RAPID NUCLEATION IN PULSED LASER HEATED AMORPHOUS Si

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Solid phase nucleation in amorphous Si is investigated at high temperatures using pulsed laser heating. At ~ 930°C the steady-state nucleation rate is found to be ~ 2×10^{18} cm^{-3} s^{-1}, which is much higher than expected on the basis of classical nucleation theory. This discrepancy is resolved by updating the theory using the current knowledge of thermodynamic properties of amorphous and microcrystalline Si. Rapid nucleation in amorphous Si which is heated to a temperature near its melting point is suggested to be the mechanism by which explosive crystallization is triggered.

1. Introduction

Amorphous silicon (a-Si) is not a stable material: when heated it will transform into crystalline Si (c-Si) [1]. During the past decades, much research has been devoted to the study of this crystallization. Seeded crystallization or solid phase epitaxial growth (SPE) is very well characterized over a wide range of temperatures; it can be described by an Arrhenius type of behavior from 450 up to about 1360°C [2,3]. Unseeded crystallization is less well understood. This process is not only governed by growth but also by another process: before growth can occur, crystalline nuclei have to appear in the amorphous matrix. This process of spontaneous formation of crystalline clusters, which is called nucleation, is up to now only investigated in a limited temperature range of 500 to 700°C [1,4–6]. In this regime the rate at which nucleation occurs shows, like SPE, an Arrhenius type of behavior. In the classical theory of nucleation [7] a-Si is treated as being undercooled with respect to c-Si at temperatures below a (virtual) coexistence temperature. At high temperatures (and small undercooling) the free energy difference between a-Si and c-Si becomes very small. Hence the driving force for both crystallization and nucleation vanishes and both phenomena will deviate from their initial Arrhenius type of behavior. Especially the rate at which crystalline nuclei are formed is extremely sensitive to this free energy difference. A few years ago, calorimetric experiments and simple thermodynamic arguments led to consid-

erable insight into the magnitude and temperature dependence of the free energy difference between a-Si and c-Si [8]. Surprisingly, these findings were never implemented in the theory of nucleation.

Recently we found [9] that the nucleation rate in a-Si which was pulsed laser heated to > 900 °C is orders of magnitude larger than expected on the basis of classical nucleation theory. In this paper, we implement the current knowledge of the free energy of a-Si in nucleation theory. This includes the effect of structural relaxation of a-Si which has recently been shown to occur [10]. In addition, the effect of lattice strain in microclusters of c-Si [11] is taken into account. With the updated theory, nucleation in a-Si can be described over a wide range of temperatures. Consequences of rapid nucleation during pulsed laser processing of a-Si will be discussed, especially those pertaining to explosive crystallization [12] and amorphous regrowth [13].

2. Available experimental data

An overview of existing data concerning nucleation in a-Si is shown in fig. 1. Solid and open triangles represent nucleation rates determined in vacuum-evaporated a-Si films [1,4,5]. Solid circles represent rates determined in ion-implanted a-Si [6]. The dashed curve is an extrapolation of these data points, taken from ref. [4]. The nucleation rate during laser heating to 930 °C is shown as an open circle; the error bar represents the uncertainty in the temperature.
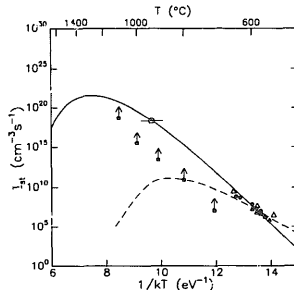

Fig. 1. Overview of nucleation rates in a-Si. Open circle: result from laser heating experiment [9]. Solid circles and triangles: taken from the literature [1,4,6]. Squares: underestimates for nucleation rates inferred from ref. [14]. Dashed curve: extrapolation of low-temperature data according to classical nucleation theory and "old" data on a-Si, after ref. [4]. Solid curve: Nucleation rate according to "updated" classical nucleation theory (see text).

Details concerning this experiment are described elsewhere [9]. Solid squares are underestimates for nucleation rates during laser induced random crystallization, deduced from crystallization times recently published [14]. These rates (squares and open circle) were determined neglecting the incubation time (see next section). Therefore, actual nucleation rates may be higher. It can be seen that the recently obtained high-temperature data deviate significantly from the theoretical curve.

