

THE NUCLEATION RATES OF SILICON NANOFILMS

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ABSTRACT

An approach for the calculation of thin film nucleation rate, J is highlighted in this paper. Nucleation is a random process in which the number of nuclei formed in a fixed interval of time is a random quantity and subjected to statistical laws. This normally applies to either the frequency of appearance at time, t of nuclei per unit volume or area of the system under consideration, based on the classical kinetic theory of nucleation. In this work, the nucleation rates, J was calculated using a visual basic programming by identifying appropriate parameters from the pre-exponential factor, contact angle, desorption energy, diffusion energy, supersaturation ratio, etc.) and performing trial and error execution. It was observed that, from the different plots of nucleation rates, J for vapour/liquid and liquid/solid transition was found to lie within the reasonable experimental ranges.

INTRODUCTION

In recent years, thin film science has grown world-wide into a major research area. The importance of coatings and the synthesis of new materials for industry have resulted in a tremendous increase of innovative thin film processing technologies. Currently, this development goes hand-in-hand with the explosion of scientific and technological breakthroughs in microelectronics, optics and nanotechnology [1]. Many semiconducting materials have been used in thin film science, but from the growth and structure aspect, silicon is perhaps the most widely studied material. Silicon thin film technology emerged as the dominant force in solid state devices in the early 1960s and has continued to progress at a rapid rate. This progress has been the result of a combination of better understanding of the materials, the devices, and the processing steps involved in their fabrication [2].

Among the whole variety of processes accompanying silicon nanofilm growth, the principal one is, undoubtedly, the new-phase nucleation of islands, that is, the first-order phase transition [3]. At first order phase transition, the free energy of two phases is equal, but the first order derivatives of the free energy are not equal. The transition is not instantaneous at equilibrium conditions. Instead, the original phase remains metastable beyond equilibrium conditions, with the new phase forming via microscopic fluctuations. Fluctuations larger than a critical size grow into the new phase. Smaller fluctuations collapse into the original phase. This activated process is called nucleation [4].

Nucleation is a random process; the number of nuclei formed in a fixed interval of time is a random quantity and is subject to statistical laws. However, the average values can be calculated and are subject to the kinetic theory of nucleation. Thus, this paper will describe the nucleation rates theory and calculation study for the vapour/liquid and liquid/solid phase transition.

METHODOLOGY OF CALCULATION

Nucleation is the first step of a phase transition and is the process by which a new, stable phase (a nucleus) forms from an unstable (or metastable) liquid, solid or vapor bulk phase. There are two general types of nucleation. Heterogeneous nucleation occurs when a foreign substrate's surface, e.g., an ion or a dust particle, acts as the site for the formation of a new phase. The other type of nucleation is called homogeneous nucleation and occurs in the absence of any nucleating agents, e.g, surfaces [5]. Our discussion is based on the capillary approximation whereby a nuclei of a nascent (stable) phase is assumed to have sharp boundaries and the same uniform physical-chemical properties as the bulk phase which called Classical Nucleation Theory [6]. Basically, the reversible work ΔG required to form a nucleus of the new phase consists of two terms: a bulk or volumetric term that stabilizes the fragmentary new phase and a surface term that destabilizes it [7]. For homogeneous nucleation, the net change of energy, ΔG is given by

$$\Delta G = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3 \Delta G_v \quad (1)$$

where r is the radius of the nucleus, γ is surface free energy per unit area and ΔG_v is the free energy change per unit volume. ΔG for heterogeneous nucleation is equal to

$$\Delta G_{het} = \frac{\pi(2 - 3\cos\theta + \cos^3\theta)}{3} r^3 \Delta G_v + 2\pi(1 - \cos\theta)\gamma_{vn}r^2 + \pi\sin^2\theta(\gamma_{ns} - \gamma_{sv})r^2 \quad (2)$$

where γ_{vn} is the surface energy per unit area between vapour-nucleus, γ_{sv} is the surface energy per unit area between substrate-vapour, γ_{ns} is the surface energy per unit area between nucleus-substrate, θ is the contact angle and r is the diameter of spherical nucleus as show in fig. 1.

