

Quantitative V-L-S Growth Model and Experiments of Fe Catalyzed Si Nanowire Formation

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ABSTRACT

We report the formation of Si nanowires (SiNWs) by vapor-liquid-solid (V-L-S) mechanism where Si atoms are pumped from Si wafer. This happens when a material has the large difference of activity in its pure (Si) and alloy state (Si-Fe). We developed a kinetic model to quantitatively describe the growth of the nanowires. The model predicts that the length of the nanowires increases linearly with the growth time.

INTRODUCTION

In the rapidly developing field of nanotechnology, formation of one-dimensional nanostructures has been intensively investigated because of their potential nano-device applications and the intrinsic interest in structures with reduced dimension. A variety of approaches, including thermal evaporation and laser ablation, have been successfully used to synthesize these one-dimensional structures, such as Si nanowires (SiNWs) and it was demonstrated that vapor-liquid-solid (V-L-S) reaction plays a key role in the formation of these structures [1-4]. The crystal growth by this mechanism involves vapor, liquid, and solid phases, and occurs in two steps. First, there is a condensation from the vapor to the liquid solution in a vapor-liquid system. The second step occurs in a liquid-solid system and is the precipitation from the supersaturated liquid solution at the liquid-solid interface. An important idea of the V-L-S growth model is that metal catalysts (Fe, Ni, Au, etc) act as liquid-forming agents, which react with the vapor phase, and form liquid solution droplets. Since the surface of the liquid droplets has a large accommodation coefficient and therefore the solution droplets are preferred sites for the condensation of vapor atoms which causes the liquid to become supersaturated. Crystal growth occurs by precipitation of the condensed materials from the supersaturated liquid at the solid-liquid interface and the unidirectional growth is the consequence of an anisotropy in solid-liquid interfacial energy. The V-L-S model was proposed in the 1960s-1970s [5-7], however, what kind of specific role of the metal catalysts is acting during the V-L-S growth is still not very clear and quantitative growth model describing the growth process is still lacking except for the nanowires generally have alloy droplets on their tips. In order to be able to rationally control the size, structure, composition, and axial direction of the nanowires, a better understanding of the V-L-S model is necessary. Hence, in this work we chose SiNWs as a model system to study the V-L-S growth. The role of metal catalysts playing in V-L-S growth was discussed and a quantitative growth model was proposed to account for the nanowire growth.

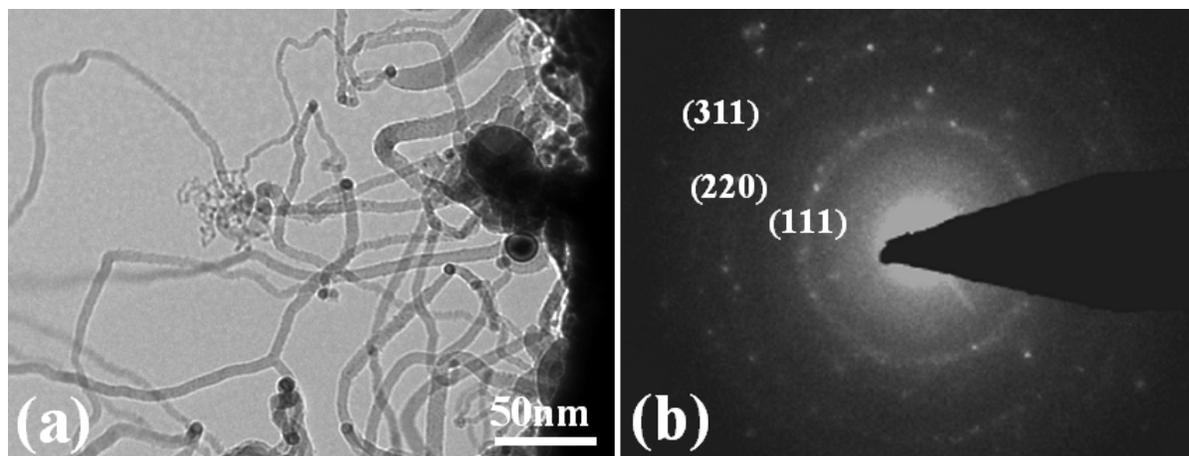


Figure 1. (a) TEM image revealing the typical morphology of the SiNWs, (b) the corresponding electron diffraction pattern from this area.

EXPERIMENTAL

Crystal silicon wafers, 350 μ m thick and 2 by 3 mm in size, with (100) orientation were used as substrate. In order for transmission electron microscopy (TEM) observation, the silicon wafer has a central hole. Single crystal 99.999% pure 700 \AA Fe films were grown on irradiated NaCl(100) substrates in an UHV e-beam evaporation system, then removed from the substrate by dissolving the NaCl in de-ionized water and physically placed onto the wafer surface. The sample was mounted in a specially modified TEM sample holder. The microscope used in this work was a modified JEOL 200CX [8]. In order to minimize the contamination, a UHV chamber was attached to the middle of the TEM column, where the base pressure was less than 10^{-8} torr without the use of the cryoshroud. The microscope was operated at 100 KeV to minimize irradiated effects. The specially designed sample holder allows for resistive heating of the sample to around 1000 $^{\circ}$ C.

