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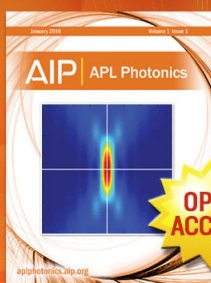
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A nanoscale temperature-dependent heterogeneous nucleation theory

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Classical nucleation theory relies on the hypothetical equilibrium of the whole nucleation system, and neglects the thermal fluctuations of the surface; this is because the high entropic gains of the (thermodynamically extensive) surface would lead to multiple stable states. In fact, at the nanometer scale, the entropic gains of the surface are high enough to destroy the stability of the thermal equilibrium during nucleation, comparing with the whole system. We developed a temperature-dependent nucleation theory to elucidate the heterogeneous nucleation process, by considering the thermal fluctuations based on classical nucleation theory. It was found that the temperature not only affected the phase transformation, but also influenced the surface energy of the nuclei. With changes in the Gibbs free energy barrier, nucleation behaviors, such as the nucleation rate and the critical radius of the nuclei, showed temperature-dependent characteristics that were different from those predicted by classical nucleation theory. The temperature-dependent surface energy density of a nucleus was deduced based on our theoretical model. The agreement between the theoretical and experimental results suggested that the developed nucleation theory has the potential to contribute to the understanding and design of heterogeneous nucleation at the nanoscale. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4922415>]

I. INTRODUCTION

Nanostructures, such as quantum dots and quantum rings, nanowires, and nanotubes, have attracted considerable interest, as a result of their great potential for microelectronic and optoelectronic nanodevices.^{1–4} The first step in the growth of a nanostructure is the nucleation process. The nucleation process, in which clusters of a new phase form from a parent phase, is a universal phenomenon in both nature and technology; for example, nucleation occurs in the basic processes of gas condensation, liquid evaporation, and crystal growth.^{5–7} In the case of the formation of nanostructures, heterogeneous nucleation is much more common than homogeneous nucleation in practice,^{8–12} and this heterogeneous process can determine the growth evolution of various nanostructures.^{13,14}

The classical nucleation theory—which is based on the collective, pioneering work of Volmer and Weber,¹⁵ Farkas,¹⁶ and Becker and Döring¹⁷—has been widely used to address various nucleation processes.^{9,18} However, the actual nucleation process is more complex at the nanometer scale than indicated by the ideal description provided by the classical nucleation theory,^{9,19} and some new nucleation phenomena cannot be explained by the classical nucleation theory. The classical nucleation theory predicts that in the heterogeneous nucleation process, the surface of a cluster that grows to form a heterogeneous nucleus is always smooth

and stable. However, the surface of such nuclei would certainly become unstable on the nanometer scale under the influence of thermal fluctuations, which are strongly temperature-dependent.⁹ The classical nucleation theory therefore cannot be applied to elucidate the heterogeneous nucleation process at the nanoscale under the influence of thermal surface fluctuations.

Motivated by this problem, we developed a temperature-dependent nucleation theory to address the heterogeneous nucleation on the nanoscale based on the classical nucleation theory. In our theory, the thermal fluctuations of the surface are taken into account within the framework of statistical mechanics and quantum mechanics. The developed theory not only brings to light novel, interesting information about heterogeneous nucleation on the nanoscale, but also hints at ways to control the nucleation.

II. THEORY

In classical nucleation theory, the surface of a nucleus is assumed to be a locally flat substrate on which the cluster grows as a spherical cap in a heterogeneous process. Considering the change of Gibbs free energy induced by the bulk and the surface, the Gibbs free energy activation barrier for the heterogeneous nucleation can be expressed as⁹

$$\Delta G = \Delta gV + F_s, \quad (1)$$

where Δg , V , and F_s are the Gibbs free energy difference per unit volume, the volume of the nucleus, and the change of surface energy, respectively. Based on Tan's model and the