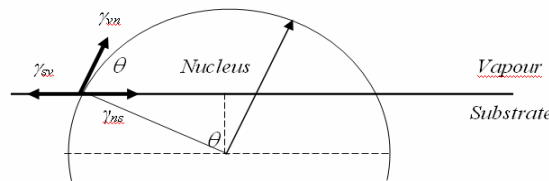


Figure 1

Eq. 3 shows the ΔG_v for vapour/liquid transition and Eq.4 shows the ΔG_v liquid/solid transition.

$$\Delta G_v = \frac{RT}{v_0} \ln \frac{P}{P_e} \quad (3)$$

$$\Delta G_v = \frac{\Delta H_f \Delta T}{T_m} \quad (4)$$

where v_o is molecular volume, R is the gas constant, p_e is saturation vapor pressure of the substance at certain temperature T , p is the vapor pressure and $S = p/p_e$ is the supersaturation ratio. T_m is the melting temperature, ΔH_f is the latent heat of fusion of the material per unit volume and in negative volume, $\Delta T = T_m - T$ is the undercooling temperature. Eq. (5) shows the critical radius, r^* which is the maximum in ΔG for both homogeneous and heterogeneous nucleation in vapour/liquid or liquid/solid transition. Between, Eq. (6) is the barrier height or critical energy ΔG^* for homogeneous nucleation while Eq. (7) is the ΔG^* for heterogeneous nucleation.

$$r^* = -\frac{2\gamma}{\Delta G_v} \quad (5) \quad \Delta G_{\text{hom}}^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} \quad (6)$$

$$\Delta G_{\text{het}}^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} \left[\frac{2 - 3\cos\theta + \cos^3\theta}{4} \right] \quad (7)$$

The nucleation rate, J based on the classical nucleation theory is defined as the frequency of appearance at time t of nuclei per unit volume or area of the system under consideration. For homogeneous and heterogeneous nucleation, nucleation rate is the combination between population of critical nuclei, critical surface area of nuclei and flux of atom impingement. But generally, the rate of nucleation, J , in Classical Nucleation Theory is an exponential function of ΔG^*

$$J = J_o \exp\left(\frac{-\Delta G^*}{RT}\right) \quad (8)$$

where the pre-exponential factor J_o is not very dependent upon the supersaturation, compared with the exponential factor, and therefore one can consider J_o as nearly a constant. Typical values of J_o for homogeneous nucleation are 10^{25} - 10^{35} $\text{cm}^{-3}\text{s}^{-1}$. J_o for heterogeneous nucleation is depends on the nucleation process. As example, J_o for the condensation from vapour nucleation process is 10^{17} $\text{cm}^{-2}\text{s}^{-1}$ and crystallization from melt is 10^{22} $\text{cm}^{-2}\text{s}^{-1}$.

Using the concept and quantitative description of nucleation theory, a computer program was developed, which covers both homogeneous and heterogeneous nucleation in vapor/liquid and liquid/solid phases.

RESULTS AND DISCUSSION

Based on the equation above, the calculation for nucleation theory would require the knowledge of additional material parameters. Silicon is the material chooses to be investigated due to its simplicity and extensive application in the electronics industry. The material parameters of silicon which used in this calculation including the enthalpy of fusion, ΔH_f (39.6×10^3 J/mol), melting temperature, T_m (1683K), atomic volume, v_o ($12.1 \text{cm}^3/\text{mol}$), surface energy, γ (0.34×10^{-4} J/cm²) and wetting angle, θ (70°). These

parameters were used to calculate the ΔG_v , ΔG_{hom}^* and ΔG_{het}^* for both vapour/liquid and liquid/solid transition of silicon.

