THE NUCLEATION AND GROWTH OF SILICON NANOFILMS IN SUPERCOOLED LIQUID/SOLID PHASE

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ABSTRACT

The formation of silicon nanofilms can be described using an approach of nucleation and island growth mechanism with enhanced supercooling. The theoretically derived parameters (ΔG, ΔG^*, r^*, ΔG_v, ΔT) were found to be in the acceptable ranges that, Si nanofilms resembling 8 nm quantum dots could be fabricated on the substrate at extremely low nucleation rates. A Volmer-Weber growth model was used to explain the growth mode, initially by the aggregation of nuclei which increase in size leading to a liquid/solid phase transition. The resulting Si nanofilms were expected to be in an unwetting oval-shaped due to stronger nuclei-nuclei interactions.

INTRODUCTION

A great interest in the application of nanostructures and quantum dots is currently found in the fields of science and engineering, in which nanofilms become the ground of their elementary base. The general description of nanofilm formation has been overwhelmingly emphasized by many nanotechnologists during the recent years [1-3], but an in depth understanding of the phenomena is still in slow progress, mainly due to lack of information on the very early stage of nanofilm, called nucleation. In general, nanofilm nucleation is defined as the creation of small clusters or nuclei that responsible for film growth, either homogenously-nuclei formed in free space, or heterogeneously-nuclei formed on a surface. The former is likely to be more straightforward solution from the mathematically-derived equations, whilst the latter seems to be more complicated and practical applications in the current nanotechnology. Classical or capillary nucleation theory is widely employed to explain the nucleation process in the gas/liquid phase [1,4]. In the case of silicon nanofilm no rigorous theory has been developed to explain its liquid/solid transitions. It is hence of prime importance in the interest of nanostructured materials to establish basic understanding of the very early process with parameters that can be theoretically predicted and experimentally measured. We investigate suitable approaches on this issue with highlight on silicon nanofilms. This paper is an extension of the works previously done on vapour/liquid nucleation of silicon [5] in that some of the simulated data will be used in order to find out important parameters expected form the theory.

NUCLEATION THEORY AND GROWTH MODEL

Unlike the vapour/liquid phase nucleation [5], both thermodynamic and kinetic approaches are slightly different. The former is concerned with thermal properties and their changes during the liquid/solid transition, whilst the latter is related to the macroscopic mechanisms that can be used to explain transition phenomena in both phases, such as nucleation and diffusion rates. Assuming that the atoms/molecules that are initially in liquid phase coalesce to each other followed by agglomeration, forming small clusters similar to nuclei of specific sizes, and the process is preceded with further increase of sizes up to their critical conditions. We further assumed that the nuclei are unstressed in their spherical shapes which accommodate several thousand of atoms depending on the nature of bonding; essentially Si that crystallites in diamond cubic structure shall accommodate less number of atoms if compared to amorphous Si within the same volume of spherical shape.

From the thermodynamic point of view, the net change in the free energy, ΔG_{hm} is associated with homogenous nucleation and with these two processes: Firstly, creation of an interface between the nuclei of the new phase and the initial phase, associated with a change in free energy, ΔS. Secondly, passage of atoms or molecules from one phase to another or from one state to another (from liquid to solid nuclei), which corresponds to the variation in free energy, ΔV. Therefore, $\Delta G_{hm} = \Delta S + \Delta V = 4\pi r^2 \gamma_{ns} + \frac{1}{3}(4\pi r^3 \Delta G_v)$. The energy per unit volume of nuclei, ΔG_v is positive if $T > T_o$, where T_o is the solidification temperature of the transition. Under these conditions, applying the Gibbs-Duhem principle, the new phase is not stable. Since γ_{ns} is a positive quantity, ΔG_v is then positive: the number of nuclei of the new phase are not stable and do not tend to grow. On the contrary, if $T < T_o$, ΔG_v is negative, the new phase (solid) is stable. There are values of r for which $\Delta G_{hm} < 0$, and the corresponding nuclei will tend to stabilize the new phase since their formation reduces the free energy of material.

If Δh_v and Δs_v are respectively the changes in enthalpy and entropy associated with the formation of a unit volume of the new phase, then $\Delta G_{hm} = \Delta h_v + T\Delta s_v$. At the solidification temperature T_m, we can postulate $\Delta h_v = -L_f$, where L_f is the latent heat of fusion of the material per unit volume and $\Delta s_v = -L_f/T_m$. We assume $\Delta T = T_m - T$, and this quantity is a measure of the degree of *supercooling* of the liquid. In a first approximation, we can hypothesize that $\Delta C_p = 0$. Eq. (1) can be calculated by assuming that difference in specific heat between the liquid and solid phases, ΔC_p is constant, i.e.

