

# Influence of gold particle size on melting temperature of VLS grown silicon nanowire\*

Jiang Yanfeng(姜岩峰)<sup>†</sup> and Zhang Yamin(张亚民)

(Microelectronic Center, College of Information Engineering, North China University of Technology, Beijing 100144, China)

**Abstract:** Based on the Lindemann melting model, a model related to gold nanoparticle size and melting temperature for VLS grown silicon nanowire is proposed. Eutectic temperatures of Au–Si with different gold sizes have been calculated using the model and are in agreement with the experimental results. This model has been demonstrated to be reasonable, and it can be used to determine the growth temperature of silicon nanowire.

**Key words:** silicon nanowire; eutectic temperature; Au  
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## 1. Introduction

With the development of microelectronic technology and integration ability, the dimensions of silicon devices have decreased to the nanoscale. Semiconductor nanowires have received increasing attention during recent years because of their possible application as future building blocks for new kinds of nanoscale devices<sup>[1–8]</sup>. Compared to nanowires from III–V- or II–VI-semiconductors, silicon nanowires have the advantage of being compatible with today's technology for integrated silicon circuits (ICs). On the other hand, silicon nanowires provide an interesting and promising system for investigating phenomena associated with low-dimensional semiconductor nanostructures. Because of the superior properties of silicon nanowire, much more attention is paid to its preparation and application.

Up to now, many different methods for the preparation of silicon nanowire have been proposed, such as laser melting<sup>[3,4]</sup>, CVD<sup>[1,5]</sup>, physical evaporation<sup>[6]</sup>, and supercritical fluid<sup>[7]</sup>. In terms of growth mechanisms corresponding to different methods, vapor–liquid–solid (VLS) growth<sup>[1,2,8]</sup>, oxide-assisted growth<sup>[4]</sup>, solid–liquid–solid growth<sup>[9]</sup> and so on are available.

One relative mature technology for silicon nanowire growth is the VLS method using gold particles as a catalyst<sup>[1,3,4]</sup>. This method has been used successfully in the preparation of silicon nanowires with different diameters, whose electrical properties have been measured, demonstrating that they can be used practically. During preparation, one key parameter is the eutectic temperature of Au–Si. If the temperature control is not suitable, silicon nanowire surface defects and an amorphous crystal nucleus of the oxide outer layer structure appear, which could affect the wire's properties. Actual experimental results have shown that the eutectic temperature is influenced by Au particle size, which in turn determines the nanowire's diameter. This means that the morphology and the structure of silicon nanowires is closely related to the growth

temperature<sup>[5,6]</sup>. Therefore, it is necessary to study the relationship between the diameter of silicon nanowires and the optimal growth temperature.

In this paper, firstly, according to the Lindemann melting criteria<sup>[10]</sup> and the relationship between melting temperature and vibration entropy derived by Mott<sup>[11]</sup>, the effect of size on Au particle melting temperature is derived. A relationship between particle size and melting temperature is obtained and is compared with actual experimental results. In the third part, an experiment is done based on the calculated melting temperature for a sample. Through comparison, it is been concluded that there is an improvement in the properties of a sample grown at the calculated temperature.

## 2. Model for the effect of size of Au particles on eutectic temperature

The phenomenon that the melting point of a metal particle is influenced by its size was discussed by Buffat<sup>[2]</sup> in 1976. It was proposed that metal particle melting points are lower compared to bulk material and are variable with different sizes.

The earliest expression for the size effect of low-dimensional material melting points was derived by Pawlow<sup>[12]</sup> and amended by Hanszen<sup>[13]</sup>, and is given as:

$$\frac{T_m(D)}{T_m(\infty)} = 1 - \frac{4}{\rho_s L D_s} \left[ \gamma_s - \gamma_l \left( \frac{\rho_s}{\rho_l} \right)^{2/3} \right]. \quad (1)$$

In Eq. (1),  $D$  is the particle diameter.  $T_m(D)$  is the particle melting temperature and  $T_m(\infty)$  is that of the bulk.  $L$  is the latent heat of fusion,  $\gamma$  is the surface tension, and  $\rho$  is the density. The subscripts s and l in Eq. (1) stand for solid and liquid, respectively.

