Variable strain energy in amorphous silicon

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Different Raman experiments on structural relaxation of a-Si and a-Ge are reviewed and discussed in relation to calorimetric measurements on a-Ge. On the basis of the correlation found between results from Raman spectroscopy and results from calorimetry in the case of a-Ge and of the strong similarity between a-Si and a-Ge in terms of their Raman spectra, it is suggested that the strain energy in a-Si may vary considerably with preparation conditions and subsequent treatments. Under this assumption the a-Si Gibbs free energy versus temperature has been constructed for material in different initial states of relaxation. It is shown that the melting temperature of amorphous silicon should increase when relaxation occurs during the heating phase prior to melting. Thus differences in apparent melting temperature, as observed under different laser heating conditions, may be explained.

I. INTRODUCTION

The history of amorphous silicon (a-Si) dates back to the early days of ion implantation into crystalline silicon (c-Si)[1] and to the pioneering experiments on vacuum deposition,[2] both roughly two decades ago. Studies of its properties and behavior upon various (heat) treatments have been carried out ever since, especially in relation to crystallization and solid-phase epitaxy. A boost in research activities occurred around 1975 when it became clear that a-Si in its hydrogenated form (a-Si:H) shows semiconducting properties and can be used as such in devices.[3] a-Si:H differs in many respects from its "clean" counterpart a-Si, but fundamental questions concerning the atomic structure are similar for the two types of material. It was only after the first reports on pulsed-laser annealing in 1975 that the possibility of melting (ion-implanted) a-Si became an issue.[4] In the years following this discovery of damage repair by pulsed-laser irradiation, it was suggested that the process does not involve simple thermal melting[5] but rather the formation of a high-density, electron-hole plasma. In the latter picture, the temperature of the Si lattice does not rise to the melting temperature.[6] More recently, there is a general consensus that indeed a-Si can be melted by pulsed-laser irradiation.[7] The temperature at which melting occurs, however, still poses major questions. In 1978 Bagley and Chen[8a] and Spaepen and Turnbull[8b] predicted that the melting temperature of a-Si should be considerably (> 200 K) lower than that of c-Si (1685 K). Their prediction was based on calculations of the Gibbs free energy versus temperature of a-Si and l-Si, in comparison to that of c-Si. Experimental indications for a difference in melting temperature were found in 1980 by Baeri et al.,[9] who studied pulsed electron beam heating of a-Si. Experiments on continuous

wave (cw) laser heating[10] and on line-source electron beam heating,[11] in contrast, did not show any significant difference: solid-phase epitaxial regrowth of a-Si was found to occur even at temperatures relatively close to the melting temperature of c-Si. Subsequently, Thompson et al.[12] performed experiments on nanosecond pulsed-laser-induced melting of a-Si and showed convincingly that under those circumstances the material melts at ≈200 K below the c-Si melting temperature. Their conclusion is now widely accepted, even though elaborate cw laser heating experiments by Olsen et al.[13,14] still have not shown any such melting point lowering.

In this paper we discuss recent measurements of structural changes in a-Si upon laser and thermal treatments, in view of their implications for the controversy concerning the melting temperature of a-Si. A model is described, which may reconcile results previously considered contradictory.

II. KINETICS OF MELTING

In the discussion concerning the melting temperature described in the Introduction, it is generally assumed that the free energy of a-Si does not vary with the preparation method or subsequent thermal treatments. Following the reasoning of the authors in Ref. 8, this implies that one may indeed speak about *the* melting temperature of a-Si, which is determined by the crossing point of the free energy versus temperature curves for a-Si and liquid Si (l-Si). Hence, apparent variations in this melting temperature can only be discussed in terms of kinetics of melting. It is known that kinetic factors are essential in the description of the reverse process, i.e., solidification of l-Si.[15,16] However, pulsed-laser experiments show that melt nucleation is possible on a nano-

second timescale without large superheating of the amorphous phase and therefore it is unclear why kinetics would prevent melting during the relatively long times (typically microseconds) involved in cw laser heating.