$$\Delta G_v = \Delta H_f \frac{\Delta T}{T_f} - \frac{1}{2}\Delta C_p^f \frac{\Delta T^2}{T_m - \Delta T} \sim -H_f \frac{\Delta T}{T_m} \tag{1}$$

where $L_f = \Delta H_f$. This approximation is justified for amorphous materials (polymer, glass). In the case of metals we assume that $\Delta C_p = 0$ and we will thus neglect the second order terms in ΔT. We took the difference in the specific heats at the melting point ΔC_p^f as the value of ΔC_p. Rewriting the free energy change,

$$\Delta G_{hm} = 4\pi r^2 \gamma_{ns} + \frac{4}{3}\pi r^3 H_f \frac{\Delta T}{T_m} \tag{2}$$

when $T < T_m$ ($\Delta T > 0$), ΔG_v has a maximum for $r = r^*$. For $r > r^*$, the formation of nuclei

of increasing size results in stabilization of the solid phase since ΔG_v decreases and even becomes negative. ΔG_{hm} also can be derived from the Maxwell-Boltzmann distribution which finally arrived at the following expression, $n_r/n_o = \exp(-\Delta G_{hm} kT)$, where n_r/n_o is the ratio between the number of nuclei formed and number of available atoms. If $n_r \ll n_o$ as in the case of $n_r/n_o = 0.007$ [6], then $\Delta G_{hm} \sim - 5kT$. The critical energy and radius can be resolved from equation (2) as

$$\Delta G^*_{hm} = \frac{16\pi\gamma_{ns}^3 T_m^2}{3\Delta H_f^2 \Delta T^2}, \ r^* = \frac{2\gamma_{ns}}{\Delta G_v} = \frac{2\gamma_{ns}T_m}{\Delta H_f \Delta T} \tag{3}$$

Nanofilm growth model can be depicted in three modes (Fig.2). In the Frank-van der Merwe or layer-by-layer growth mode - Fig 2(i), the nucleus-substrate interaction dominates the nucleus-nucleus interaction and thus a new layer begins to grow only when the previous layer is completed – the nuclei tend to be in a wetting condition (Fig.2 a). The Stranski-Krastanov or layer plus island growth mode - Fig 2(iii), is a process whereby the first few layers is initially formed followed by a 3-dimensional islands nucleate and grow on top of the complete layers. In the Volmer-Weber or island growth mode - Fig 2(ii), the adsorbate-adsorbate interaction dominates and thus deposition produces multilayer islands. This requires $\gamma_{ns}-\gamma_{sl} > \gamma_{nl}$ for island to occur (the free energy of the substrate surface is low and therefore the adsorbed layer does not wet the substrate surface). Volmer-Weber growth model in Fig 2 (b to c) further illustrates the transformation to an oval-shaped nucleus when $r > r^*$. The energy, γ_{ns} pulls inside thus resembling the structure of a 3-D quantum dot.
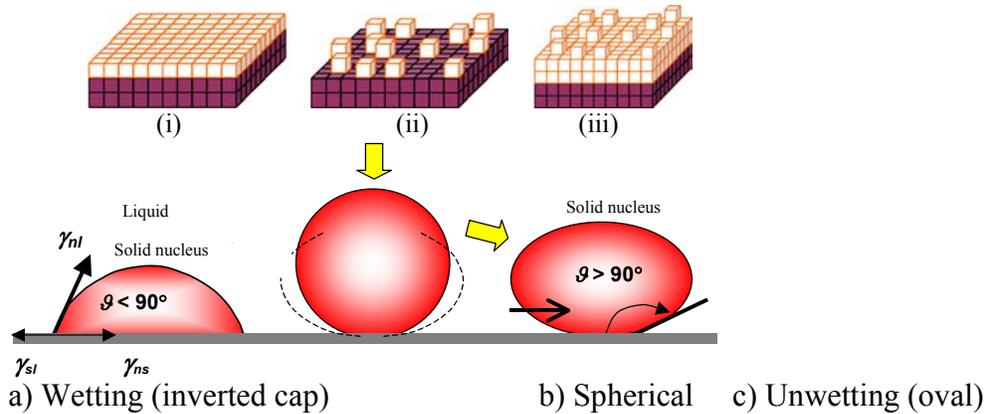

a) Wetting (inverted cap)　　　　b) Spherical　　c) Unwetting (oval)

Figure 2: Growth of silicon nanofilms

Plot of ΔG-r is shown by a curve with ΔG^* equivalent to the potential barrier that must be lowered for nuclei of critical size r^* to be formed more easily. It seems that from equation (4) the more important supercooling is, the more this barrier is lowered. The Volmer thermodynamic model shows that a complete phase transition by nucleation is only possible if the liquid is *supercooled*. In fact, nucleation is initiated with lower supercooling because the impurities (e.g. substrate, particle) present in the liquid phase, even in low concentration, induce nucleation, normally referred to *heterogeneous nucleation*.

