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Measurement of the specific heat and determination of the thermodynamic functions of relaxed amorphous silicon

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The specific heat, c_p, of two amorphous silicon (a-Si) samples has been measured by differential scanning calorimetry in the 100–900 K temperature range. When the hydrogen content is reduced by thermal annealing, c_p approaches the value of crystalline Si (c-Si). Within experimental accuracy, we conclude that c_p of relaxed pure a-Si coincides with that of c-Si. This result is used to determine the enthalpy, entropy, and Gibbs free energy of defect-free relaxed a-Si. Finally, the contribution of structural defects on these quantities is calculated and the melting point of several states of a-Si is predicted. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4803888]

INTRODUCTION

Amorphous silicon (a-Si) and its hydrogenated version (a-Si:H) hold a high scientific interest because of their use in many applications such as solar cells and thin film transistors for large area displays, and because they are taken as a model to understand the structure of tetrahedral amorphous materials.

At present, the theoretical models of a-Si can be tested against a large amount of experimental data obtained from structural techniques, such as neutron and x-ray diffraction, Raman spectroscopy or electron paramagnetic resonance, which give key details about short-range and medium-range order or structural defects.[1] In contrast, knowledge of its thermodynamic properties is very poor.

This situation may be due to the difficulty of doing thermal measurements on thin films and because a-Si is intrinsically unstable under heating as it tends to relax to microscopic configurations of lower energy and, ultimately, to crystallize.[2] Consequently, thermodynamic data are scarce and not reliable enough to serve as solid tests for the microscopic models or to be used in practical applications where a-Si coexists in thermal equilibrium with other phases like in a-Si nanoparticles embedded in SiO_2.[3]

Determination of a-Si thermodynamic functions needs its entropy and enthalpy at a given temperature and its specific heat to be determined. The enthalpy at the crystallization temperature has recently been shown to vary between 5.6 and 13.5 kJ/mol for relaxed a-Si, depending on the particular a-Si material,[4] with the minimum value being below ½ the value usually taken as standard.[5] All calculations made so far[6,7] rely on this "standard" value, on a theoretical value of the entropy at 0 K (Ref. 8) and on specific heat values estimated from those of amorphous Ge.[9] The specific heat of a-Si has only been measured at cryogenic temperatures and significant discrepancies arise between the several published values.[10–12] Measurements above room temperature are more difficult to do because, in fact, one is interested in the small excess specific heat with respect to crystalline silicon (c-Si).

In this paper, we will report on the experimental determination of the excess specific heat of a-Si in the 100–900 K temperature range. After a brief description of the experimental methods, our results will be given and the discrepancy with those values already published in the literature will be discussed. Our values will be then used to determine the excess Gibbs free energy of a-Si relative to c-Si and to predict its melting temperature. Finally, some concluding remarks will follow.

EXPERIMENTAL METHODS

Two samples of a-Si:H were deposited on the inner walls of a plasma enhanced chemical vapor deposition (PECVD) reactor chamber and were collected in the form of flakes. X-ray diffraction (Bruker AXS Smart Apex diffractometer) revealed that they were 100% amorphous. Their hydrogen content, n_H/n_{Si}, was determined by elementary analysis (EA2400 Perkin Elmer). Hydrogen desorption during heating ramps was monitored by evolved gas analysis (EGA) experiments carried out in vacuum. Hydrogen was detected with an MKS quadrupole mass spectrometer (Microvision Plus).

The excess specific heat of a-Si with respect to c-Si, $\Delta c_p \equiv c_p(a-Si) - c_p(c-Si)$, was measured by differential scanning calorimetry (DSC) with the procedure described elsewhere[13] that allows detection of Δc_p values as low as 1%. For these experiments, large amounts of sample (20–60 mg) were kept in platinum crucibles. Independent tests have been carried out to calibrate the apparatus sensitivity at these conditions. Two DSC apparatus were used: Mettler Toledo DSC821 and TA Instruments Q2000. The last DSC allowed us to do experiments at cryogenic temperatures.

RESULTS: THE EXCESS SPECIFIC HEAT OF a-Si

We studied two samples. Since they differ on their crystallization enthalpy [9.6 kJ/mol (sample A) and 7.3 kJ/mol (sample B)], they give us the opportunity to analyze if this property has an effect on Δc_p or not.