In this context it is noted that a-Si is a covalently bonded, fourfold coordinated material with semiconducting properties, while liquid Si (l-Si) is 6.5- to 12-fold coordinated and metallic.[7b,17] Therefore the a-Si to l-Si transition is assumed to be discontinuous and of first order.[7b] In this respect a-Si should be clearly distinguished from many other amorphous materials (glasses), which upon heating show a continuous transition to the melt.

III. STRUCTURE AND OTHER PROPERTIES OF AMORPHOUS SILICON

Ever since the beginning of research on a-Si, it is a well-known fact that many properties of this material vary strongly with preparation conditions and subsequent treatments. Among these are optical, electrical, and spin properties.[2,18-29] It is generally acknowledged that these variations are related to the atomic structure of the a-Si random network.[23,29] A complete description of this structure should at least involve bond angle and length distortions,[30,31] topology (distribution of five-, six-, and seven-membered rings),[32-34] voids (local and global),[35] and under- or overcoordination of atoms in the network (dangling or floating bonds).[36]

Model building experience has shown that angular distortion and topology are closely related[37]: the average angular distortion obtained after a Keating minimization[34,38] of the distortion energy is determined by the topology and ranges roughly from 7° to 13°, which is 6% to 12% of the ideal value of the bond angle of 109.5°. The absolute minimum angular distortion for any true continuous random network appears to be $\approx 6.6°$ (Ref. 37), which illustrates the structural gap between a-Si and c-Si. Note that the estimated maximum distortion observed for crystalline material is $< 3°$ (Refs. 39 and 40). According to most reports, bond-length distortions are insignificant[31,34,39,41] ($\approx 1\%$). This is a direct consequence of the fact that the spring constant for bond stretching is much larger than that for bond bending.[38,42,43] Small voids, corresponding to the size of a few atoms, and dangling bonds are probably inherent to real random networks but are usually not included in models.[30] The existence of floating bonds has only been suggested recently and has been a subject of debate.[44] Large voids are sometimes present in low-temperature-deposited (porous) a-Si films,[2,18,35,45,46] but not in films formed by ion implantation into c-Si and are considered irrelevant to the present discussion concerning the melting temperature.

From the foregoing it is concluded that variations in a-Si material properties can be mainly attributed to variations in bond-angle distortion (and network topology) or to variations in the density of small voids and dangling or floating bonds. The key question in relation to the melting temperature of a-Si is whether or not these variations have any influence on the free energy of the material. The major contribution to the difference in free energy (at 0 K) between a-Si and c-Si comes from distorted bond angles.[31] Hence, variations in bond-angle distortion will inevitably have a clear influence on the free energy. The energy associated with dangling or floating bonds is not accurately known, but an upper limit can be roughly estimated assuming a density of 10^{20} cm^{-3} (Ref. 47) and an energy per bond of 0.5 eV.[36] This yields 0.1 kJ/mole, which is only $\approx 1\%$ of the energy associated with distorted bond angles,[31] as will be discussed in detail in the next section. This indicates that variations in the density of dangling or floating bonds have only minor influence on the free energy. The energy of voids can be divided into a part related to distortion and a part related to under- or overcoordination and therefore needs not be treated separately.

The (tacit) assumption that the free energy of a-Si does not vary with preparation conditions or thermal treatments[7-14] thus implies that the average bond-angle distortion is constant. This assumption is mainly based on extensive calorimetric studies of high-energy ion-implanted a-Si by Donovan and co-workers,[48] who claim that this material does not show any heat release prior to crystallization and find a constant heat of crystallization for a whole range of samples (11.9 ± 0.7 kJ/mole). In the same experiments it was found that a-Ge did show a large release of heat prior to crystallization: ≈ 6.0 kJ/mole,[48b,48c] which is approximately half of the heat released upon crystallization (11.6 ± 0.7 kJ/mole). This is clear evidence for a substantial decrease of the distortion energy in the a-Ge random network. Although the elastic properties of Si and Ge are not the same,[42] it is very difficult to understand why a-Ge and a-Si would behave qualitatively different, that is, why a-Ge shows large changes upon annealing while a-Si does not at all. Fan and Anderson[49] have suggested that also a-Si may show low-temperature heat release prior to crystallization. Unfortunately this interpretation of their results is questionable, since the films were sputter deposited at low substrate temperatures and therefore probably were porous and contained a high concentration of impurities.