Later, Buffat *et al.*<sup>[2]</sup> extended Pawlow's model into second order. Since in the melting state, solid and liquid states of the same material have the same surface potential, a more detailed model using the Gibbs–Duhem equation combined with

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<sup>†</sup> Corresponding author. Email: yfjiang@ncut.edu.cn

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the Laplace theorem and the Clapeyron equation was obtained, given as:

$$\frac{T_m(D)}{T_m(\infty)} = 1 - \frac{4}{\rho_s L} \left[ \frac{\gamma_{sl}}{D - \delta} + \frac{\gamma_l}{D} \left( 1 - \frac{\rho_s}{\rho_l} \right) \right], \quad (2)$$

in which  $\delta$  is the thickness of the liquid layer and  $\gamma_{sl}$  is the interfacial energy difference between the solid and liquid phases.

In the above models, only the surface atoms have been considered to have an influence on the melting point. But the relaxation and restructuring processes of surface atoms during melting should be considered, too. Moreover, the interface energies in Eqs. (1) and (2) are difficult to determine. So, in this paper, a suitable model is proposed based on Lindemann's proposal.

Lindemann<sup>[10]</sup> proposed a melting model using the theory of simple harmonic vibration of an atom. An assumption was made that when the amplitude of the atomic thermal vibration in a crystal exceeds the atom's minimum distance, melting will occur. The model in this paper is also based on the above assumption.

The average atomic thermal vibration energy in Lindemann's model can be expressed as in Eq. (1):

$$M(2\pi\nu_E)^2 \sigma^2 = kT, \quad (3)$$

in which  $M$  is the mass of the atom,  $\nu_E$  is the Einstein frequency,  $\sigma^2$  is the root-mean-square amplitude,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature.

According to Lindemann's assumption, when the root-mean-square amplitude  $\sigma$  reaches the atom's minimum distance, melting occurs. So, Equation (4) can be obtained, which relates to the bulk melting point  $T_m(\infty)$ , that is,

$$\Theta_D = c \left[ T_m / MV^{1/2} \right]^{1/2}. \quad (4)$$

In this equation,  $\Theta_D$  is the Debye temperature,  $c$  is a constant,  $M$  is the mass of the atom, and  $V$  is the volume of the atom.

First of all, the mean square displacement of a gold nanocrystal atom  $\sigma^2(D)$  has been calculated, and the relationship to the size can be expressed as<sup>[14, 15]</sup>

$$n\sigma^2(D) = n_v\sigma_v^2(D) + n_s\sigma_s^2(D),$$

or

$$\sigma^2(D) = \frac{n_v}{n}\sigma_v^2(D) + \frac{n_s}{n}\sigma_s^2(D). \quad (5)$$

In this equation, s and v denote surface and interior.  $\sigma^2(D)$  is the average value of the vibration mean square displacement.  $n_s$  denotes the number of atoms at the surface.  $n_v$  is the number of interfacial atoms.

Equation (5) shows that the total mean square displacement of atom vibration can be divided into two parts, surface and interior. Because the interfacial atoms have a higher free energy, melting often starts at the interface<sup>[15]</sup>.

With particle size  $D$  increasing, on condition that the volume of the lattice is fixed, the relative ratio of surface to interior  $n_s/n_v$  is increased. Because the interior atoms have a higher free energy, melting temperature is also increased accordingly.

Below we discuss the direct relationship between amplitude  $\sigma^2(D)$  and  $D$  based on Eq. (5).

Two assumptions are made:

(1) The ratio between  $\sigma_s^2(D)$  and  $\sigma_v^2(D)$  is a constant value, denoted as  $\sigma_s^2(D)/\sigma_v^2(D) = \sigma_s^2(\infty)/\sigma_v^2(\infty) = \alpha$ . Here  $D = \infty$  corresponds to the bulk material.