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Hydrogen atoms introduce more vibrational modes in the material. Consequently, it is natural to observe a diminution of Δc_p when hydrogen content is reduced. We measured Δc_p of sample A as a function of hydrogen content. To this aim, the sample was previously annealed at 10 K/min up to 870 and 920 K. We verified that, according to previous results,[14,15] after annealing at 920 K the crystalline fraction was negligible. Fig. 1 makes clear that, as expected, annealing reduces Δc_p considerably: after annealing at 920 K, Δc_p is reduced to 1/5 of its as-grown value. Since elemental analysis and the EGA curve of Fig. 2 allows the hydrogen content to be determined, the dependence of Δc_p on n_H/n_{Si} can be plotted (inset of Fig. 1). From this plot, one can deduce that a large fraction of Δc_p of the as-grown sample is due to the hydrogen atoms. Furthermore, extrapolation to $n_H/n_{Si} = 0$ seems to indicate that Δc_p for pure a-Si is near zero. This prediction has been verified experimentally; in a similar experiment, n_H/n_{Si} has been further reduced by heating sample A up to 920 K six times (now, n_H/n_{Si} is under the sensitivity limit of the experiment, 0.2%). The result is that, in this condition, Δc_p becomes zero above 570 K and has a very small value [<0.2 J/K/mol, i.e., $<1\% c_p$(c-Si)] below this temperature (Fig. 1).

Finally, sample B delivered similar results. Here again, we verified that Δc_p diminished when n_H was reduced by thermal annealing and its value became negligible after complete dehydrogenation. In this state, Δc_p of sample B was measured within a wider temperature range (120–770 K). The results that are shown as star symbols in Fig. 3 agree with those of dehydrogenated sample A (Fig. 1). To better appreciate the significance of our results, we should say that previous estimations of Δc_p based on measurements on a-Ge gave values of 1.4 J/K/mol at 570 K.[6]

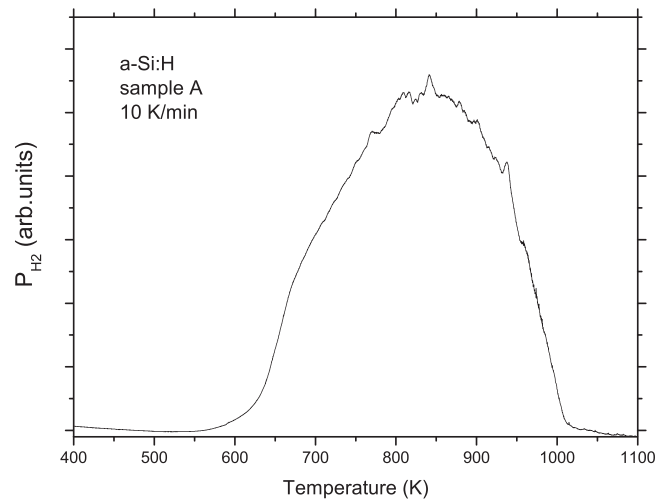

FIG. 2. Evolved gas analysis curve of dehydrogenation for sample A.

ANALYSIS: THERMODYNAMIC FUNCTIONS AND MELTING TEMPERATURE OF RELAXED a-Si

In this section, we want to determine the thermodynamic functions of "defect-free relaxed a-Si" (henceforth labeled with a superscript "df"). This state corresponds to a microscopic configuration with minimum bond-angle strain (the so-called "relaxed state") and with negligible density of structural defects; it can be viewed as the microscopic configuration closest to c-Si. We will show that our experimental values of Δc_p, together with published values of the crystallization enthalpy[4] and the entropy of a-Si,[8] make it possible to propose the most reliable values of its thermodynamic functions, published so far. In a second step, we will estimate the contribution of structural defects and, finally, the melting temperature of relaxed a-Si will be predicted. It is worth noting that melting is the only reversible transformation of a-Si that has been detected so far[16] and that it could be used to test our proposed thermodynamic functions.

The enthalpy of a-Si relative to c-Si is given by

$$\Delta H_{ac}(T) = \Delta H_{ac}(T_0) + \int_{T_0}^{T} \Delta c_p dT', \quad (1)$$

where $\Delta H_{ac}(T_0)$ can be taken as the heat released during crystallization at T_0. The entropy difference with c-Si can

