

DEFECTS, ENTROPY, AND MELTING OF AMORPHOUS SILICON

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Structural relaxation of amorphous Si (a-Si) is thought to be fully controlled by annihilation of point defects quenched in during preparation. The density of defects in unrelaxed a-Si is estimated from a wide variety of published experimental data to amount to several atomic %. The enthalpic and entropic contributions of these defects to the excess Gibbs free energy difference of a-Si over c-Si is estimated. The variation in free energy due to defects may lead to a further melting temperature depression of 40 - 200 K for unrelaxed a-Si in addition to the 200 K depression already present between c-Si and relaxed a-Si.

INTRODUCTION

It has recently been established that structural relaxation of amorphous Si (a-Si) is in fact fully controlled by non-equilibrium point defects and clusters of point defects [1 - 3]. This insight in the physical mechanism underlying variable short range order in a-Si makes it possible to assess the effect of structural relaxation on several other properties of a-Si. One such property is the Gibbs free energy of a-Si. Estimates of the difference in free energy between a-Si and c-Si (ΔG_{ac}) have led to the prediction [4] that a-Si should melt at a ≈ 200 K lower temperature (T_{ma}) than c-Si (T_{mc}) if heated fast enough. Time resolved conductivity (TRC) measurements have convincingly shown this to be the case [5].

Raman spectra of a-Si which has received thermal treatments (200 - 600 °C) have been interpreted as an indication that ΔG_{ac} depends on the state of relaxation [6]. This led to the prediction that T_{ma} is a function of the state of relaxation [7]. Transient conductance (TRC) measurements have not shown such a difference [5, 8] but from reflectivity measurements of Ge-implanted a-Si Grimaldi *et al.* [9] inferred a difference of ≈ 50 K between T_{ma} of relaxed and unrelaxed a-Si. Solid phase crystallization studies on a μs timescale showed that a-Si did not melt up to ≈ 50 K below T_{mc} [10], which is possibly due to relaxation.

In this paper we will try to improve our estimate of the effect of relaxation on ΔG_{ac} and relate this to T_{ma} . To do this we will first review some literature and find a reasonable value for the number of defects in unrelaxed a-Si. We will then estimate the enthalpic and entropic contribution of these non-equilibrium defects to ΔG_{ac} and from there continue to find the effect of defects on T_{ma} . We will restrict ourselves to pure a-Si prepared by ion implantation, because in that case the discussion is obscured neither by chemical effects (*e.g.* hydrogen) nor by macroscopic densification which has been shown to be negligible in this material [11].

DENSITY OF DEFECTS IN UNRELAXED AMORPHOUS SILICON

When we want to assess the effect of defects on the properties of a-Si, an obvious requirement is that we should know the number. Several estimates have been made for the maximum (or saturation) non-equilibrium defect concentration in a-Si at room temperature.

1) From the amount of heat released as measured by differential scanning calorimetry (DSC), the defect density can be estimated when the (average) stored energy per defect is known. From channeling measurements in c-Si, this amounts to 0.56 eV per displaced atom [12]. The formation enthalpy for the monovacancy in c-Si has been reported to amount to 3.6 eV [13]. Combining these numbers with the total heat release (4 - 5.8 kJ/mole) yields defect densities ranging from 1 to 7 at. %.

Table I Estimates of defect concentrations in unrelaxed amorphous silicon.

method	defect conc. (at. %)	reference
DSC	1 - 7	[12]
impurity diffusion	1	[14]
Raman spectroscopy	< 5	[3]
bevel / optical profile	8 (bonds)	[15]
positron lineshape	2 - 5	[16]
carrier dynamics	...	[18]
ESR	> 0.04	[19]

2) The diffusivity of Cu and Pd, both fast diffusers in a-Si (and in c-Si), has been observed to depend on the state of relaxation [2]. Under the assumption that in trap-free a-Si the diffusivity of these elements equals that in c-Si, a trap (or defect) density in unrelaxed a-Si of ≈ 1 at. % has been estimated [14].