RESULTS

Figure 1a is a typical TEM micrograph revealing the morphology of the SiNWs formed at 1000 $^{\circ}$ C. The average diameter of the SiNWs is about 15nm, and length can reach a few hundred nanometers. Each wire has a longitude uniformity in diameter along its axis and shows a smooth side wall. The selected area diffraction pattern (SAED) taken from the SiNWs is shown in the figure 1b, where the sharp rings can be perfectly indexed as Si structure. It is also found that all the SiNWs are virtually terminated at the end of the nanowires by nano-clusters which show different structure from Si as revealed by the electron diffraction in figure 1b, where the weak spots are from the diffraction of these nanoparticles and can be ascribed to Fe-Si alloy.

We have also observed that the length of SiNWs varied with the growth time. With continuous growth the SiNWs protruded the edges of the central hole of the Si wafer and were imaged by TEM. Figure 2a-d shows the four SiNW samples obtained for different growth time, 3, 15, 25, and 40 mins, respectively. From these experiments, the relative growth rate of the nanowires can be roughly estimated.

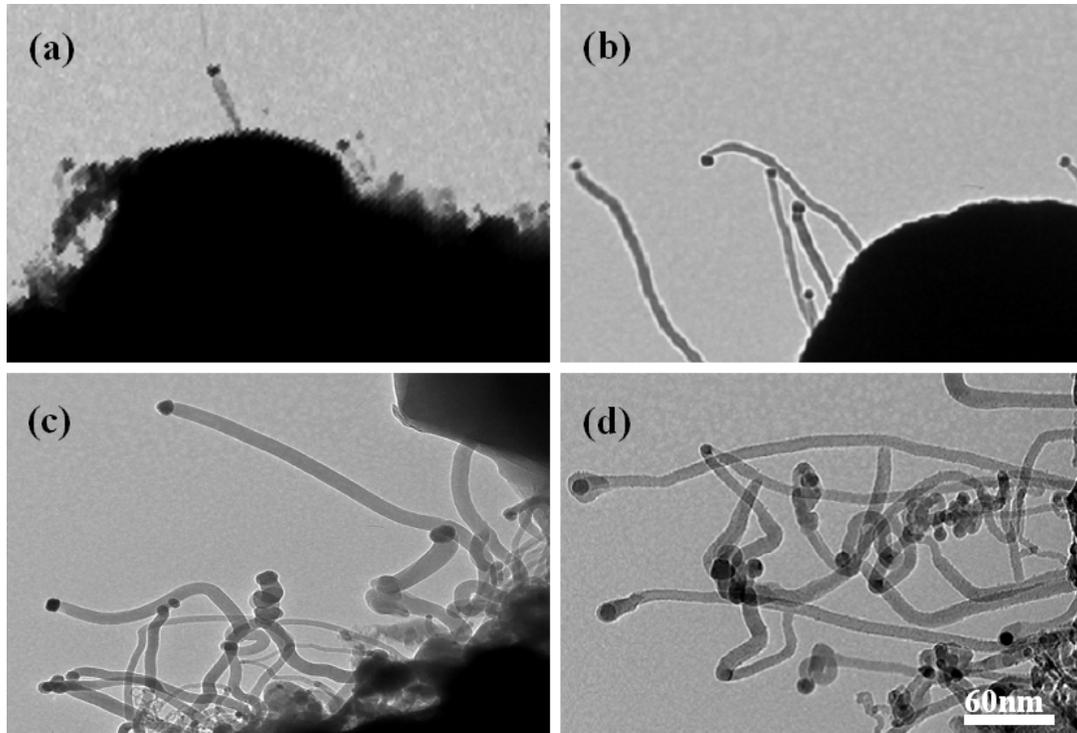


Figure 2. SiNWs formed under different growth time. (a) 3 mins; (b) 15 mins; (c) 25 mins, and (d) 40 mins.