(2) A new parameter  $D_0$  is defined, which corresponds to the case that all atoms are located at the surface. According to Friedel's nucleation theory<sup>[16]</sup>, when particle size is less than a critical dimension of the crystal nucleus, the melting temperature will be zero. So there exists a critical size for a crystal, which can exist only when the diameter is greater than this size. Based on this assumed parameter, the ratio between  $n_s$  and  $n_v$  is:

$$x = n_s/n_v = D_0/(D - D_0)$$

Based on the above two conditions, we can get:

$$\sigma^2(D)/\sigma^2(\infty) = \exp[(1 - \alpha)/(D/D_0 - 1)]. \quad (6)$$

According to the Lindemann criteria, when the mean-root-square displacement of atomic  $\sigma(D)$  is more than 10% of the atom's distance, the crystal will melt. That is, the melting temperature can be given by the relation:  $\sigma/h = 10\%$ .

From the above equations, we derive:

$$\Theta_D^2 = c^2 T_m / MV^{1/2},$$

$$T_m(D)/\Theta_D^2(D) = T_m(\infty)/\Theta_D^2(\infty),$$

$$\sigma^2(D)\Theta_D^2(D) = \sigma^2(\infty)\Theta_D^2(\infty) = \text{const.}$$

So we can also derive the following equation:

$$T_m(D)/T_m(\infty) = \exp[(1 - \alpha)/(D/D_0 - 1)]. \quad (7)$$

It can be seen that in cases where  $\alpha$  and  $D_0$  are known, the melting temperature can be determined. The method for calculation of the two parameters is discussed below.

Assuming that the shape of the nanoparticle is spherical,  $D_0$  is the diameter when all the atoms of the crystal are located at the surface, by

$$4\pi(D_0/2)^2 h = 4\pi(D_0/2)^3/3. \quad (8)$$

In this equation,  $h$  is the height of the surface atom layer of the bulk crystal, which approximately equals the atom's diameter. So,

$$D_0 = 6h. \quad (9)$$

According to Mott's theory<sup>[11]</sup>, crystal melting entropy can be expressed as

$$S_m(\infty) = 2R \ln(\nu_s/\nu_l). \quad (10)$$

$\nu_s$  and  $\nu_l$  are the vibration frequency of the solid and liquid crystal at the melting temperature, respectively.  $R$  is a gas constant. At the melting temperature, the maximum frequency of the crystal can be calculated by the following formula:

$$\nu_s = F[T(\infty)/MV^{2/3}]^{1/2}. \quad (11)$$

$M$  is the mass of the atom,  $T_m(\infty)$  is the melting temperature of the bulk crystal,  $V$  is the atom volume,  $F$  is a constant with a value of  $2.06 \times 10^{12} \text{ kg}^{1/2} \cdot \text{m}/(\text{s} \cdot \text{K}^{1/2})$ <sup>[17]</sup>. The

frequency of the liquid can be calculated by the following formula:

$$v_l = \frac{3}{4} \eta [N_0^2 / \rho M^2]^{1/2}. \quad (12)$$

$\eta$  is the dynamic viscosity coefficient,  $N_0$  is the Avogadro constant, and  $\rho$  is the density of the liquid.

The relationship between the crystal vibration entropy  $S_{vib}(\infty)$  and the melting temperature  $T_m(\infty)$  can be derived from Eqs. (10)–(12) as:

$$S_{vib}(\infty) = 3R \ln \frac{C(\infty)}{C_l(\infty)} \left( \frac{\pi^4}{6N_0} \right)^{3/2} \left[ \frac{T_m(\infty)}{M} \right]^{1/2}. \quad (13)$$