3) Raman measurements of relaxed a-Si which was again subjected to ion bombardment have shown that the material returns to the unrelaxed state when the calculated displacement damage due to the ion beam amounts to ≈ 5 at. % [3]. It is likely that a fraction of the defects produced in a collision recombine, therefore this number may be taken as an upper limit estimate for the defect density in unrelaxed a-Si.

4) Optical profiles of beveled samples which were prepared by H⁺ implantation of (implanted and annealed) a-Si have been interpreted as depth profiles of 'Si bonding defects' [15]. The maximum defect density estimated from these measurements was 8 at. %. If more than one bonding defect is associated with a structural defect then this number would be an overestimate of the defect density.

5) A study of positron annihilation in ion implanted Si employing a variable energy slow positron beam and line shape analysis can also be understood in terms of defects [16]. Vacancy type defects may trap positrons and the spectra of a-Si could not be distinguished from c-Si containing 'a few at. % defects' [16]. We will interpret 'a few' as 2 - 5. Another study employing positron annihilation is the lifetime study of Dannefaer *et al.* [17]. They find much lower defect densities but since those results are obtained on partially relaxed material prepared by deposition techniques they will not be considered here.

6) Very recently, Stolk *et al.* measured carrier lifetimes in optically excited a-Si (both relaxed and unrelaxed) using a femtosecond pulsed laser pump and probe technique, and found that the lifetime in relaxed a-Si is much longer than in as-implanted a-Si. Although there is little doubt that the changes in carrier lifetime are related to changes in the defect density, a quantitative interpretation will not be given here because the cross sections for recombination at defects are unknown and may vary over several orders of magnitude. A more elaborate discussion of these measurements and estimates can be found elsewhere in these proceedings [18].

7) Electron spin resonance measurements of a-Si prepared by ion implantation has been used by many researchers to measure the density of unpaired dangling bonds in the network. It amounts to 0.04 at. %, most of which can be annealed out when the material is relaxed [19].

All estimates are displayed in Table I. None of the probes mentioned above is universally sensitive and each of the quoted numbers may therefore represent the concentration of only a subset of all the defects present. Nevertheless, the agreement between the first five techniques is striking and we will therefore use a defect concentration of 1 - 5 at. % in unrelaxed a-Si in the remainder of this paper with 5 at. % as an upper limit. This value is much higher than the density of uncharged dangling bonds as measured by ESR. In our opinion this indicates that ESR is not sensitive to the majority of the defects, as is the case in c-Si, and therefore 0.04 at. % represents a lower limit.

To summarize this section, a range of experiments using very different techniques have indicated that the (saturated) defect concentration in unrelaxed a-Si is on the order of several atomic percent.

THERMODYNAMICS OF NON-EQUILIBRIUM DEFECTS

The Gibbs free energy difference between a-Si and c-Si consists of two temperature dependent contributions, namely the enthalpy (ΔH_{ac}) and entropy (ΔS_{ac}):

$$\begin{aligned}\Delta G_{ac}(T) &= \Delta H_{ac}(T) - T \cdot \Delta S_{ac}(T) \\ &= H_0 + \int C_p dT - T \cdot S_0 - T \cdot \int \frac{C_p}{T} dT\end{aligned}\quad (1).$$

Using the experimentally determined heat of crystallization, a specific heat C_p ($0.275 \cdot T - 21.6$ eV/atom \cdot K) scaled from that of a-Ge [20] and a configurational entropy S_0 determined from a model building study of an ideal CRN [21], Donovan *et al.* calculated ΔG_{ac} corresponding to that of relaxed a-Si [22]. Fig. 1 shows the curve (labeled 'relaxed') calculated in the same way using a more recent value of the heat of crystallization [12]. The temperature at which this curve intersects that of l-Si (1351 K) determines (the estimated) T_{ma} for relaxed a-Si. Since it is considerably below the measured temperature of 1460 K [5] it must be concluded that at least one ingredient of the calculation is still quantitatively not correct. The discrepancy can be fixed by using a larger value for S_0 and/or C_p and/or by assuming that the l-Si curve is steeper than shown in the figure. Since there is no compelling reason to choose either one of these alternatives, we will leave it as it is and come back to this issue later.

