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Observation of Incubation Times in the Nucleation of Silicon Nanowires Obtained by the Vapor–Liquid–Solid Method

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We report the observation of a characteristic incubation time in the growth of silicon nanowires using the vapor–liquid–solid growth mechanism. This incubation time manifests itself during the growth process as a characteristic time delay in the range of several seconds to minutes, prior to which no nanowires are formed. The observation is in excellent agreement with a theoretical model based on the diffusion of silicon through the catalyst, which predicts the presence of an incubation time, as determined by diffusion of the growth constituent through the solid catalyst. Furthermore the theoretical dependence of the incubation time on the activation energy is derived, and validated experimentally for the first time by measuring the incubation times of silicon nanowires obtained by chemical vapor deposition for both gold and copper as a catalyst. The experimentally observed incubation times are in excellent agreement with the theoretically predicted incubation times. The reported incubation times are a universal feature of vapor–liquid–solid growth and can be applied to any other metal/semiconductor system for the synthesis of nanowires and provide a novel route to determine the phase space for nanowire-synthesis.   [DOI: 10.1143/JJAP.45.L190]

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Silicon nanowires have attracted significant attention in the last few years owing to their reduced dimensionality, which is of interest in both fundamental and applied studies. On a fundamental side, the nanoscale dimensions lead to inherently quantum mechanical effects such as the Coulomb blockade effect.[1,2] On the applied side silicon nanowires hold the promise for the realization of high device density chips[3,4] and complementary metal–oxide–semiconductor (CMOS) technology compatibility. To date silicon nanowires have been synthesized and a wide range of electronic devices[5–11] with nanoscale dimensions, highly sensitive biochemical sensors, dye sensitized solar cells as well as novel thermo-electric properties have been demonstrated. In light of the growing number of research and application areas, an physical understanding of the growth process of silicon nanowires is becoming increasingly important. The generally accepted theory of silicon nanowire growth is the vapour–liquid–solid (VLS) growth mechanism, based on growth from a liquid metal seed particle.[12–15]

Here we analyze the temporal characteristic of the initial phase of the VLS growth mechanism and demonstrate for the first time that the growth of nanowires occurs with a characteristic, strongly temperature dependent time delay on the order of several seconds to minutes. This novel mechanism has not been reported before, and is shown to be an inherent property of the VLS growth mechanism and of particular importance when carrying out growth at low temperatures. Furthermore, it is demonstrated that measurement of the incubation time as a function of temperature yields the activation energy of the diffusion coefficient through the catalyst, and thereby provides a quantitative analysis of the growth kinetics. To confirm these findings, silicon nanowires were grown using the VLS method with different catalytst, gold and copper respectively and the incubation times recorded. The inferred activation energy is in excellent agreement with tabulated bulk values, and therefore shows for the first time the important role that the solid catalyst plays in determining the temporal behaviour and onset of the growth process. Besides providing a physical understanding of the Cu–Si and Au–Si system the presented model and methodologies can be further extended to other alloys of technological and scientific interest, such as aluminum, gallium, titanium and indium.

Silicon nanowires are most commonly synthesized using the VLS growth mechanism. In brief, the synthesis proceeds in the following steps. The fusion temperature of an element can be lowered by alloying it with other elements. The eutectic temperature is the lowest temperature at which the mixture of two or more elements liquefies. Fusion temperature of pure gold is $1064°C$ and as low as $363°C$ when alloyed with 18% of silicon. At other mixture proportions and/or higher temperatures, liquid mixtures of Au and Si and their solid phases may coexist as a function of the impurity content. The VLS method for synthesizing silicon nanowires is based on the precipitation of silicon in a liquid Au–Si droplet. A good understanding of the thermodynamic phase diagram of the Au–Si alloying system is therefore fundamental in the understanding of the nucleation mechanism of silicon nanowires, as well as for finding the conditions of optimal synthesis.

The thermodynamic phase diagram of the gold-silicon alloying system presents a simple eutectic form,[16] and is presented schematically in Fig. 1. On the diagram, the arrow indicates the evolution of the composition of gold droplets during the VLS process. The origin of the arrow represents the starting point of VLS synthesis: Indeed, substrates are covered with Au nanoparticles and are usually heated under vacuum at a temperature higher than the eutectic. Au nanoparticles are initially solid. Subsequently, a silicon source in the vapor phase is preferentially adsorbed at the surface of the gold droplets. Due to the concentration gradient at the surface, silicon diffuses through the gold droplet. Following the thermodynamic phase diagram, a phase separation of the liquid Au–Si alloy and solid Au occurs. The composition of the liquid mixture is denoted c_1, as shown in the thermodynamic diagram. In order to model