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Kelvin equation, taking the capillary effect of the nanosized curvature of the nuclei on the Gibbs free energy of the nucleation into account, Δg can be defined as $\Delta g = -\frac{1}{2} \frac{R_m T}{V_m} \ln \frac{P}{P_e} - \frac{\sigma_0}{R_0}$, where T , σ_0 , and R_0 are the temperature, the nucleus-vapor interfacial energy, and the radius of the nucleus, respectively.^{9,13,19} R_m and V_m are the gas constant and the molar volume of the nucleus, respectively. P and P_e are the vapor pressure and the equilibrium vapor pressure, respectively. The effect of the bulk on the change in the energy barrier is shown in the first term of Eq. (1); the second term represents the influence of the surface. The influence of the thermal fluctuations is mainly reflected in the surface of the nucleus. Thus, we only considered the change in the surface energy of the nucleus. The change in the surface energy F_s was always considered as $F_s = \sigma_0 S$, where σ_0 and S are the constant surface energy density and the surface area, respectively. However, before the formation of the nucleus, the surface of cluster does not remain smooth and stable as described in the classical nucleation theory, especially in the presence of thermal fluctuations. The classical nucleation theory relies on the hypothetical equilibrium of the whole nucleation system, and neglects thermal fluctuations of the surface, because high entropic gains of the (thermodynamically extensive) surface would lead to multiple stable states.⁹ In fact, at the nanometer scale, the entropic gains of the surface are high enough to destroy the stability of the thermal equilibrium during the nucleation, in comparison with the whole system. Thus, the surface energy would be different from that predicted by classical nucleation theory. To address the influence of the thermal fluctuations on the surface energy, we introduced a temperature-dependence to the surface of cluster; i.e., considering the thermal fluctuations, the surface of the cluster was not kept smooth. Here, we assumed only small deviations from the spherical shape, and we therefore took the radius of the sphere to be $r = R_0(1 + \varepsilon)$, in which ε could be expanded in real spherical harmonics as $\varepsilon = \sum_{l=1}^{\infty} \sum_{m=-l}^l x_{l,m} Y_{l,m}(\theta, \varphi)$.²⁰ We used the surface Hamiltonian to represent the thermal fluctuations on the surface, and expressed it as

$$H_s = \int_0^{2\pi} \int_0^{\theta_0} \sigma_0 R_0^2 (\varepsilon^2 + 2\varepsilon + 1) \sin \theta d\theta d\varphi, \quad (2)$$

where θ and φ are the characteristic angles of the cluster.

Based on the surface Hamiltonian, we obtained the partition function of the surface energy as

$$Z = \int D \sum \delta(\nu[\sum] - V) e^{-\beta H_s}, \quad (3)$$

where $\nu[\sum]$ is the volume enclosed by the surface \sum , and the integral measure $D \sum$ can be written as $\int D \sum = \int_{-\infty}^{+\infty} \prod_{l>0,m} (\frac{\xi}{s} dx_{l,m}) \int_0^{+\infty} \frac{dR_0}{a}$. a is a characteristic system length of the nucleus materials, while the characteristic surface is $s = 4\pi a^2$.

According to the partition function and the behavior of the spherical harmonics, we obtained the surface energy, including the effects of temperature:

$$F_{ST} = 2\pi\sigma_0 R_0^2 (1 - \cos \theta) - \frac{1}{\beta} \ln \frac{S}{as} - \frac{1}{\beta} \sum_{m=0}^{\infty} \ln \sqrt{\frac{1}{\beta\sigma_0 R_0^2 (f_1 + f_2 + f_3)}}, \quad (4)$$

where f_1 , f_2 , and f_3 are factors of the characteristic angle of the nucleus.²¹ The surface energy was therefore temperature-dependent in our approach; the surface energy did not remain constant with the same radius of nucleus, as predicted by classical nucleation theory. Furthermore because of the temperature-dependent surface energy, the Gibbs free energy activation barrier for heterogeneous nucleation was also temperature-dependent

$$\Delta G_T = \Delta g V + F_{ST}. \quad (5)$$

Moreover, based on this adjusted Gibbs free energy activation barrier, we obtained the nucleation rate in our model as

$$I_T = I_0 e^{-\beta \Delta G_T}, \quad (6)$$

where I_0 is a kinetic prefactor; $\beta = \frac{1}{kT}$, where k is the Boltzmann constant. The nucleation rate I in the classical nucleation theory can be obtained by the same way, except the energy barrier, ΔG , is different.