Figure 2 and 3 shows the nucleation rates as function of supersaturation ratio at different temperature for homogeneous nucleation and heterogeneous nucleation in vapour/liquid transition. These graphs were plotted based to the eq.(8). Supersaturation ratio, $S=p/p_e$ is the variable parameter choose due to its important roles in vapour/liquid transition. The pre-exponential factor, J_0 used for both homogeneous and heterogeneous nucleation is $10^{25} \text{ cm}^{-3}\text{s}^{-1}$ and $10^{17} \text{ cm}^{-2}\text{s}^{-1}$.

Nucleation rates remains negligibly small until the supersaturation reaches a critical value, the Ostwald metastable limit, at which point Nucleation Rates suddenly and dramatically increases. Hence, this critical supersaturation level can be arbitrarily set as the rate at which the rate is equivalent to $1 \text{ nucleus cm}^{-3}\text{sec}^{-1}$ (or any other suitable experimentally detectable limit) with little loss of accuracy [8]. The existence of critical supersaturation leads to the conclusion that condensation of vapors will be experimentally observed only at $p > p_e$. In the opposite case the vapors will be in a metastable state, i.e. due to kinetic reasons no condensation will take place for the time of the experiment. Thus we identify the critical supersaturation with the limit of metastability of the ambient phase [9]. Besides, nucleation rate increases very steeply as a function of the Supersaturation at any given temperature. But when the temperature is higher, the critical value of supersaturation becomes smaller. So, the calculation results of nucleation rates are in good agreement with the experimental results reported by Wolk and Strey [10].

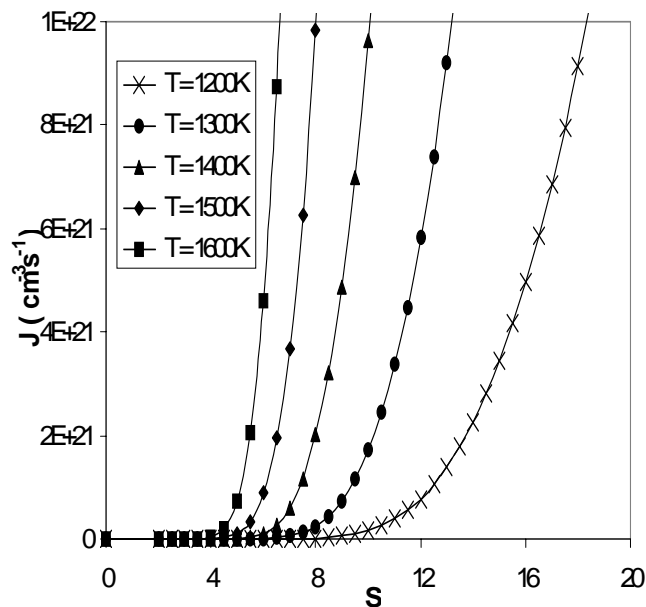


Figure 2: Graph J vs S with different T (Homogeneous Nucleation) for Vapour/liquid Transition

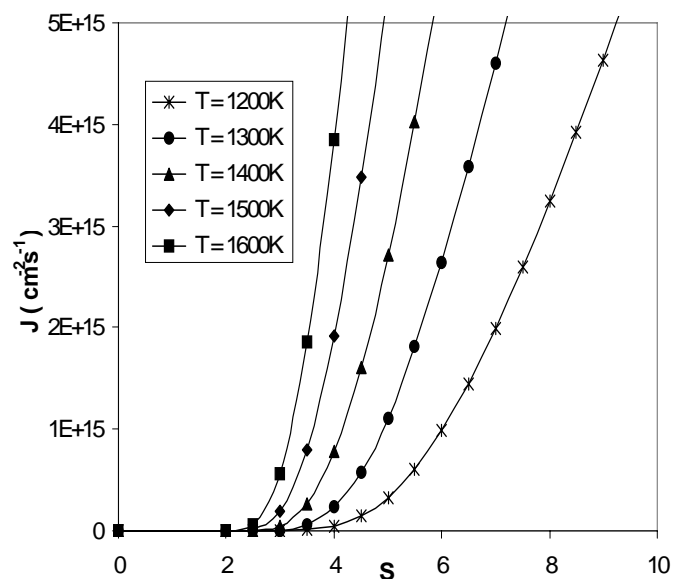


Figure 3: Graph J vs S with different T (Heterogeneous Nucleation) for Vapour/liquid Transition