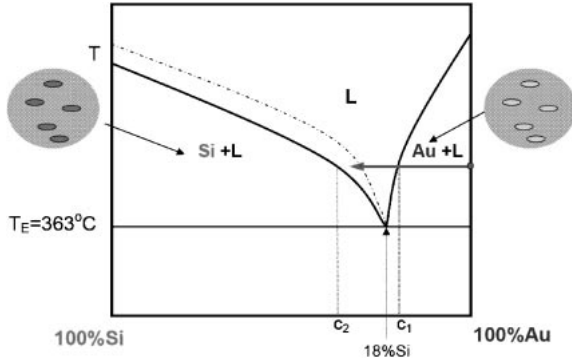*E-mail address: annafm@wsi.uni-muenchen.de

Fig. 1. Schematics of the thermodynamic phase diagram of the Au–Si system. The dotted line represents the modification of the solid–liquid line induced by the interaction with the substrate.
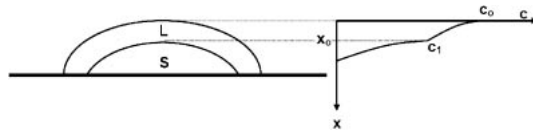

Fig. 2. Definition of the geometry considered for the unidimensional model of diffusion of the liquid Au–Si alloy through the initially solid Au droplet.

this process, we assume that the silicon content profile in the droplet during nucleation can be represented as in Fig. 2. As schematized, the gold droplet consists of a liquid shell and a solid center. The liquid front advances as silicon diffuses further in solid gold. Upon contact with the substrate the whole droplet is in the liquid phase with concentration c_1. Simplifying the geometry in one dimension, the movement of the liquid–solid interface can be described by a diffusion equation with a moving boundary:

$$\frac{\partial c_L(x,t)}{\partial t} = D_L \frac{\partial^2 c_L(x,t)}{\partial x^2}, \quad 0 \le x \le x_0(t), \quad (1)$$

$$\frac{\partial c_S(x,t)}{\partial t} = D_S \frac{\partial^2 c_S(x,t)}{\partial x^2}, \quad x \ge x_0(t), \quad (2)$$

Where D_S and D_L are respectively the diffusion coefficients of silicon through solid and liquid gold, c_S and c_L the silicon content of the solid and liquid phase, and $x_0(t)$ the moving liquid–solid boundary. As boundary conditions, we assume that: c_{L0} is the silicon content at the liquid surface of the droplet ($x=0$), c_1 is the silicon content at the liquid–solid interface $x = x_0$, and that the silicon content at the solid boundary with the substrate is zero at $t=0$. By solving the equations with this boundary conditions, it can be shown that the profiles of silicon content in the droplet are:

$$c_L(x,t) = c_{L0} + (c_{L0} - c_1) \frac{1}{\operatorname{erf}\left(\frac{\beta^2}{D_L}\right)} \operatorname{erf}\left(\frac{x}{2\sqrt{D_L t}}\right) \quad (3)$$

$$c_S(x,t) = c_1 \left(1 - \frac{1}{\operatorname{erf}\left(\frac{\beta^2}{D_S}\right)} \operatorname{erf}\left(\frac{x - x_0(t)}{2\sqrt{D_S t}}\right) \right), \quad (4)$$

Which implies that the movement of the liquid–solid interface $x_0(t)$ is necessarily of the form:

$$x_0(t) = 2\beta\sqrt{t}. \quad (5)$$

By assuming continuity of the silicon flow at the liquid–solid interface, and by considering that $D_S \ll D_L$, an expression for β can be obtained. Together with eq. (5), it can be shown that the characteristic time for the solid–liquid interface to reach the substrate follows as:

$$\tau \approx \frac{h^2}{\beta^2} \approx \frac{h^2}{\langle D_{S0} \rangle \exp[-E_a/(KT)]},$$

where

$$\langle D_{S0} \rangle = D_{S0}\left(1 + \ln \frac{c_1}{c_0 - c_1}\right), \quad (6)$$

where h is the height of the nanoparticle. This result indicates that the liquid–solid interface advances with the bulk diffusion coefficient of silicon through solid Au, modulated by the silicon concentration gradient at the liquid phase.

It is instructive to compare the phase evolution of the Au–Si droplets during VLS to a bulk Au–Si alloy. In bulk Au–Si, the alloy remains liquid for silicon contents between c_1 and c_2 (see Fig. 1). For contents equal or higher than c_2, silicon precipitates homogeneously in the form of lamellae within the melt. In the case of Au–Si liquid droplets on a substrate, the precipitation of silicon is induced by the substrate and occurs necessarily at concentrations below c_2:

$$c_{\text{precip}} = c_1 + B(\gamma, T) < c_2, \quad (7)$$

where B is a function of the interface energy, γ, and temperature, T. In terms of the thermodynamic phase diagram, the 'early' silicon precipitation can be represented by the displacement of the liquid–solid (Si) line towards lower silicon concentrations, which is indicated by the dotted line.