When the radius of the cluster reached a critical value, the nucleus would form; the formation of the nucleus indicates the start of nanostructural growth. Thus, the critical radius R_{CT} is an important indicator for nucleation, and can be obtained by

$$\frac{\partial \Delta G_T}{\partial R_0} = 0. \quad (7)$$

Similar to the nucleation rate, the critical nucleus radius R_{CT} in our model was different from R_C , which is obtained using ΔG in the classical nucleation theory. At the critical nucleus radius, the Gibbs free energy barrier achieved maximum values ΔG_T^* and ΔG^* . When the radius of the cluster exceeds the critical radius size, the cluster can be called a nucleus. It is the time to grow to the nanostructures.

Based on the surface energy, and taking account of the thermal fluctuations and the surface area of the nucleus, we obtained the average surface energy density as

$$\sigma_T = \sigma_0 - \frac{1}{S\beta} \ln \frac{S}{as} - \frac{1}{S\beta} \sum_{m=0}^{\infty} \ln \sqrt{\frac{1}{\beta\sigma_0 R_0^2 (f_1 + f_2 + f_3)}}. \quad (8)$$

The first term is the constant surface density σ_0 identified in classical nucleation theory, which can be obtained via first principle calculations.²² The other terms in Eq. (8) relate to the thermal fluctuations. Thus, the surface energy density was shown to be temperature-dependent.

According to the analysis above, and as a result of the introduction of the thermal fluctuations on the surface, the surface energy was shown to be temperature-dependent. Hence, the temperature not only affected the volume term of the Gibbs free energy activation barrier, but also influenced the surface term. The adjusted Gibbs free energy activation

barrier indicated that the nucleation rate and the critical nucleus radii, which characterized the nucleation process, varied as a function of the adjusted Gibbs free energy activation barrier. The surface energy density in our model also showed a temperature dependence. Our model therefore elucidated the further dependences of the nucleation behavior on changes in the temperature, over those disclosed by the classical nucleation theory.

III. RESULTS AND DISCUSSION

We took the Ge/Si heterogeneous system as an example to verify our theory. In the following calculations, the surface energy density and molar volume of the Ge nucleus were taken as $\sigma_0 = 6.05 \text{ eV/nm}^2$ (Refs. 23 and 24) and $V_m = 13.636 \times 10^{21} \text{ nm}^3/\text{mol}$,²⁵ respectively. Taking into account the thermal fluctuations on the surface, the surface energy was obtained using Eq. (4), with the critical nucleus radius. As shown in Fig. 1(a), the surface energy decreased with the temperature in lines with square. The surface energy is invariant with changes in temperature in the classical nucleation theory; this is shown as a solid line. We elucidated the influence of changes in temperature on the surface energy by introducing the thermal fluctuations to the surface of the cluster before the formation of the nucleus. The thermal fluctuations destroyed the stability of the surface and the nucleus. When the temperature was increased, the thermal fluctuations were stronger, and the loss of energy in the equilibrium was greater. Therefore, the surface energy decreased with the temperature.

According to the temperature dependence of the surface energy, the Gibbs free energy activation barrier was different from that predicted by the classical nucleation theory. The Gibbs free energy activation barrier is shown for different radii at 300, 600, and 900 K in Fig. 1(b). The Gibbs free energy activation barrier was different for different radii. The energy barrier was at a maximum when the radius achieved the critical value; this value was obtained using Eq. (7). The critical radius and critical energy barrier varied with changes in the temperature. To illustrate the influence of the temperature-dependent surface energy, we compared the critical energy barrier with and without thermal fluctuations, and the results are shown in Fig. 1(c). The critical energy barrier with thermal fluctuations was smaller than that without thermal fluctuation. Furthermore, the gap between the two models became larger with the temperature because of the stronger thermal fluctuations at higher temperatures.

