, the VLS model could also be extended into a solid-liquid-solid (SLS) model, in which the liquid droplet of Ni(Fe)Si gets the supply of silicon atoms not from the gas phase but through solid diffusion from the solid silicon substrate.[5] Due to the high solubility of Si in $FeSi_2$ and $NiSi_2$ eutectic alloys, silicon atoms can diffuse through the solid-liquid interface into the droplet and precipitate out again through the liquid-solid interface between the supersaturated droplet and SiNWs. This process results in the SiNWs growth from the heat treatment of a silicon substrate covered by a vapor-deposited Ni layer. Based on a systematic analysis of the growth mechanism of semiconductor nanowires, Lee *et al.*[11] proposed an oxide-assisted model in which the SiNWs were formed by two steps. Firstly, amorphous nano-particles of SiO were nucleated on the surface of SiO matrix particles, followed by phase separation and successive silicon precipitation due to the disproportion of amorphous SiO within the temperature zone of 950–1250°C. Secondly, the amorphous nano-particles of SiO_x at the tips of SiNWs continuously absorb Si–O clusters from the gas phase, which ensures the continual phase separation and precipitation and results in formation of SiNWs clad with a SiO_2 outer layer. The favorable one-dimensional growth of SiNWs are facilitated by the SiO_2 sheath which retards the lateral growth of SiNWs, and the high absorptivity for Si–O clusters of the molten SiO_x nano-particle at the tip as a growth front. The semi-liquid nature of the SiO_x tip can be understood by considering that the effective melting point of the amorphous SiO_x nano-particle should be much lower than its bulk counterpart due to the high surface/volume ratio. Actually, phase separation and/or precipitation of both silicon and SiO_2 crystallites in nano-meter size have been well documented in the literature.[12–14]

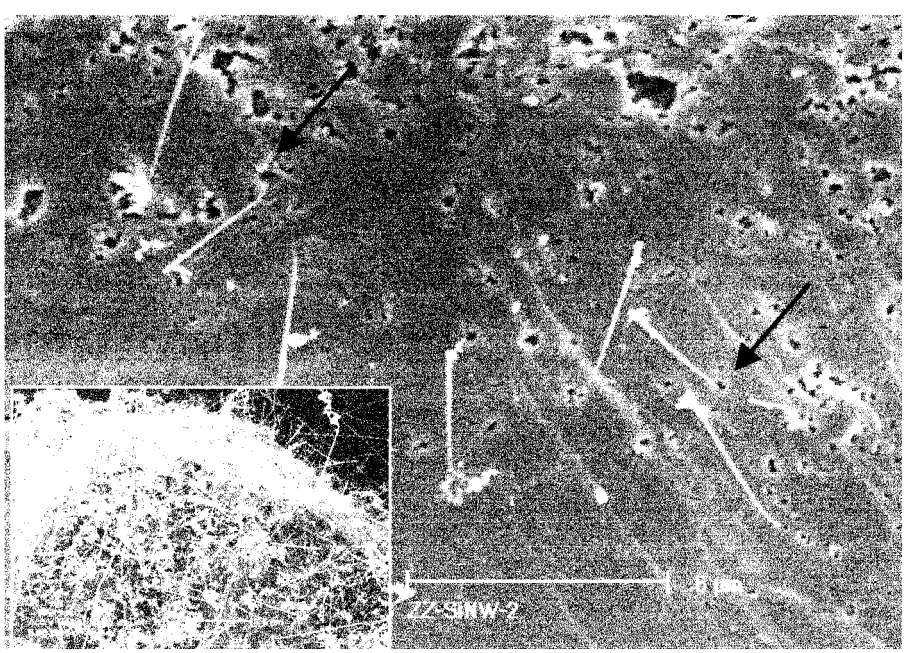


Fig.5. An evidence of the early stage of the SiNWs grown from the SiO_x particles. Note the roots of SiNWs connected to holes in the particle, denoted by arrows. A further developed stage shows an abundance of more curved SiNWs wrapped onto the particles (inset).

An evidence of growth mechanism of SiNWs wrapped onto particles can be seen from Fig.5, which shows an early growth stage of SiNWs nucleated directly from the surface of a SiO_x particle and its root is normally connected with a hole (pointed by black arrows) on the particle surface. A further developed growth stage can also be seen, for example, from the inset of Fig.5, where more curved SiNWs have developed on the surface of the SiO_x particle. Supporting the transmission electron microscopic (TEM) study,[15,16] the above SEM results provide a further experimental evidence for the nucleation site of SiNWs to be on the surface of a SiO_x matrix, where an amorphous SiO_x nano-particle is formed and successive phase separation (or decomposition) and precipitation occurs under suitable temperature and chemical composition.

From the above experimental results, we can conclude that the SiNWs on the surface of two types of particles are not formed individually in the gas phase first and then deposited on the surface of the particles. Instead, they are nucleated directly from the surface of the SiO_x particles or matrix, and grown continuously by phase separation and precipitation from the nano-sized amorphous particles on the tip, which serves as a growth front. The precipitation (or disproportionation) induced SiO_2 outer layer prevents further lateral growth, thus facilitating the favored growth of SiNWs along one dimension.

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