In order to determine the Gibbs free energy difference between unrelaxed a-Si and c-Si (ΔG_{uc}) it would be necessary to add to ΔG_{ac} both the enthalpic and entropic contributions of the quenched-in defects:

$$\Delta G_{uc}(T) = \Delta G_{ac}(T) + H_{def}(T) - T \cdot S_{def}(T) \quad (2).$$

The total enthalpy associated with defects, H_{def} , is known from DSC studies [12] and amounts to ≈ 5.8 kJ/mole. If we completely ignore any possible entropy effects and assume the same temperature dependence for H_{def} and ΔH_{ac} , then ΔG_{uc} would be similar to ΔG_{ac} but shifted upwards by 5.8 kJ/mole. This is also plotted in Fig 1, see curve number 1 labeled 'unrelaxed'. The entropy (at 0 K) of defects, S_{def} , can be estimated. For a first order estimate, it is assumed that only one type of defect occurs. The entropy is then given by:

$$S_{def} = 1/N \cdot k \cdot \ln(W) \quad (3)$$

where k is Boltzmann's constant and W is the number of ways that n defects can be distributed over N atoms:

$$W = N! / ((N-n)! \cdot n!) \quad (4).$$

Using Stirling's formula, this gives

$$\ln(W) \approx N \cdot \ln(N) - (N-n) \cdot \ln(N-n) - n \cdot \ln(n) \quad (5).$$

Which can be rewritten as

$$-\ln(W) \approx (N-n) \cdot \ln(N-n)/N + n \cdot \ln(n/N) \quad (6).$$

Defining the concentration of defects as $x = n/N$ and assuming $x \ll 1$, it is thus found that

$$S_{def} \approx -x \cdot k \cdot \ln(x) \quad (7).$$

For $x = 0.05$, this gives $S_{def} = 0.15$ k/atom. This may be compared with the configurational

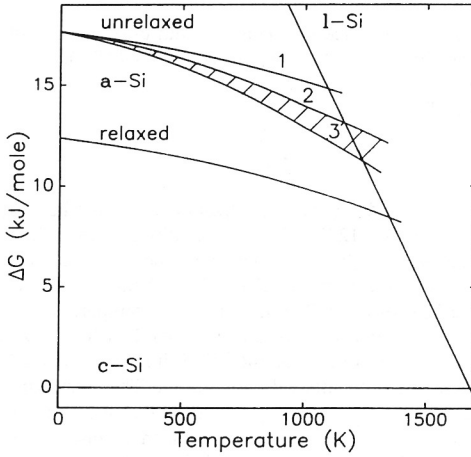


Fig. 1: Gibbs free energy difference curves for a-Si and l-Si relative to c-Si. The curve labeled 'relaxed' is essentially the same as that calculated by Donovan et al. [22]. The curves marked 'unrelaxed' were calculated taking the effect of defects into account (see text). 1: Enthalpy effect only. 2: Defect-entropy added. 3: Entropy contribution to specific heat added.

excess entropy S_0 of a fourfold coordinated CRN over that of the diamond crystal structure. S_0 has been determined by Spaepen [21]; it amounts to 0.2 k/atom at most. For point defect populations of more than one type of defect, S_{def} may be somewhat larger, but the above estimate indicates in which range of values S_{def} will fall. For our first estimate, we neglect the effect of defects on C_p (ΔC_p). This assumption results in curve number 2 plotted in Fig. 1.