In a situation where nucleation is heterogeneous, the intervention of new interfaces must be taken into consideration: those between the solid nucleus-substrate surface, liquid-solid nucleus and liquid-substrate surface, each of which is shown by the respective surface energies per unit area, γ_{ns}, γ_{nl}, and γ_{sl} as shown in Fig. 2(a). The total change of energy, ΔG_{ht} is the functions of, in addition to energy changes due to surface and volume, the contact area of nucleus–substrate and energy loss at liquid-substrate interface which are rather more practical with the presence of a wetting angle θ, i.e.,

$$\Delta G_{ht} = \frac{\pi\left(2 - 3\cos\theta + \cos^3\theta\right)}{3}r^3\Delta G_v + 2\pi\left(1 - \cos\theta\right)\gamma_{nl}r^2 + \pi\sin^2\theta\left(\gamma_{ns} - \gamma_{sl}\right)r^2 \quad (4)$$

The critical parameters ($\Delta G_{ht}*$ and $r*$) are respectively given by

$$\Delta G_{ht}^* = \Delta G_{hm}f(\theta) \ , \ f(\theta) = \frac{1}{4}(2 + \cos\theta)(1 - \cos\theta)^2 \ \text{ and}$$

$$r* = \frac{-2\left[2\pi(1 - \cos\theta)\gamma_{nl} + \pi\sin^2\theta\left(\gamma_{ns} - \gamma_{sl}\right)\right]}{\Delta G_v\left(2 - 3\cos\theta - \cos^3\theta\right)} \quad (5)$$

RESULTS AND DISCUSSION

Using suitable computer programming the total change of energy, ΔG for both homogenous and heterogeneous nucleation and the related parameters ($\Delta G*$, $r*$, ΔG_v, ΔT) were calculated and the computed results are shown in Figures 3 to 6. The following initial parameters were substituted: H=39,600 J/mol, T_m=1683 K, v_o=12.1 cm^3/mol, $\gamma_{vn} = \gamma_{ns}$ =0.34 x 10^{-4} J/cm^2, and θ=70°, with other data included from reference [5]. It is observed that the resulting nucleation parameters for silicon were found to be realistic and within the measurable ranges.
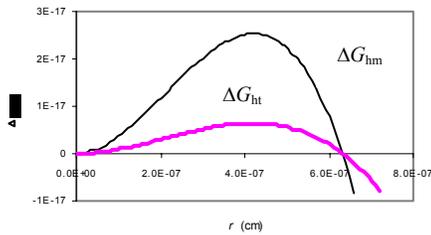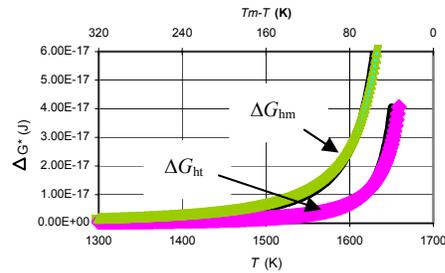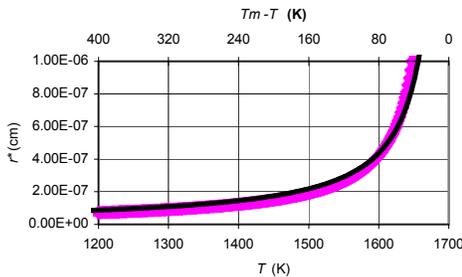

Figure 3: ΔG versus r

Figure 4: $\Delta G*$ versus T

Figure 5: $r*$ versus T
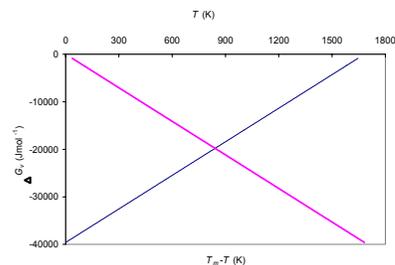
Figure 6: ΔG_v versus T, T_m-T

A light curve in Fig. 3 (at T_m=1600 K) shows the lower energy of ΔG_{ht} if compared to ΔG_{hm} (heavy line) due to the contribution of contact angle, θ, and a further reduction of these energies with higher degree of supercooling, ΔT (Fig.4). It can also be seen that r^* is constant irrespective of ΔG^*. Different plots of ΔG^* and r^* as a function of T are shown in Figs. 4 and 5 for a range of T=1300-1600 K or an equivalent of ΔT from 320 - 80 K. The following parameters were estimated from the graphs: r^* =1-4 nm and the associated ΔG_{hm}^*=1×10^{-18}–3×10^{-17}J and ΔG_{ht}^*=1×10^{-19}– 7×10^{-18}J over the same temperature range, respectively. The results suggest practical size of r =4 nm (or d=8 nm) occurring at a supercooling of ΔT=83 K. The energy, ΔG_v appears to increase linearly with temperature, T or linearly inverse with supercooling, ΔT over the entire melting temperature of silicon, T_m =1683 K (Fig. 6).

CONCLUSIONS

The nucleation in supercooled liquid/solid Si nanofilms were found to obey the thermodynamic approach with the predicted parameters: ΔG_{hm}^*=1×10^{-18}–3×10^{-17}J and ΔG_{ht}^*=1×10^{-19}– 7×10^{-18}J over the supercooling temperatures of 80-320 K, and the associated r^* =1 - 4 nm. There was a linear relationship between the energy, ΔG_v and supercooling, ΔT. The Volmer-Weber growth model was found to be reasonably acceptable in explaining the growth of Si nanofilms.

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