3. Theory of nucleation

In this section we briefly review classical nucleation theory [15], applied to crystallization in a-Si. When a-Si is heated to a certain temperature, atoms may rearrange themselves to form small crystalline clusters. To evaluate the probability for a cluster of a certain size to be formed, the Gibbs free energy of formation ΔG of such a cluster is calculated. This energy is determined by the gain in volume free energy Δg for atoms in the crystalline phase relative to atoms in the amorphous phase and by the cost of the free energy σ necessary to form an interface between the crystalline cluster and the amorphous matrix:

$$\Delta G = a\sigma r^2 - b\Delta g r^3,\tag{1}$$

where r is the cluster radius and a and b are geometrical factors. For a spherical cluster, $a = 4\pi$ and $b = 4\pi/3$. When a cluster grows, ΔG initially increases until it reaches a maximum ΔG_c for $r = r_c$. Upon further growth ΔG will decrease and eventually change sign. r_c is obtained by solving $d\Delta G/dr = 0$, which yields:

$$\Delta G_c = (16\pi/3)s^3/\Delta g^2.\tag{2}$$

A cluster of this size and with this energy is called a critical cluster, because for smaller clusters it is energetically unfavorable to grow, while for clusters larger than r_c, growth leads to an energy gain. After a period during which a steady-state distribution of clusters of different sizes is established, the number of stable nuclei produced per unit of time is constant. This period is referred to as the incubation time or transient time. The number of grains produced in the steady-state regime is the steady-state nucleation rate I_{st}. I_{st} is proportional to the number of critical nuclei which appear in the film per unit of time, and it can be shown that I_{st} depends exponentially on $-\Delta G_c/kT$. Furthermore, I_{st} depends on the "interface rearrangement rate" which is a measure for the frequency of growth events. This term is generally assumed to show approximately the same temperature behavior as does seeded crystal growth, i.e. it is thermally activated with an activation energy E_a of about 2.8 eV [16]. However, seeded crystal growth occurs at a planar a-Si/c-Si interface.

For growth at the irregular and strongly curved interface of a small crystalline cluster, E_a may deviate from this value. I_{st} is thus given by:

$$I_{st} = I_0 Z \exp(-E_a/kT) \exp(-\Delta G_c/kT), \tag{3}$$

where I_0 is a prefactor which depends on the atomic density, on the atomic vibration frequency and on the surface area of a critical nucleus. Z is the Zeldovich factor. Note that I_{st} depends exponentially on the square of the free energy difference Δg between a-Si and c-Si. In order to extrapolate low temperature data of nucleation rates to higher temperatures, it is necessary to know the temperature dependence of Δg with sufficient accuracy.

4. Properties of a-Si and small crystalline clusters

4.1. Structural relaxation of a-Si

For most glasses, which are a common group of amorphous materials, Δg decreases with temperature until melting occurs and the curve describing Δg of the solid shows a smooth transition into the curve describing Δg of the liquid. If this were the case for a-Si, the driving force for crystallization would vanish as the temperature approaches the melting temperature. However, semi-empirical calculations show that even at the melting point of c-Si, Δg still amounts to at least 5 kJ/mol [8]. Actual values for Δg depend on the thermal history of the a-Si film under consideration. It has been suggested that the strain energy stored in bond angle distortions in a-Si varies between 10 and 19 kJ/mol [10]. These changes are due to structural relaxation. Strain energies of 10 and 19 kJ/mol correspond to completely relaxed and completely unrelaxed a-Si, respectively. These strain energies are thought to be the main contribution to the enthalpy difference Δh between a-Si and c-Si, and consequently an important factor when evaluating Δg. Calculated values for Δg versus temperature are shown in fig. 2. Straight lines represent the free energy differences of c-Si and ℓ-Si with respect to c-Si. Curved lines are calculated values for Δg of a-Si, where different curves correspond to different states of structural relaxation. Curves 1 to 4 correspond to strain energy of 19, 16, 13 and 10 kJ/mol, respectively. Details of these calculations are described elsewhere [16].