In the VLS process, the substrate induced silicon precipitation is a crucial ingredient, as for concentrations equal or higher than c_2, silicon will precipitate within the droplet and not necessarily only on the substrate. Once precipitation of silicon starts, and provided that the external synthesis conditions are maintained, equilibrium is established between the flux of silicon through the droplet and the precipitation underneath in the form of nanowires.

We call incubation time, τ, the time required for the starting of nanowire growth. τ mainly corresponds to the time required for the fused Au–Si phase to advance through the catalyst nanoparticle. Importantly, this parameter can be measured by monitoring the surface at the first stages of growth by scanning electron microscopy (SEM). This observation can be realized by *in situ* SEM or by realizing chemical vapor deposition (CVD) runs of increasing durations and analyzing them. The accuracy of the method is determined by the time interval chosen between growth runs, the capability of reaching the same temperature on the wafer, and the accuracy of gas handling system to introduce and stop the silane flow in the tube furnace.

To experimentally determine the incubation time, silicon nanowires were synthesized by catalytic CVD. The substrates were thermally oxidized silicon wafers covered with
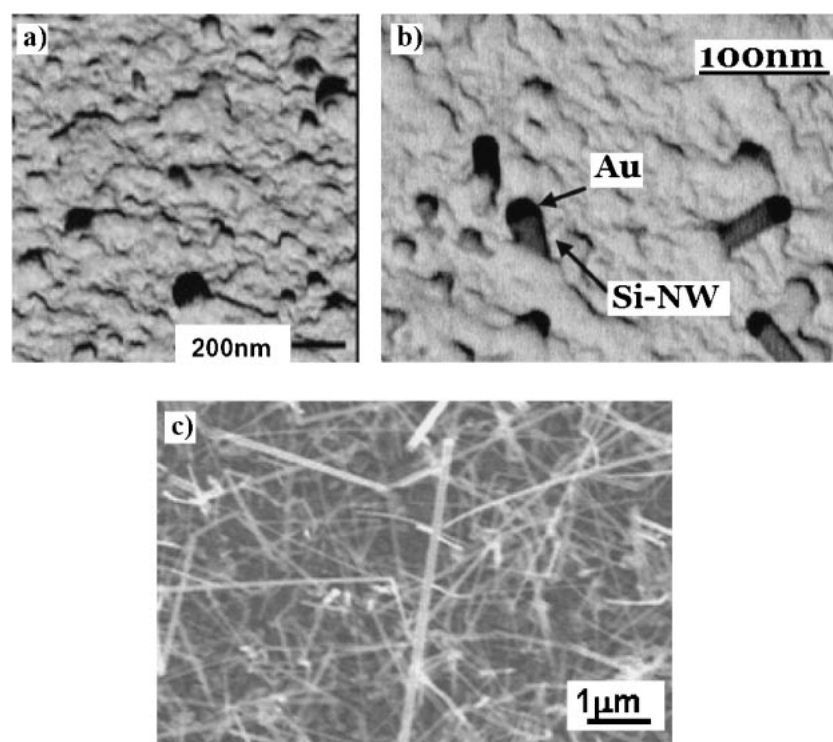
Fig. 3. SEM micrographs of the surface of three CVD runs at 550°C, representing the stages just prior to nucleation, 30 s (a), just after nucleation, 45 s (b) and steady growth (c).

a 3 nm Au layer. Copper was also used as a catalyst, with similar initial thickness. The substrates were heated under vacuum and under flow of 100 sccm of H_2 during 5 min prior to deposition for the sake of getting a uniform temperature through the substrate. For the silicon nanowire synthesis, 2.5% silane was added to the hydrogen flow in the furnace. Silane is decomposed only at the surface of the metal, thanks to an Au-mediated catalytic decomposition of silane. Indeed, it has been shown that at temperatures equal or higher than 200°C this reaction occurs in the form:[17]

$$SiH_4 + Au(s) \rightarrow Si + Au + H_2 \qquad (8)$$

In the case of Cu, a similar catalytic decomposition reaction is expected to occur. Systematic CVD runs were realized with durations varying between 5 and 300 s at temperatures ranging between 450 and 650°C. Deposition time could be accurately controlled with a flow-meter and a gas valve connected in series at the entrance of the furnace. The surface topology was measured with SEM. In order to validate the reproducibility of the growth, selected depositions were realized twice and excellent reproducibility of the growth stage was found. Moreover, the ratio between the total silane partial pressure P_{Si} and gas temperature T_g was kept constant, according to the ideal gas law ($P_{Si}V = NRT_g$), resulting in a constant silane density in the gas phase for the entire range of temperatures used in the experiments. In our experimental set up, we believe that the accuracy in finding the incubation time is determined mainly by the time interval within the different CVD runs.