DISCUSSION

The key factor in V-L-S model is formation of liquid droplets during the initial growth of nanowires. Therefore, the appearance of solid nanoclusters at any end of the nanowires is the most remarkable characteristics of V-L-S mechanism. The presence of Fe-Si nanoclusters at the growth end of the SiNWs in our case suggests that the growth of the nanowires proceeds by the V-L-S mechanism and the reaction process can be described as follows. When the Si wafer was resistively heated to the temperature of 1000°C, the thin Fe film alloyed with silicon substrate and formed a layer of liquid Si-Fe solution on the wafer surface. However, surface tension caused a breakup of the film and the formation of a multitude of fine alloy droplets of roughly uniform size and each droplet was the seed for V-L-S growth. Since the surface of the liquid droplets has a large accommodation coefficient and therefore each alloy droplet is the preferred site for Si atom condensation. When the liquid droplets become supersaturated with the Si atoms supplied from the vapor, the coexisting Si phase precipitates and crystallizes as nanowires at the solid-liquid interface. The process is illustrated in Figure 3. The precipitation and growth of SiNWs pushes the alloy droplet up so that the liquid droplet remains at the growing end of the nanowires, allowing the wire growth to continue. It is noted that the observation of the Si nanowire formation is at the temperature below the bulk solidus line as predicted in binary Fe-Si equilibrium phase diagram. This phenomenon was also observed by other investigations and was attributed to the lower melting points of the nanoclusters as compared with the bulk solids [1-3].

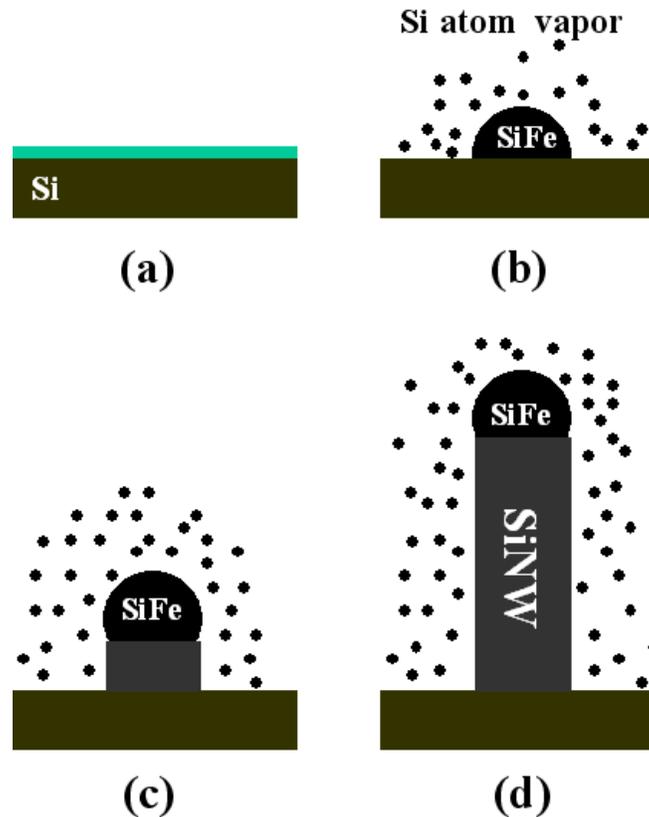


Figure 3. Schematic diagram of V-L-S growth of SiNWs on Si wafer, (a) a thin layer of Fe film with thickness of 700Å on Si(100) substrate; (b) formation of Fe-Si liquid droplet through the Fe alloying process with Si substrate at 1000°C; (c) the solution droplet becomes supersaturated with Si vapor, crystalline Si precipitates out from the droplet and pushes the droplet up; (d) the nanowires grows further due to the continuous pumping of Si atoms from the substrate by the liquid droplet.

During the V-L-S growth the liquid alloy is always constitutionally supercooled due to the vapor condensation. The composition difference in the droplet is $\Delta C = C_L - C_E$, where C_E is the equilibrium concentration without vapor condensation, and C_L is the composition of the liquid next to the gas interface. The concentration difference, ΔC , in the liquid corresponds to a liquidus supercooling ΔT . C_S is the composition at the solid-liquid interface and is the supersaturation required for nucleation and growth of new crystal. Si crystal can nucleate in the liquid when the liquidus supercooling exceeds the critical value for heterogeneous nucleation. The stability of the liquid droplet can be obtained by the continuous precipitation of Si during the V-L-S reaction. Therefore, there is a flux of silicon atoms due to a concentration difference ΔC across the liquid alloy droplet to the growth front of the nanowires. For the stable droplet the steady state growth conditions should be reached, i.e., the number of silicon atoms that enters the liquid interface through condensation on the vapor-liquid interface is same as precipitated at the solid-liquid. For a condensation reaction of vapor atoms evaporated from the substrate, the flux J (atoms/nm² sec) of vapor atoms condensed into the liquid alloy droplet can be estimated from gas kinetics as:

$$J_c = \alpha \sigma \gamma_{Si} X_{Si} (2\pi mkT)^{-\frac{1}{2}} \quad (1)$$

where α is the accommodation coefficient, usually the surface of the liquid droplets has a large accommodation coefficient, $\sigma = (1 - \gamma_{Si} X_{Si}) / \gamma_{Si} X_{Si}$ is the supersaturation of the liquid droplet in which γ_{Si} is the activity coefficient of Si, and X_{Si} is its mole fraction in the liquid alloy. From equation (1) we can know that the role of Fe catalyst acting is to reduce the activity of Si by the Si-Fe alloying process, and a force capable of driving Si atoms from substrate onto the free surface of Fe-Si droplet is present in the difference between the activity of Si atoms in pure and alloy state. As a result, the silicon substrate is progressively depleted by transfer of Si atoms into the Fe-Si droplets, this continues as the precipitation of SiNWs until the liquid droplet is elevated to a low temperature zone where the liquid droplet is solidified and the transfer of Si atoms is kinetically hindered. It is known that pure Si has very low equilibrium vapor pressure up to 1000°C, however, the presence of Fe-Si droplets enhances the evaporation of Si from its substrate driven thermodynamically. As a result, a large flux of Si atoms can be transferred from a pure Si reservoir to Si-Fe droplet.

At the steady-state growth conditions, the precipitation of Si atoms into the nanowire from the liquid droplet creates a growth rate of the nanowires which is equal to the speed of advancement of the S-L interface,

$$\frac{dN(t)}{dt} = AJ_c, \quad (2)$$

where $N(t)$ is number of Si atoms in the SiNW at time t , A is the area of the V-L interface. We assume that the nanowire has cylinder shape with diameter of d , the liquid droplet at the growth end has a cap shape with radius of R . By solving the above differential equation, the nanowire length increases linearly with respect to growth time

$$L = \frac{8\Omega R}{d^2} \left(R + \sqrt{R^2 - \frac{d^2}{4}} \right) \times \frac{\alpha(1 - \gamma_{Si} X_{Si})}{\gamma_{Si}} (2\pi mkT)^{-\frac{1}{2}} \times (t - t_0), \quad (3)$$

where Ω is the atomic volume of Si in SiNW. In the model we assume that no surface migration of Si atoms on the side faces of the growing crystals to the liquid occurs, and the diameter of the

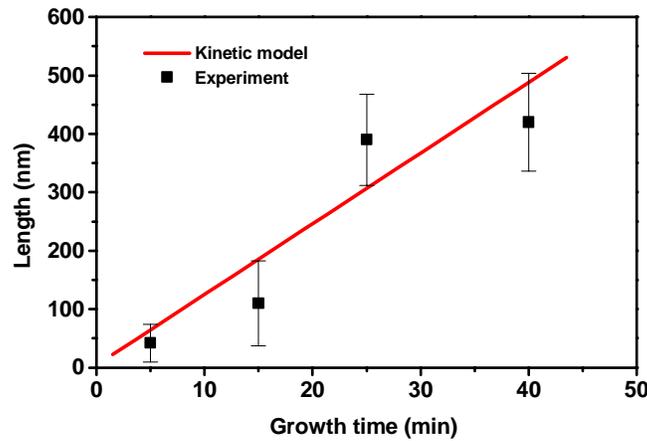


Figure 4. Dependence of the nanowire length on the growth time and fit to the kinetic model.

nanowires is only determined by the size of the S-L interface. From equation (3) it is known that the growth rate is closely related to the Si activity coefficient in the Fe-Si alloy, low activity in alloy state will give rise to fast growth rate. The activity coefficient can change with the composition of the alloy, therefore, during the alloying process of the Si-Fe system, γ_{Si} is not constant. However, for the stable liquid droplet, the composition of the droplet won't change and γ_{Si} will keep constant when SiNWs are precipitated from the supersaturated liquid droplet. Therefore, equation (3) can be practically applied to predict the length of the nanowires grown by V-L-S mechanism. The thermodynamic data about Fe-Si system indicate that the activity coefficient of Si, γ_{Si} , is much smaller than 1 ($\gamma_{\text{Si}} \sim 10^{-5} - 10^{-4}$ at 1000°C for $X_{\text{Si}} < 0.3$) [9, 10]. The radius (R) of the droplet and the diameter (d) of the nanowires can be measured experimentally, and we have obtained a reasonable accordance of this model with our experimental measurements as shown in Figure 4.

CONCLUSION

We have described quantitatively the formation of SiNWs by V-L-S mechanism. The liquid droplet of Fe-Si alloy pumps Si atoms from its substrate to SiNWs driven by the large difference of activity coefficient of Si in its pure and alloy state. A kinetic model was developed to predict the length of the nanowires.

Acknowledgements: This research project is funded by National Science Foundation (# 9902863), Department of Energy–Basic Energy Science and National Association of Corrosion Engineers seed grant. The experiments were performed at the Materials Research Laboratory, University of Illinois at Urbana-Champaign, which is supported by the U.S. Department of Energy (#DEFG02-96-ER45439). The authors kindly thank I. Petrov, R. Twesten, M. Marshall, K. Colravy, and N. Finnegan for their help.

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