4.2. Lattice strain in microcrystalline clusters

All considerations above concern the free energy difference between a-Si and monocrystalline c-Si. However, random crystallization yields initially nanometer sized crystalline clusters. This implies that it is questionable to use bulk values for the thermodynamic properties. A first refinement can be the
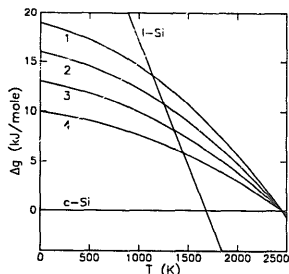
Fig. 2. Gibbs free energy curves of a-Si and ℓ-Si relative to c-Si [16]. Curves 1–4: curves for a-Si in different states of relaxation, with a strain energy at 0 K of 19, 16, 13 and 10 kJ/mol respectively.

inclusion of an energy term due to lattice strain in the clusters. Raman and X-ray measurements have shown that for clusters of 15 Å radius, the lattice constant is expanded up to 1% [11]. From this, a strain energy Δg_{strain} in the cluster of 1–2 kJ/mol can be calculated, which has to be subtracted from Δg. Another indication for a free energy difference between single- and micro-crystalline Si is the enhancement of SPE of microcrystalline Si with grain sizes smaller than 100 Å [17].

The energy due to lattice strain in the crystalline clusters was calculated in the following way: first the lattice expansion for clusters of 2–15 Å radius was extrapolated from the data in ref. [11], assuming a linear dependence between the radius of the cluster and the lattice expansion $\Delta d/d_0$. A relation $\Delta d/d_0(\%) = 1.4 - 5.5 \times 10^{-3} r$ was used. The lattice expansion thus obtained was converted to a volume change using $\Delta V/V_0 \approx 3(\Delta d/d_0)$ and combined with the bulk modulus B of c-Si to give the strain energy according to $\Delta g_{strain} = \frac{9}{2} B (\Delta d/d_0)^2$.

4.3. Surface energy

The surface free energy σ (the excess free energy of interface atoms relative to atoms in bulk c-Si) is generally taken to be constant over a large range of temperatures. However, it is very unlikely that this is a correct assumption. Since I_{st} depends very strongly on σ it is important to use the correct temperature dependence of σ. σ can be written as $\sigma = \Delta h_s - T \Delta S_s$ where Δh_s and ΔS_s are the surface enthalpy and surface entropy, respectively. We suggest to use $\Delta h_s = \Delta h$ and $\Delta S_s = \Delta S/2$, where Δh and ΔS are the enthalpy and entropy of a-Si with respect to c-Si. This comes about by reasoning that the

enthalpy is largely due to strained bonds at the interface which may store the same amount of energy as the a-Si itself; but the interface is partially ordered, therefore the entropy is taken intermediate between the values for a-Si and c-Si. All interface energy is attributed to one atomic layer. Extension of surface energy over more than one atomic layer can be taken into account by scaling the value of σ thus obtained.

5. Results of nucleation rate calculations

In order to evaluate the sensitivity of I_{st} on the different parameters, I_{st} was calculated for different values of Δh, Δg_{strain}, and σ. Fig. 3 shows I_{st} versus $1/kT$ on a logarithmic scale, for three different values of the surface free energy. In this plot, σ was taken to be $f(\Delta h_s - T\Delta S_s)$ with $f = 0.95$, 1 and 1.05. It can be seen that small changes in f give differences of several orders of magnitude in the calculated nucleation rate. In addition, small changes in the slope of the calculated curves can be observed. A similar set of curves is obtained for temperature independent surface free energies of 0.40–0.45 J/m^2 but for temperatures higher than ~ 1200°C these curves deviated somewhat from the curves shown in fig. 3.

Lattice strain in small clusters of crystalline Si depends on the size of the cluster. As a result, expression (2) for the energy of formation of a critical nucleus, ΔG_c, is no longer valid. Therefore, a calculation was made where I_{st} was determined from numerically obtained values of ΔG_c. This is shown in fig. 4 as a solid curve. This curve is compared in the same figure with three curves obtained using cluster size independent values for the lattice strain energy (0,
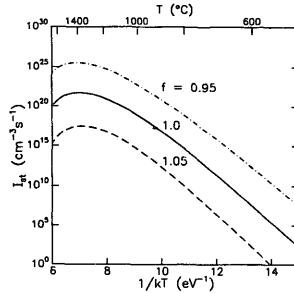

Fig. 3. Nucleation rate in a-Si versus $1/kT$ calculated for three different values of surface free energy σ, namely 0.95, 1.0 and 1.05($\Delta h_s - T\Delta S_s$).
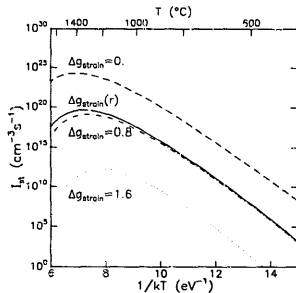
Fig. 4. Calculated nucleation rate in a-Si versus $1/kT$ for different values of Δg_{strain}. Solid curve: cluster-size dependent Δg_{strain}. Other curves: Δg_{strain} taken constant at 0, 0.8 or 1.6 kJ/mol.