IV. RAMAN SPECTROSCOPY AND STRUCTURAL RELAXATION

A. Amorphous silicon

The first systematic indications for variations in bond-angle distortion in a-Si and hence, in free energy, came from recent experiments[24-26,45,50,51] in which Ra-

man spectroscopy is used to study structural changes in a-Si upon annealing. Raman scattering is extremely sensitive to crystallization, since the spectrum of a-Si basically reflects the full vibrational Density-Of-States (DOS),[52,53] while that of c-Si is determined by selection rules and shows (in first order) only one strong characteristic peak around 520 cm^{-1}. Therefore changes in the a-Si network can easily be distinguished from partial crystallization.[50,54] These experiments indicate that the average bond-angle distortion in a-Si is not constant, but varies considerably with preparation conditions and thermal or laser treatments. Therefore the Gibbs free energy of a-Si should also vary.

Because the Raman spectrum of a-Si directly reflects the vibrational DOS of that material[52,53] it can be used to probe changes in vibrational frequencies induced by local strain (bond bending).[37,50,55–57] The width Γ of the main (transverse optic) peak in the Raman spectrum of a-Si is related to the distribution of vibrational frequencies in the random network and thereby to the average bond-angle distortion $\Delta\Theta$. Several authors have attempted to quantify the relationship between Γ and $\Delta\Theta$.

(i) Beeman[37] has performed direct calculations of the Raman spectrum for different network structures. Using a Born potential to describe forces on an atomic scale, he arrived at

$$\Gamma/2 \approx 3.2 \cdot \Delta\Theta + 7.4, \tag{1}$$

in which Γ is in cm^{-1} and $\Delta\Theta$ is in degrees. Here, $\Gamma/2$ is measured at the high-frequency side of the transverse optic peak in the Raman spectrum. Values of $\Gamma/2$ obtained in different experiments range from 32 to 49 cm^{-1} (Refs. 24,29,37,45,50,and 51) corresponding to values for $\Delta\Theta$ of 7.7° to 13.0°. [From model-building experience the absolute minimum for any true continuous random network is estimated to be 6.6° (Ref. 37).] It is noted, however, that in none of the individual experiments is the full range of $\Gamma/2$ values found. Beeman himself assumes the range of 32–41 cm^{-1} given by Tsu and co-workers,[50] which corresponds to 7.7°–10.5°.

(ii) Using a different approach, based on a Keating potential and parameters obtained from deformation of c-Si, Tsu et al.[50] found

$$\Gamma/2 \approx [(3.37 \cdot \Delta\Theta)^2 + 16^2]^{1/2}. \tag{2}$$

Experimental values of $\Gamma/2$ thus correspond to bond-angle distortions of 8.2°–11.2°.

(iii) Wong and Lucovsky[55] have constructed random network models with an average bond-angle distortion of 7° and 10°, respectively. Using a Born potential they calculated the main features of the corresponding Raman spectra and found $\Gamma/2$ values of 30 and 45 cm^{-1}. It is noted, however, that these authors did not pretend to give an absolute range of $\Delta\Theta$ or $\Gamma/2$, but rather wanted to illustrate the relation between

these quantities in a range which is of practical interest.

(iv) Lannin et al.,[57] finally, obtained a relation beteen $\Gamma/2$ and $\Delta\Theta$ by comparing results from Raman spectroscopy with those from x-ray diffraction (i.e., radial distribution functions). Although this comparison has only been made for a-Ge, it is claimed that the relation for a-Si can be obtained by simple scaling. This yields a range of $\Delta\Theta$ values of $\approx 9°$ to 11°–12°.

From the foregoing it is clear that there is no agreement about the quantitative relation between $\Gamma/2$ and $\Delta\Theta$. Nevertheless, all studies[37,50,55,57] indicate that there is indeed a fundamental relation between features in the Raman spectrum and the average bond-angle distortion in the a-Si random network. In summary, it is consistently found that the average bond-angle distortion differs by 20%–40% for maximally ordered and maximally disordered networks, respectively.