The nucleation rate also showed differences in our model because of the changes in the Gibbs free energy activation barrier. As shown in Fig. 2, we compared the nucleation rate obtained using our model and that obtained using the classical nucleation theory. The nucleation rate increased with the temperature; because of the decrease in the energy barrier, the nucleation rate determined using our model was larger than that predicted by the classical nucleation theory.

The change in the surface energy and the Gibbs free energy activation barrier also affected the evolution of the critical nucleus radius. The critical radius is defined as the size at which the Gibbs free energy activation barrier reaches

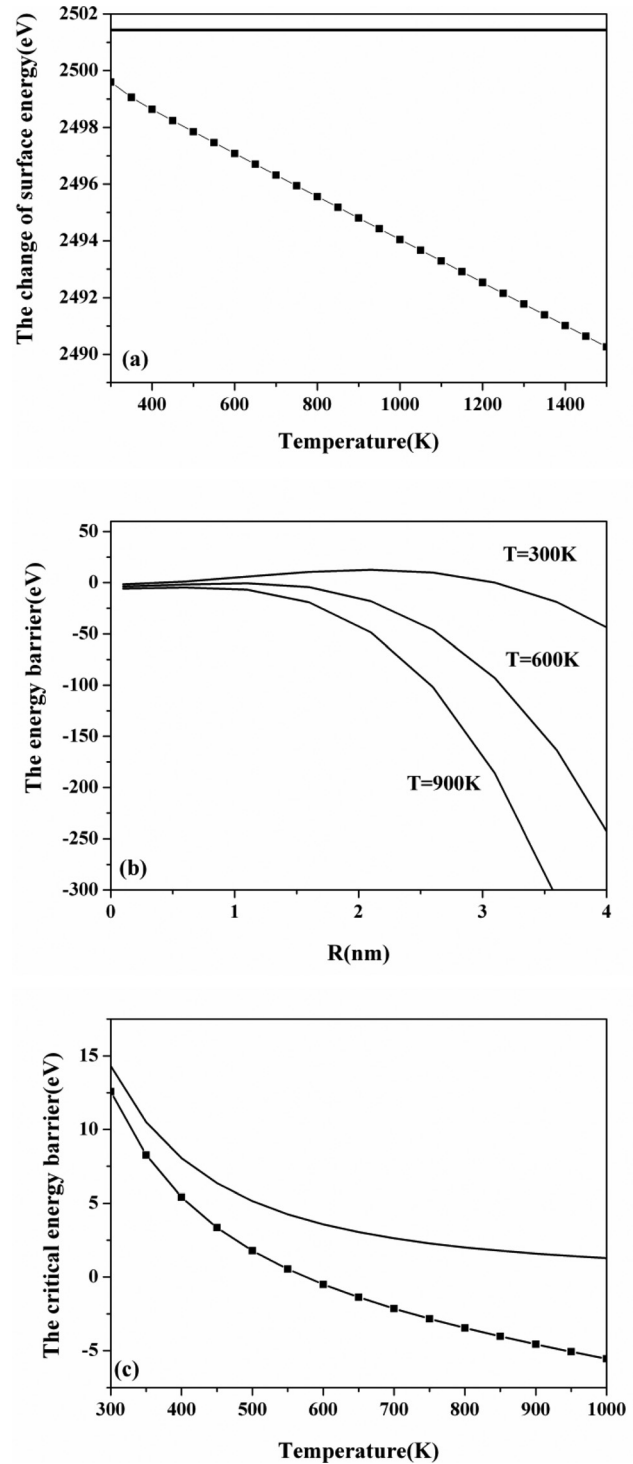


FIG. 1. (a) The surface energy as function of temperature. The line with square represents the surface energy obtained by our model, while the solid line represents the surface energy in classical nucleation theory. (b) The behavior of Gibbs free energy activation barrier with various radii of nucleus at the temperature of 300 K, 600 K, and 900 K. (c) The comparison of the critical energy barrier with critical radius under various temperature conditions. The line with square represents the critical energy barrier in our model, while the solid line represents the critical energy barrier in classical nucleation theory.