$C(\infty)$  and  $C_l(\infty)$  is the ultrasonic velocity of the macro-crystal and liquid, respectively. According to Eq. (7), the ratio of the macro-crystal's melting temperature to that of the nano-crystal equals to the ratio of the square of Debye temperatures. Because the relationship between vibration entropy and Debye temperature is linear, the square of a particle's vibration entropy is also proportional to melting temperature. For the nanoparticle, from Eq. (13), the relation between melting vibration entropy  $S_{vib}(D)$  and melting temperature  $T_m(D)$  can be expressed as in Eq. (14):

$$S_{vib}(D) = 3R \ln \frac{C(D)}{C_l(D)} \left( \frac{\pi^4}{6N_0} \right)^{3/2} \left[ \frac{T_m(D)}{M} \right]^{1/2}. \quad (14)$$

Combining Eqs. (13) and (14), Equation (15) is obtained:

$$S_{vib}(D) - S_{vib}(\infty) = \frac{3R}{2} \ln \frac{T_m(D)}{T_m(\infty)}. \quad (15)$$

Combining Eqs. (7) and (15), we get:

$$S_{vib}(D) = S_{vib}(\infty) - \frac{3R}{2} \left( \frac{\alpha - 1}{D/D_0 - 1} \right). \quad (16)$$

Because vibration entropy is the main contributor to crystal melting entropy, we obtain:

$$S_m(D) = S_m(\infty) - \frac{3R}{2} \left( \frac{\alpha - 1}{D/D_0 - 1} \right). \quad (17)$$

Because the crystal structure is in long-range order, at least half of atoms in crystal will locate inside the atom. That means the smallest  $D$  should be  $2D_0$ .

When  $D$  approaches  $2D_0$ , the crystal and the liquid have the same structure, and so  $S_m(D_0)$  will be zero. From Eq. (17), one can get:

$$\alpha = [2S_{vib}(\infty)/(3R)] + 1. \quad (18)$$

For metals, the main contribution to melting entropy comes from vibration, so  $S_{vib}(\infty) = S_m(\infty)$ .

For Eq. (18),  $\alpha = 1$  corresponds to bulk material, so the melting temperature is unchanged. When the vibration from surface atoms is more than that from internal atoms, the melting temperature will decrease, so  $\alpha > 1$ . Combining Eqs. (7), (9) and (18), a relationship between nanoparticle melting temperature and size can be obtained as shown in Eq. (19):

$$T_m(D)/T_m(\infty) = \exp \{-4hS_m(\infty)/[R(D - 6h)]\}. \quad (19)$$

The above equation is the result of the model which we derived. The relationship between nano-size melting temperature and that of the bulk material has been established.

Table 1. Related experimental results from References.

Response agents	Catalyst	Growth mechanism	Growth temperature	Diameter (nm)	Length ( $\mu\text{m}$ )
SiH <sub>4</sub>	Au	VLS	638–768	3–12	1–3
SiH <sub>4</sub>	Au	VLS	643–773	3–15	1
Si <sub>2</sub> H <sub>6</sub>	Au	VLS	873	50	10–20
SiH <sub>4</sub>	Au	VLS	673–873	20–100	10

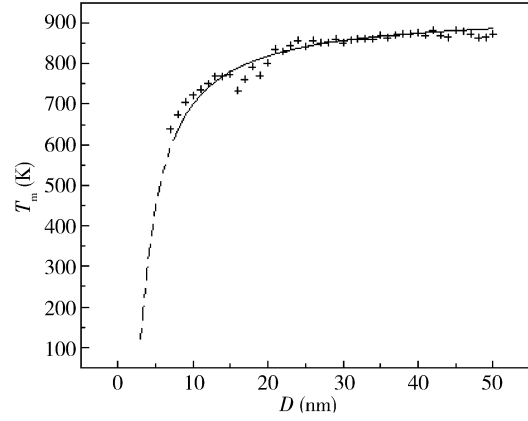


Fig. 1. Comparison of model prediction values and experimental results.