The strain energy $U_{\Delta\Theta}$ associated with bond-angle distortions is in first approximation given by[31]

$$U_{\Delta\Theta} = \sum 6 \cdot [\tfrac{1}{2} \cdot k_\Theta \cdot (r \cdot \Delta\Theta)^2], \tag{3}$$

in which k_Θ is a bond-bending force constant and r is the Si–Si atomic distance (2.35 Å). The factor 6 represents the number of bond pairs per atom while the summation is over all atoms in the network. Here, k_Θ can be expressed in terms of the force constant β as it appears in Keatings potential[31,38,42]: $k_\Theta = 2/3\beta$. Keating originally calculated β to be 13.8 N/m for Si but in later papers other authors use $\beta = 6.7$–9.7 N/m.[31,53,58,59] This illustrates that it is difficult to obtain an accurate value for β by comparing experimental results on elastic and vibrational properties with calculations using the relatively simple Keating potential.[34,53]

Tsu et al.[50] used the value of β originally given by Keating in combination with formula (2) and found that the strain energy stored in the a-Si network varied from 40–50 kJ/mole for as-deposited a-Si to 15–20 kJ/mole for annealed a-Si (which should be compared to an absolute minimum of 12 kJ/mole for $\Delta\Theta = 6.6°$).

Using $\beta = 9.7$ N/m and a linear interpolation of the numbers given by Wong and Lucovsky,[55] Sinke et al.[45,51b] arrived at 19 kJ/mole for as-implanted a-Si and 13 kJ/mole for a-Si annealed at 600 °C for 20 s. Nanosecond laser annealing at energy densities just below the threshold for surface melting yields $U_{\Delta\Theta} = 15$ kJ/mole (the absolute minimum in this approach is 10 kJ/mole for $\Delta\Theta = 7°$).

The decrease of the strain energy upon annealing is usually referred to as structural relaxation[60] and has two characteristic features: (i) relaxation shows transient behavior and a-Si may melt or crystallize before full relaxation occurs[45,51b]; (ii) relaxation saturates at a temperature-specific level.[45,50,51]

Since the minimum bond-angle distortion in ran-

dom network models appears to be determined by the topology,[37] it is likely that relaxation in a real network proceeds by changes in the ring structure. Therefore relaxation may involve rearrangement of bonds and could be mediated by defects such as dangling bonds, floating bonds,[36] and small voids. The apparent activation energy for relaxation increases as the relaxation proceeds,[45,51] which gives rise to a (pseudo) saturation in the behavior of relaxation versus time. Whereas Raman spectroscopy shows that the state of relaxation of a-Si may vary continuously,[50] measurements of the refractive index indicate that there are only two distinct states: one as-prepared and one anneal stabilized.[19-22] This suggests that the network property that is probed using Raman scattering is different from that governing (changes in) the refractive index.

B. Amorphous germanium

Except for a scaling factor, the vibrational properties of a-Ge are very similar to those of a-Si.[53] This includes the observation of relaxation upon annealing. The full experimental range of $\Gamma/2$ values is 18.5–31 cm^{-1} (Refs. 50 and 57). The relation between $\Gamma/2$ and $\Delta\Theta$ has been quantified by Tsu et al.,[50] who give

$$\Gamma/2 \approx [(2.65 \cdot \Delta\Theta)^2 + 9^2]^{1/2}, \qquad (4)$$

in which $\Gamma/2$ is in cm^{-1} and $\Delta\Theta$ is in degrees. Note that $\Gamma/2$ is again measured at the high-frequency side of the TO peak. Using this equation their experimental range of $\Gamma/2$ (18.5–25 cm^{-1}) is found to correspond to $\Delta\Theta$ values of 6.1° to 8.8°. By comparison with results from x-ray diffraction, Lannin[57] suggests that 23–31 cm^{-1} corresponds to 9.3°–11.5°.