0.8 and 1.6 kJ/mol). It can be seen that a lattice strain energy of 0.8 kJ/mol yields a curve which is quite close to the solid curve. This indicates that it is not necessary to evaluate ΔG_c numerically and that the energy due to lattice strain in small crystalline clusters can be taken cluster size independent.

Now we come back to the solid curve in fig. 1. This curve, which is obtained using $E_a = 2.8$ eV, $\Delta h_0 = 15$ kJ/mol (partially relaxed a-Si), $\sigma = 0.43$ J/m^2 (fixed value for all temperatures), and a fixed strain energy $\Delta g_{strain} = 0.8$ kJ/mol, describes all nucleation data reasonably well over a wide range of temperatures. It can be used to estimate the nucleation rate in a-Si which is heated to a temperature close to its melting point, which yields $\sim 10^{22}$ cm^{-3} s^{-1}.

6. Explosive crystallization and amorphous regrowth

Explosive crystallization (XC) [12] is a form of random crystallization involving ℓ-Si, which is undercooled with respect to c-Si but not to a-Si. This is possible because a-Si has a lower melting temperature then c-Si; it can occur when a-Si is heated ultra-fast (5–50 ns) to its melting point. Molten a-Si will solidify rapidly into polycrystalline Si. Heat of crystallization which is released during solidification flows to neighboring a-Si, increasing the temperature. Under favorable conditions this leads to melting of additional a-Si which then also solidifies, and thus a self-sustaining process is initiated. Although XC is well understood in terms of heat flow and interface motion [18], one of the unanswered questions is by which mechanism XC is triggered. We suggest that

XC is initiated via solid phase nucleation in a-Si during the heat-up phase prior to melting. A strong indication that this is indeed the case is the following: after XC, relatively large textured grains of ~ 0.1 μm size, spaced about 1 μm apart, can be found in the resulting polycrystalline Si material [18]. These so-called flakes have been related to the events which initiate crystallization. Assuming that every single flake results from one nucleation event in a layer of 10–100 nm just below the surface and assuming the time available for nucleation is 1–10 ns, the mechanism by which these flakes are formed should give 10^{21}–10^{23} events/cm$^3 \cdot$ s. From the solid curve in fig. 1, the nucleation rate in a-Si at 1200°C is estimated to be $\sim 10^{22}$ cm^{-3} s^{-1}, which corresponds very well with the observed flake density. We now suggest the following process: during heating of a-Si to its melting point, solid phase nucleation leads to the formation of crystalline nuclei in the a-Si film. When the amorphous material is melted, these nuclei – which have a higher melting temperature then a-Si because they are crystalline – remain solid and start to grow rapidly, consuming the undercooled liquid. Now it can be understood why there exists a threshold pulse duration of 5–10 ns, necessary for XC to be triggered [13], irradiation with shorter pulses leading to solidification into a-Si. Namely, only after a short (incubation) period has passed stable nuclei do exist and XC can be triggered. Thus the threshold pulse length for XC is directly related to the incubation time for nucleation in a-Si. Consequently the incubation time for nucleation in a-Si near its melting point is about 5–10 ns. This is extremely short: from an extrapolation of incubation times observed in the low temperature range [4,6] one would expect an incubation time at the melting point of a-Si of several milliseconds.

7. Conclusions

Solid phase nucleation in a-Si under pulsed laser irradiation is observed to occur at a rate of about 2×10^{18} cm^{-3} s^{-1} at a temperature of ~ 930°C. This is considerably higher than expected on the basis of an extrapolation of low-temperature data using the presently available classical nucleation theory. Recently obtained knowledge of thermodynamic properties of a-Si and micro-crystalline Si is inserted in this theory. With this updated theory, nucleation in a-Si can be described by one expression over a wide range of temperatures. Solid phase nucleation in a-Si is suggested to be the mechanism by which explosive crystallization is triggered. The observed threshold laser pulse length of 5–10 ns for explosive crystallization is then related to the incubation time for this nucleation process.

Acknowledgements

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