a maximum value. When $R > R_c$, the cluster becomes a true nucleus, and begins to grow. Thus, the critical nucleus radius is an important indication of progress in the nucleation process. We obtained the critical radius using Eq. (7), and

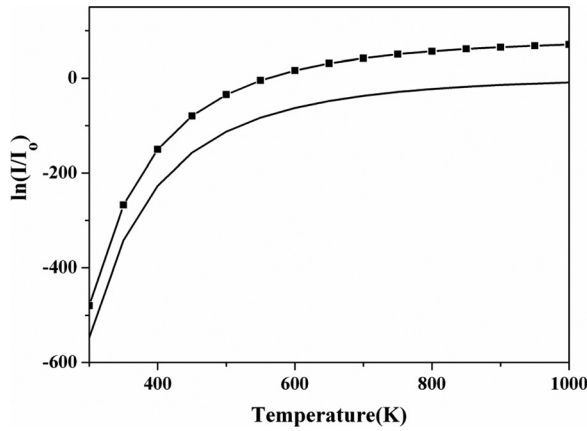


FIG. 2. The ratio of nucleation rate obtained by the two models as function of temperature. The line with square denotes the ratio of nucleation rate in our model, while the solid line denotes the ratio of nucleation rate in classical nucleation theory.

compared our results with those predicted by classical nucleation theory. As shown in Fig. 3(a), the critical radius of the nucleus decreased with increases in temperature, which indicated that the nucleus was formed more easily at higher

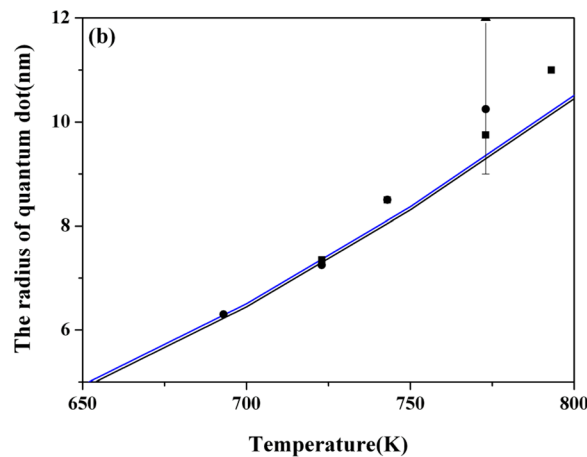
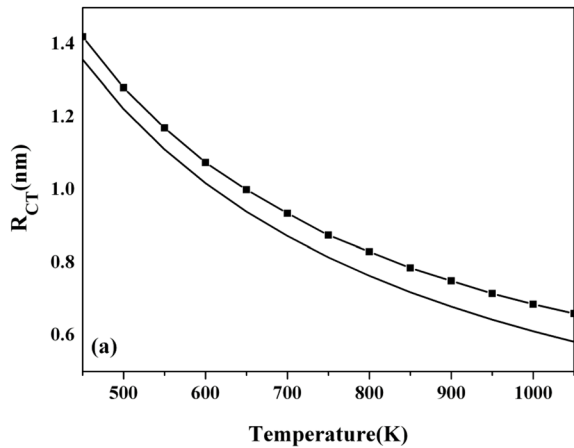


FIG. 3. (a) The relationship curves between the critical radius of nucleus and the temperature. (b) According to the critical radius of nucleus by our theory and classical nucleation theory, the radius of quantum dots after 180 s growth at various temperatures. The experimental data are from Refs. 25, 28, and 29.