The strain energy associated with bond-angle distortions is again given by Eq. (3), using constants appropriate for Ge. The Ge–Ge atomic distance is 2.44 Å. $\beta = 3/2k_\Theta$ was calculated by Keating[38] to be 12 N/m, but lower values are also used [7.7 (Ref. 34)–11.4 N/m (Ref. 42)]. Lannin[61] has recently compared Raman measurements on ion-implanted a-Ge with calorimetric determinations of the heat released upon relaxation of the same material. His data show an excellent correlation between the degree of bond-angle disorder as inferred from the Raman spectrum and the heat released upon relaxation. Maximally disordered material ($\Delta\Theta \approx 12°$ on the scale set by the author) shows a heat release of 7–9 kJ/mole upon full relaxation. Assuming Eq. (3) can be used to estimate the total strain energy in a-Ge, these numbers imply that β should be taken to be roughly 5–7 kJ/mole to obtain reasonable values of the strain energy. If the maximum value of $\Delta\Theta$ is assumed to be $\approx 9°$, as is done by Tsu,[50] best β values are between 9 and 12 kJ/mole.

Although it is not possible to decide on the exact range of $\Delta\Theta$ values on the basis of Lannin's[61] experi-

ments, they provide strong support for the qualitative relations between $\Gamma/2$, $\Delta\Theta$, and $U_{\Delta\Theta}$ expressed by formulas (1)–(4). It is acknowledged that until now, calorimetry has not shown heat release due to relaxation for a-Si. Clearly, additional measurements are needed to check whether this difference between a-Ge and a-Si is consistently found under different experimental conditions. In view of the many Raman experiments that indicate that a-Si shows structural relaxation, and awaiting conclusive evidence for the absence or presence of relaxation from calorimetry, it is interesting to evaluate the implications of relaxation for the controversy concerning the melting temperature of a-Si as discussed in the Introduction. This is done in the following sections.

V. GIBBS FREE ENERGY

As mentioned before, the difference in melting temperature between a-Si and c-Si is due to a difference in free energy between the two materials,[7,8,48] which is given by

$$\Delta G_{ac}(T) = \Delta H_{ac}(T) - T \cdot \Delta S_{ac}(T), \qquad (5a)$$

in which $\Delta G_{ac}(T)$ is the temperature-dependent difference in Gibbs free energy between a-Si and c-Si, $\Delta H_{ac}(T)$ is the enthalpy of crystallization, and $\Delta S_{ac}(T)$ is the entropy difference between a-Si and c-Si. Formula (5a) is equivalent to

$$\Delta G_{ac}(T) = \Delta H_{ac}^0 - T \cdot \Delta S_{ac}^0$$
$$+ \int_0^T \Delta C_{p,ac}(T)dT$$
$$- T \int_0^T \frac{\Delta C_{p,ac}(T)}{T} dT, \qquad (5b)$$

in which $\Delta C_{p,ac}(T)$ is the difference in heat capacity and ΔS_{ac}^0 is the residual entropy difference between a-Si and c-Si.