For liquid/solid transition, the graph nucleation rates versus temperature for both homogeneous and heterogeneous nucleation were plotted as shown in Fig. 4 and 5. The pre-exponential factor, J_0 used are $10^{25} \text{ cm}^{-3}\text{s}^{-1}$ and $10^{22} \text{ cm}^{-2}\text{s}^{-1}$, respectively.

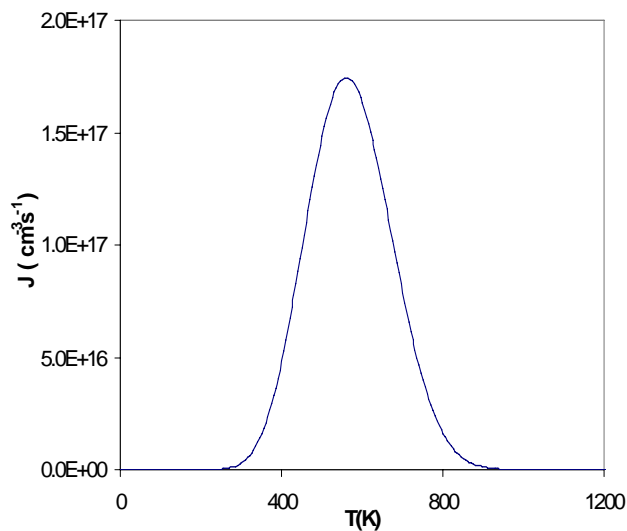


Figure 4: Graph J vs T (Homogeneous Nucleation) for liquid/solid Transition

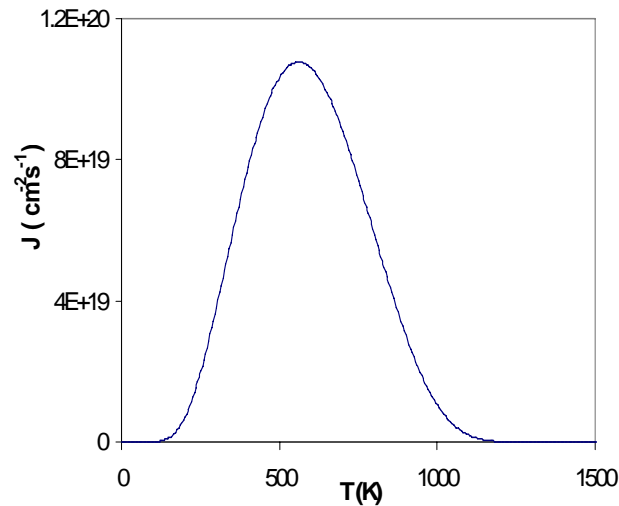


Figure 5: Graph J vs T (Heterogeneous Nucleation) for liquid/solid Transition

Based on the Fig. 4 and 5, the nucleation rate passes through a maximum at 561K for both homogeneous and heterogeneous nucleation. The high temperature branch is determined by the activation energy for nucleus formation while the low temperature branch is determined by the transport processes in the melt/liquid. If a liquid is very rapidly cooled, a temperature region beyond the maximum nucleation rate can be attained and the phase transition can in principle be blocked [11].

CONCLUSION

In conclusion, Classical Nucleation Theory can be used to describe the dynamic of first order phase transition. The effects of the supersaturation ratio and temperature parameters are significant for quantitative descriptions of homogeneous and heterogeneous nucleation in vapour/liquid and liquid/solid transitions. The graphs of calculation results are in a good agreement with the theory and partly verified by the experimental evidence.

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