### 3. Analysis and discussion

For a silicon nanowire grown by the VLS method catalyzed by gold particles, there are a lot of relevant results, as shown in Refs. [1–9]. For the process of SiNW growth, it can be formed by the Au–Si eutectic temperature, and at the point where the nano-cluster and Si are super-saturated, a solid–liquid Si/Au–Si alloy interface appears. In order to reduce the interfacial free energy and the occurrence of solid growth in the initial interface, the nanowire forms along the anisotropic direction.

Through actual measurement of eutectic temperatures at different Au particle sizes, it can be found that when the Au size changes, the eutectic temperature also changes. In fact, controlling the bath temperature during nanowire growth is to adjust the Au–Si alloy eutectic temperature, which depends on the particle size. According to the model in the previous discussion, with decreasing size, the ratio of surface atom number to internal number is increased. Because surface atoms have higher free energy than internal ones, the total mean square amplitude should increase, which eventually results in the reduction of melting temperature.

Table 1 shows some related experimental results from Refs. [1–9]. It can be seen that the growth temperature is varied with the same diameter in different work. The authors of this paper think that the nanowire's quality could be improved if it is grown at a suitable temperature.

Figure 1 shows a comparison between the model and the experiment. The curve in Fig. 1 corresponds to Eq. (19) with eutectic temperatures of different sizes, in which the atom diameter  $h = 0.3118$  nm, bulk gold crystal melting temperature  $T_m(\infty) = 1203$  K, melting entropy  $S_m(\infty) = 15.38$  J/(mol · K)<sup>[18]</sup>. From the curve we can observe that the particle's melting temperature drops with decreasing particle size. When the

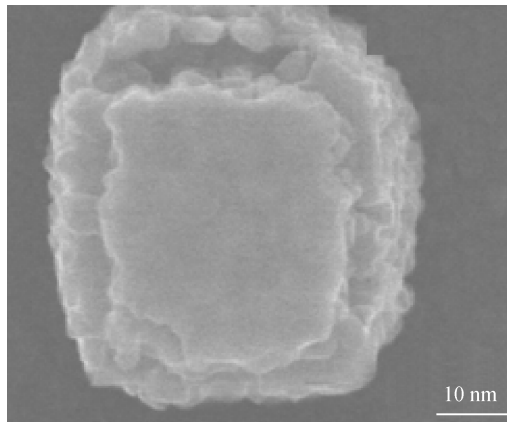


Fig. 2. Terminal section profile of the grown SiNW.

size is smaller than 30 nm, there is an obvious decrease in temperature.

The dots correspond to the actual data from Refs. [1–9]. It can be seen that our curve fits the data quite well.

According to Fig. 1, it can be seen that the Au–Si alloy melt temperature is consistent with Eq. (19) when the size of the Au–Si alloy particle is larger than 22 nm. However, some differences exist between theory and experiment when particle size is smaller. This may be attributed to two causes. The first may lie in the fact that the model only considers the size effect, neglecting others, which leads to the deviation from the experimental results. The other reason is that an assumption has been made that the silicon nanowire diameter and the Au–Si alloy diameter are fully consistent. In fact, the silicon nanowire diameter fluctuates from 1–2 nm compared with the Au particle size<sup>[3,4]</sup>. When the diameter is large, for example above 22 nm, the fluctuation can be neglected. However, at small sizes, its influence can be prominent.

The model can be used to determine the growth temperature on condition that the particle size is known. Initially, the eutectic temperature is unknown. Different groups have used different temperatures and grown nanowires of the same diameter. In our experiment, we have made a comparison according to the following: silicon nanowire with diameter 30 nm would be grown by the VLS method. According to the model, the eutectic temperature should be 843 K. So a sample is grown under these conditions. For comparison, another sample with the same diameter is grown at 873 K.