Since $\Delta G_{ac}(0) = \Delta H_{ac}^0 \approx U_{\Delta\Theta}$ (Ref. 31), the curve of ΔG_{ac} vs T changes with the state of relaxation of a-Si. This is illustrated in Fig. 1, which shows the Gibbs free energy of a-Si and l-Si in comparison to that of c-Si. Curves 1 to 4 have been constructed for a-Si prepared in different states of relaxation, assuming that it can be heated to all T without any (additional) relaxation. The values of $U_{\Delta\Theta}$ have been taken from Ref. 51b, since these are comparable to values verified experimentally for a-Ge.[61] Thus curve 1 corresponds to unrelaxed a-Si ($\Delta H_{ac}^0 \approx U_{\Delta\Theta} = 19$ kJ/mole), curves 2 and 3 to partially relaxed a-Si (16 and 13 kJ/mole, respectively), and curve 4 to fully relaxed a-Si (10 kJ/mole). Experimental values for $\Delta H_{ac}(T)$ determined at $T \approx 900$ K roughly range from 11 to 12 kJ/mole,[48] which corresponds to $\Delta H_{ac}^0 \approx 10$–11 kJ/mole. Since strong relaxation is expected to occur at 900 K (Refs. 45, 50, and 51), these
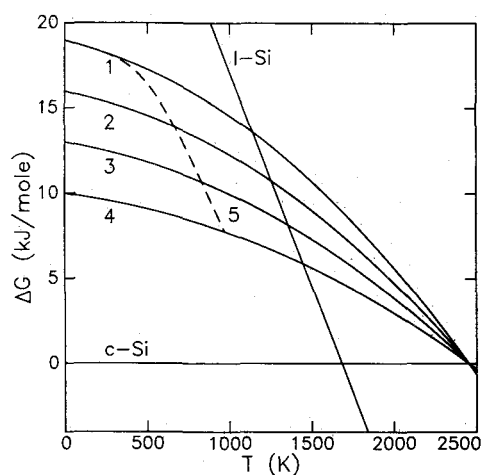
FIG. 1. Calculation of the isobaric Gibbs free energy of a-Si (curves 1 to 5) relative to that of c-Si. The Gibbs free energy of l-Si, as calculated by Donovan *et al.* (Ref. 48), is also shown. The curves 1 to 4 correspond to a-Si prepared in different states of relaxation and have been constructed under the assumption that no (additional) relaxation occurs. Curve 5 has been constructed for a-Si prepared in an unrelaxed form, assuming that it relaxes to a (pseudo) equilibrium state at each temperature. Values of the strain energy $\Delta G(0)$ have been inferred from Raman spectra (see Ref. 51b).

values should correspond to (at least partially) relaxed a-Si, which indicates that the value for ΔH^0_{ac} used in curve 4 is reasonable. Curve 4 is basically that obtained by Donovan *et al.*[48] Curve 5 has been constructed assuming that a-Si is prepared in an unrelaxed form but is allowed to relax to the temperature-dependent (pseudo) saturation level[45,50,51] at all T. This level is given by[50]

$$U_{\Delta\Theta,\mathrm{sat}}(T) = U_0 - U_1 \exp(-E_a/kt), \qquad (6)$$

in which $U_{\Delta\Theta,\mathrm{sat}}(T)$ is the temperature-dependent, pseudo-saturation level of the strain energy stored in the a-Si network, U_0 and U_1 are constants, E_a is the activation energy associated with relaxation to pseudo-saturation [≈ 0.2 eV (Ref. 50)], k is Boltzmann's constant, and T is the absolute temperature. Formula (6) has been evaluated for typical annealing times in the range of minutes to hours. For that reason, curve 5 cannot be constructed for $T > 1000$ K, since a-Si crystallizes very fast in that regime.

In constructing curves 1 to 4 it has been assumed that ΔG_{ac} scales with the degree of relaxation at $T = 0$ K. This corresponds to the assumption tht $\Delta C_{p,ac}(T)$ and ΔS^0_{ac} in formula (5b) scale with the degree of relaxation. Thus $\Delta C_{p,ac}(T)$ and ΔS^0_{ac} have been chosen as described in Refs. 7 and 48, but multiplied by the ratio of ΔH^0_{ac} ($\approx U_{\Delta\Theta}$) to $\Delta H^0_{ac,\mathrm{min}}$ (≈ 10 kJ/mole). It is noted that neither $\Delta C_{p,ac}(T)$ nor ΔS^0_{ac} is accurately known. $\Delta C_{p,ac}(T)$ as used in Refs. 7 and 48 is based on results for Ge, which are scaled to obtain those for Si and extrapolated over a wide temperature range. ΔS^0_{ac} is taken

from calculations by Spaepen,[62] which are based on model building. Therefore considerable uncertainty exists in the curvature of ΔG_{ac} vs T. The relative trend of the curves, however, is not influenced by this uncertainty.

Curve 5 has been constructed in the following way. First $U_{\Delta\Theta,\mathrm{sat}}$ is calculated at all relevant T according to formula (6). Each value of $U_{\Delta\Theta,\mathrm{sat}}$ is taken to be ΔH^0_{ac} in a curve similar to the curves 1 to 4. The saturation value of $\Delta G_{ac}(T)$ is then given by the value of $\Delta G_{ac}(T)$ at this curve. For material prepared in a partially relaxed state $U_{\Delta\Theta}$, a curve similar to curve 5 can be constructed assuming no additional relaxation occurs in the temperature range where $U_{\Delta\Theta} < U_{\Delta\Theta,\mathrm{sat}}(T)$, while $\Delta G_{ac}(T)$ follows curve 5 for higher temperatures. For instance, in the case of material with $U_{\Delta\Theta} = 13$ kJ/mole, the curve follows curve 3 up to the crossing point with curve 5 and follows curve 5 beyond that point.