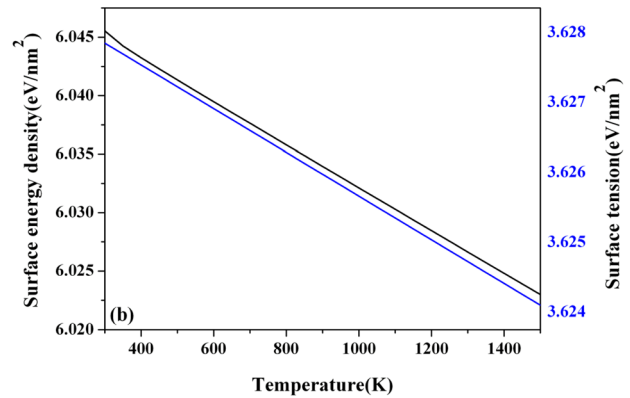
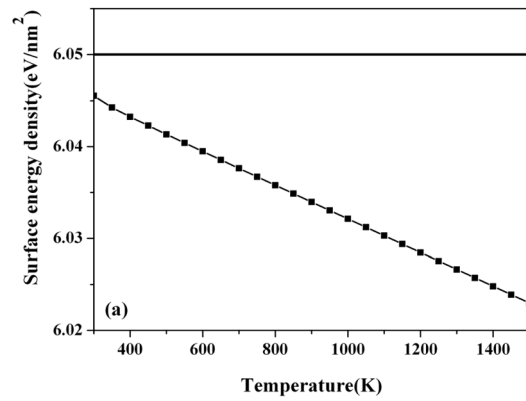


FIG. 4. (a) The surface energy density obtained by our theory and classical nucleation theory with the temperature. (b) The dependence of the surface energy density and surface tension on the temperature. The black line represents the surface energy density, while the blue line is the surface tension.

temperatures. Relative to the classical nucleation theory, the critical radius in our model seemed slightly larger at the same temperature. This increment critical radius is an amendment to the classical nucleation theory.

To further check the validity of our model, we took the size of a ripened quantum dot as an indirect reference object, while the growth of quantum dot induced by strain is not our purpose. When the radius exceeded the critical radius, the nucleus formed, and the nucleus began to grow and ripen to form a quantum dot. We took the critical radius as the origin of the growth of the quantum dot, and obtained the radius of the quantum dot as $R_t = R_{CT} + R(\Delta t)$. The increment of growth length $R(\Delta t)$ was dependent on the growth time and the temperature based on a kinetic model.²⁶⁻²⁸ We chose the growth time for the lateral size of the quantum dot to be 180 s. As shown in Fig. 3(b), the lateral size of the quantum dot changed with temperature, because of the temperature-dependent growth rate, and the critical radius. With the same growth rate and growth time, the difference in the lateral size between the two models was a result of the temperature-dependent critical radius. The size of quantum dots determined in experiments is always bigger than the size predicted by classical nucleation theory.^{26,29,30} The results of our model (which incorporated the thermal fluctuations) were closer to the results of the experiments.

Based on Eq. (8), we compared the surface energy density predicted by the classical nucleation theory with that

predicted by our model, as shown in Fig. 4(a). In contrast with the constant surface energy density predicted by classical nucleation theory, the surface energy density in our model decreased with temperature because of the introduction of the thermal fluctuations. The surface energy density used in classical nucleation theory is always calculated from first principles, at an ideal temperature. In the first-principle calculations, the surface energy function is mainly dependent on the orientation and the strain of the surface, but is rarely linked to the temperature.^{22,31,32} The surface energy density as a function of temperature is typically obtained using the semi-empirical formula $\gamma = \frac{\gamma_m + \Delta\gamma \cdot T}{\xi}$, based on the determined value of broken bonds ξ , and the surface tension at the melting point γ_m .³³ Based on this semi-empirical formula, the determined fraction of broken bonds ξ and the variation $\Delta\gamma$ can be treated as content. The surface tension obtained using the semi-empirical formula is shown as a blue line in Fig. 4(b). The surface energy density calculated using our theory is shown as a black line in Fig. 4(b). Interestingly, the dependence of the surface tension on the temperature was the same as that shown by the surface energy density, confirming the validity of our theoretical model.

IV. CONCLUSION

We developed a quantitative thermodynamic model to address temperature-dependent heterogeneous nucleation by introducing thermal fluctuations to the classical nucleation theory, within the statistical mechanics and quantum mechanics framework. The theoretical results not only provided interesting information on the heterogeneous nucleation at the nanoscale, which does not appear in classical nucleation theory, but also hinted at ways to control the heterogeneous nucleation. The agreement between theory and experiments indicated that the developed theory could improve the understanding of heterogeneous nucleation and heteroepitaxial growth on the nanometer scale.

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