The calculation of S_{def} in the preceding paragraph can now be used to estimate ΔC_p . The change in C_p is estimated indirectly, under the assumption that the disorder induced excess specific heat consists of two contributions. One from S_{def} and one from S_0 , each contributing proportional to their value. The estimated excess specific heat can thus be expressed as

$$\Delta C_p = (S_{def} + S_0) / S_0 \cdot C_p \quad (8),$$

where C_p is the experimentally determined value of C_p for a-Ge [20] scaled to a-Si [22]. From the maximum values of $S_{def} = 0.15$ k/atom (for $x = 0.05$) and $S_0 = 0.2$ k/atom [21], it can be seen immediately that this will almost double C_p . The calculated ΔG_{uc} curve (labeled 3) incorporating changes in C_p according to (8) is also plotted in Fig. 1. The dashed region between curves (2) and (3) represent our estimate of the free energy of unrelaxed a-Si where the estimate of ΔC_p is used as an upper limit.

The applicability of these entropy models is limited by the non-equilibrium nature of the defects involved. It is emphasized that we have assumed mobile defects which do not, however, annihilate. Annihilation of defects during heating would lead to a simultaneous enthalpy release and entropy decrease such that eventually the material is again described by the curve labeled 'relaxed'. Experimental tests to verify the validity of the curves shown in Fig. 1 could (apart from melting temperature measurements) include measurements of the specific heat and latent heat of melting of both relaxed as well as unrelaxed a-Si.

MELTING TEMPERATURE OF AMORPHOUS SILICON

The intercept of the free energy curves of a-Si with that of undercooled l-Si determines the melting temperature under rapid heating conditions. To evaluate these melting temperatures, a few remarks should be made. First, we have used a simple straight line to extrapolate the free energy curve of l-Si; strictly speaking specific heat effects of the undercooled liquid should be taken into account [23]. Second, the melting temperature for relaxed a-Si determined from Fig. 1 is already much lower than the experimental value of 1460 K [5]. The free energy curve for relaxed a-Si can be forced to intersect that of l-Si at 1460 K by increasing C_p or S_0 (or both by a factor of ≈ 1.4). Using these modified values to calculate the curves for unrelaxed a-Si leads to smaller melting temperature reductions than shown in Fig. 1.

The calculated melting temperature difference (ΔT_m) between unrelaxed a-Si and c-Si ranges from 1.3 to 1.6 times ΔT_m for relaxed a-Si, where the uncertainty corresponds to the dashed region between curve (2) and (3). We have also determined ΔT_m for unrelaxed a-Si using the modified C_p and S_0 values; it ranged from 1.2 to 1.9 times that of relaxed a-Si. It is concluded, therefore, that the melting temperature of a-Si containing the maximum concentration of point defects is expected to be at least 40 K and at most 200 K below that of relaxed a-Si. This estimate is based on the assumption that the heating rate is rapid enough to prevent crystallization and defect annihilation during heating. It is emphasized that the range of melting temperatures is not a melting trajectory as would be the case for normal glass. Instead, it represents a range of first order phase transition temperatures corresponding to a range of a-Si structures.

The experimental accessibility of this difference is limited for a similar reason which makes it difficult to measure the melting temperature of relaxed a-Si: In the latter case the a-Si tends to crystallize, in the former it tends to relax during the heating phase of the experiment. It has been found that a-Si relaxes already on a nanosecond timescale [6] and also that a-Si prepared by nanosecond laser quenching [24] is formed in the relaxed state [12]. This would imply that for optimal experimental conditions the heat up time should be less than a nanosecond.

SUMMARY AND CONCLUSION

In summary, we have examined some of the literature on amorphous (a-) Si. From a wide variety of experimental results it was concluded that the density of point defects and point defect clusters in unrelaxed a-Si amounts to several at. %. The enthalpic and entropic contributions of these defects to the excess free energy of amorphous over crystalline Si has been estimated. It was found that the melting temperature of unrelaxed a-Si is at least 40 K and at most 200 K lower than that of relaxed a-Si. Discrepancies in the literature may well come from defect annealing during heating.

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