The l-Si line in Fig. 1 was directly taken from Refs. 7 and 48. Since this curve is constructed by linear extrapolation of results obtained for melting of c-Si, it may not be very accurate for low temperatures of the liquid.

VI. IMPLICATIONS OF VARIATIONS IN FREE ENERGY

Figure 1 shows that the apparent melting temperature $T_{m,a}$ of a-Si, as defined by $\Delta G_{ac}(T_m) = \Delta G_{lc}(T_m)$, is different for each of the curves 1 to 4. Qualitatively one can conclude that $T_{m,a}$ is low if a-Si can be heated without full relaxation. This is probably the case for very fast (nanosecond) pulsed-laser- and electron-beam-induced melting.[9,12] During relatively slow heating procedures such as cw-laser annealing, relaxation is possible and the apparent $T_{m,a}$ is high.[10,13,14] The actual curve $\Delta G_{ac}(T)$ for a certain heating procedure will be intermediate between the extreme cases (no relaxation during heating versus full relaxation) sketched in Fig. 1, i.e., during heating partial relaxation occurs.

As has been mentioned in the foregoing, the apparent melting temperature of a-Si as deduced from experiments varies from < 1485 K (Ref. 12) to > 1625 K (Refs. 10, 13, and 14). Assuming the highest value of $T_{m,a}$ is associated with fully relaxed a-Si, curve 4 of a-Si and the curve of l-Si in Fig. 1 should cross at $T > 1625$ K. Analogously, curve 1 for unrelaxed a-Si should cross at $T < 1485$ K. Since curve 4 resembles that constructed by Donovan[7,48] (which shows a crossing point at $T \approx 1460$ K) it is concluded that quantitative agreement between theory and experiment cannot be obtained using data presently available. This is not surprising in view of the crude estimates and extrapolations necessary to construct the free-energy curves in the temperature range of interest. Clearly there is a need for reliable information

on the behavior of the free energy of a-Si and l-Si in the temperature range of interest.

Due to the assumptions made in constructing curves 1 to 4, they all cross the c-Si line at the same temperature T_{ac}. This temperature (≈ 2500 K) is a virtual coexistence temperature at which a-Si and c-Si have equal free energy. Note that T_{ac} has never been determined experimentally and even its very existence has not been proven so far, but its value is of practical importance because it appears in a simple description of crystallization,[63] where it is used to describe the "undercooling" of a-Si with respect to c-Si for $T < T_{ac}$. As T closely approaches T_{ac}, the driving force of crystallization vanishes and the crystallization rate will decrease dramatically.[13] It is, however, very difficult to measure the crystallization rate for unrelaxed a-Si, since heating to induce crystallization will inevitably induce relaxation as well. Only when the behavior of relaxation has been investigated over the same range of temperatures as that of solid-phase epitaxial regrowth (that is, up to ≈ 1360 °C) will it be possible to predict under which experimental conditions the initial state of relaxation becomes apparent in crystal growth experiments.

VII. CONCLUSIONS

Different Raman scattering experiments on structural relaxation of a-Si and a-Ge have been discussed and compared to data obtained from calorimetry of a-Ge. On the basis of the correlation between results from Raman scattering and calorimetry, in the case of a-Ge, and of the strong similarity in behavior of a-Si and a-Ge in terms of their Raman spectra, it is suggested that the strain energy in a-Si may vary considerably with preparation conditions and subsequent treatments. Curves of the a-Si Gibbs free energy versus temperature have been constructed for material in different states of relaxation and have been used to discuss differences in melting temperature, as observed under different experimental conditions. It is suggested that the apparent melting temperature of a-Si increases with the state of relaxation.

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