The Si nanowire in this paper was synthesized by the vapor–liquid–solid method, in which Au clusters were used as a solvent at high temperature. The Si and Au formed a liquid alloy and when the alloy became supersaturated with Si, Si nanowires grew by precipitation at the liquid–solid interface. SiNW was grown from 30 nm Au nanoclusters and the average nanowire diameter was  $30 \pm 2$  nm, according to the authors' experience. The length of well-defined nanowires can be controlled by adjusting the growth time during synthesis. The CVD reactor was evacuated to less than 100 mTorr.  $\text{SiH}_4$  was 50 sccm flow. The profile structure of the terminal of the grown SiNW is shown in Fig. 2. The scale bar in the image is 10 nm. It can be observed that the grown structure is similar to the shell–core structure.

Since the samples from the VLS growth method always

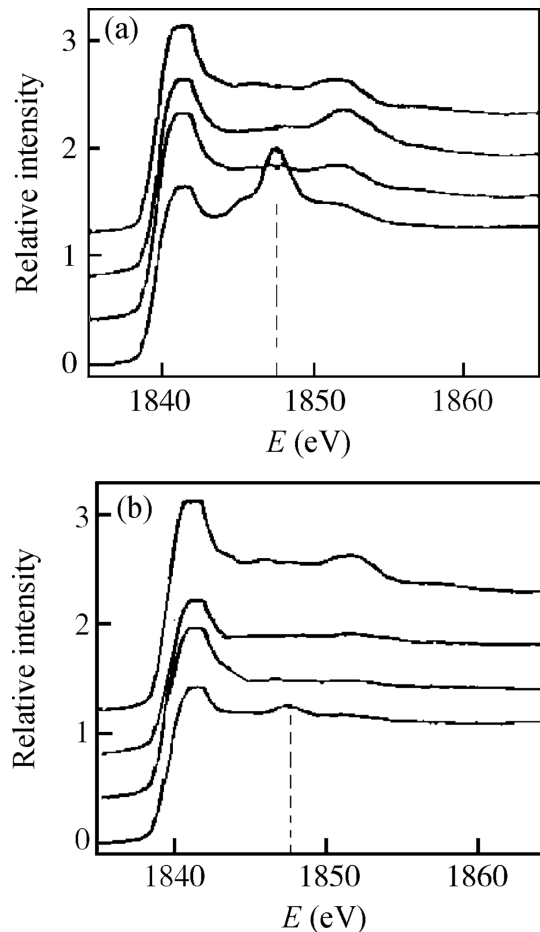


Fig. 3. XAFS spectra of the silicon nanowire grown at (a) 873 K and (b) 843 K.

have a shell–core structure, we use the XAFS (X-ray absorption fine structure spectroscopy) method to measure the samples.

XAFS refers to the modulation of the absorption coefficient above an absorption threshold (edge) of a core level of an element in a chemical environment. These spectral features are intimately related to the extended local shells of neighboring atoms. Figure 3(a) shows a normal specimen grown at 873 K, which is higher than the theoretical value. All spectra have been normalized to unity edge jump and shifted vertically for clarity. As noted above, the as-prepared SiNWs are encapsulated by a relatively thick oxide layer and are generally chemically inert. The first resonance at 1840 eV arises from the unoxidized crystalline Si core of the nanowire. It can be seen that a peak resonance appears at 1848 eV, corresponding to the oxide.

For comparison, the sample grown at 843 K was measured, as shown in Fig. 3(b). It shows a much-reduced oxide signal in the sample grown at 843 K, compared to that at 873 K, which indicates that the intensity of the oxide is very much reduced. This means that the growth conditions under theoretical values can have a good effect on the quality of the grown sample.

Based on the results in Fig. 3, a conclusion can be drawn that using a suitable eutectic temperature during growth can indeed improve the nanowire's quality. So, the feasibility of the model is demonstrated.

#### 4. Conclusion

In this paper, a model which can be used to describe the eutectic temperature under different nanowire diameters has been proposed. It has been compared with experimental results, and coincides with experiment when the diameter is larger than 22 nm. Reasons for errors at small sizes have also been discussed.

Through actual experiment, it can be observed that the model can be used to determine the precise eutectic temperature. Thus, the nanowire's quality can be increased with the reduction of surface defects and the amorphous crystal-nuclear oxide outside layer.

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