In Fig. 3, three SEM micrographs of the surface of three CVD runs at the early stages of silicon nanowire synthesis are shown. For contrast purposes, in Figs. 3(a) and 3(b) we chose to present the negatives of the SEM measurements.

Table I. Nucleation times measured for temperatures ranging from 450 to 700°C.

T (°C)	Au, τ (s)	Cu, τ (s)
450	180 ± 20	—
500	60 ± 10	120 ± 20
550	37 ± 10	45 ± 10
600	20 ± 10	
650	15 ± 5	10 ± 5

All three depositions were obtained at 550°C. Micrographs 3(a) and 3(b) correspond respectively to CVD runs at 30 and 45 s. As evident, in the figure the growth of nanowires occurs after 30 s and prior to 45 s. In the present example the nucleation time was therefore chosen to be 37 s. A similar procedure was used for all temperatures and for substrates covered with Cu. In Table I the obtained nucleation times for Au and Cu are presented, and a clear temperature dependence emerges: while at high temperatures (e.g., 650°C of CVD) nanowires already form after 15 s, reducing the temperatures causes a significant increase in the nucleation time. For instance, at a temperature of 450°C one needs to wait more than 180 s in order to observe nanowire growth. In Fig. 4, the nucleation times are plotted as a function of the inverse of temperature in a semi-logarithmic scale. From the plot in Fig. 4, an activation energy of 0.68 eV was deduced. According to eq. (6) the activation energy corresponds to the activation energy of the diffusion of silicon through solid Au. This is a relatively low value, 0.45 eV lower than the diffusion of Au through Si.[18] In the case of copper, the temperature dependence of τ indicates a slightly higher incubation energy of 0.98 eV. This
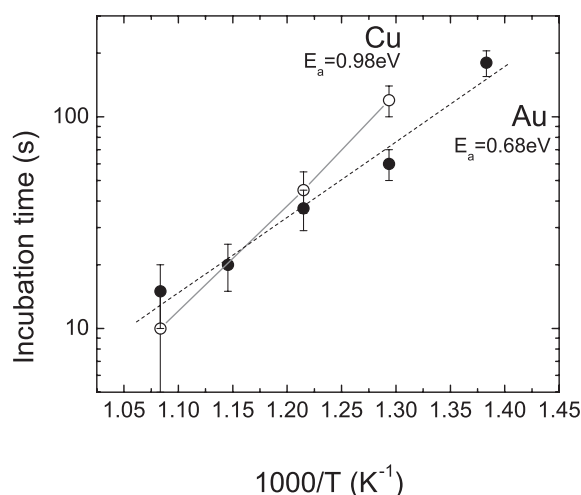
Fig. 4.   Incubation times for silicon nanowires grown separately with gold and copper as catalysts plotted as a function of the inverse of temperature on a semi-logarithmic scale. The activation energy is determined from the slope.

value coincides remarkably well with the activation energy measured by Chromik *et al.* for the diffusivity of silicon in Cu for the formation of $Cu_3Si(s)$.[19] Therefore the presented results are the first reported measurements of both incubation time and activation energy for the nucleation of silicon nanowires. Our results indicate that by comparing tabulated values of diffusion of silicon through other metals, it should be possible to deduce the nucleation kinetics of silicon nanowires in other metal-silicon systems. The presented method can therefore be used for understanding the kinetic limitations of silicon nanowires growth with other metal catalysts and/or synthesis techniques.

In summary, using a theoretical model and experimental results, we have shown that the diffusion of silicon through the solid catalyst determines an incubation time for the onset of silicon nanowire growth. This newly discovered mechanism is an inherent property of the VLS growth method. We have experimentally observed these incubation times in the growth of nanowires, synthesized by CVD at temperatures between 450 and 650°C. The recorded incubation times as a function of temperature agree well with the presented theoretical model, and allow the determination of activation energies of 0.68 and 0.98 eV respectively for gold and copper as a catalysts. Both, the model and experimental observations are important as they demonstrate the kinetic limitations for the nucleation of silicon nanowires when different catalysts are used. The reported findings should furthermore also be applicable to other semiconductor nanowires, as long as their synthesis is based on the VLS growth method.

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