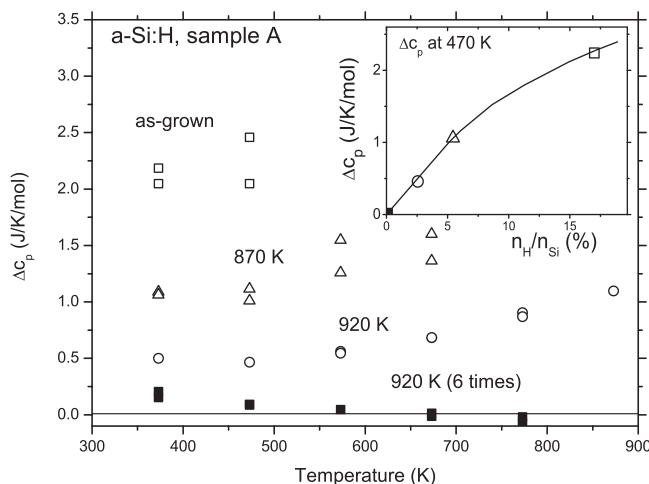

FIG. 1. Excess specific heat of a-Si:H, Δc_p, as a function of the temperature measured after annealing sample A at different temperatures to reduce the hydrogen content. After annealing it 6 times at 920 K, n_H became negligible. Inset: dependence of Δc_p on the hydrogen content.

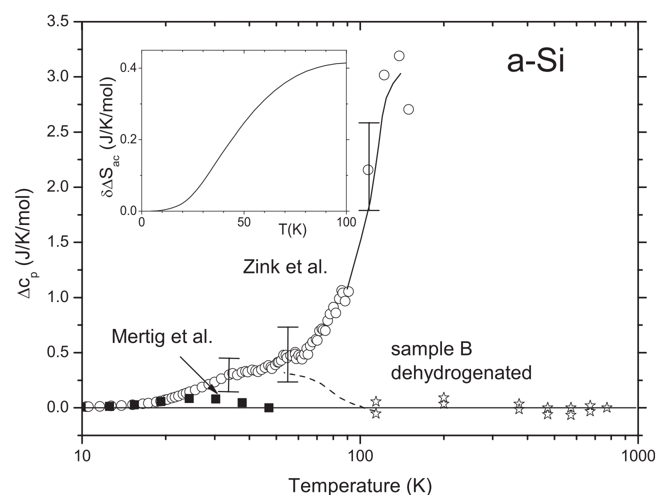

FIG. 3. Excess specific heat of dehydrogenated sample B for T > 120 K (stars). The open points and full squares are taken from the literature. Inset: upper bound for the entropy variation up to 100 K.

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also be evaluated if we know Δc_p and the difference at a single temperature,

$$\Delta S_{ac}(T) = \Delta S_{ac}(T_0) + \int_{T_0}^{T} \frac{\Delta c_p}{T'} dT'. \tag{2}$$

And, finally, the Gibbs free energy can be calculated from its definition,

$$\Delta G_{ac}(T) = \Delta H_{ac}(T) - T\Delta S_{ac}(T). \tag{3}$$

The first difficulty one encounters when trying to determine the thermodynamic functions of a-Si is that they are not unique. It is well known that the energy of a-Si obtained by ion implantation diminishes steadily upon thermal annealing due to structural relaxation.[2] Even for well relaxed material (i.e., material with minimum bond strain[17]), the crystallization enthalpy varies within a factor of two due to the varying densities of structural defects.[4] So, the minimum value of the crystallization enthalpy is 5.6 kJ/mol at $T_0 = 1000$ K and corresponds to $\Delta H_{ac}^{df}(T_0)$. The excess enthalpy above this value is the contribution of structural defects.[18] It can be as high as 7 kJ/mol. Although the nature and formation energy of these structural defects has not been elucidated, we know that they are not paramagnetic and, consequently, they cannot contain an odd number of dangling bonds. Single vacancies have formation energy around 4 eV (Ref. 19), they should have a density of $n_d = 1.7\%$ to explain the excess crystallization enthalpy. This value agrees with the density of defects that remain in a-Si obtained by ion implantation after thermal annealing[20] and will be taken as representative of the contribution of defects to the a-Si thermodynamic functions.

The second difficulty is the entropy value of a-Si at a single temperature, $\Delta S_{ac}(T_0)$. A theoretical estimate obtained from defect-free microscopic models of a-Si is 1.7 J/K/mol.[8] No other value has been proposed in the literature neither from experimental nor from theoretical grounds. So, we take it as being $\Delta S_{ac}^{df}(0\,\mathrm{K})$. The entropy increases above this value due to structural defects according to

$$\Delta S_d = -R n_d \ln(n_d), \tag{4}$$

where R is the gas constant (8.31 J/K/mol) and subindex *d* refers to "defects." For $n_d = 1.7\%$, $\Delta S_d = 0.58$ J/K/mol.

The third difficulty comes from the uncertainty in the value of Δc_p. In Fig. 3 we have plotted, in addition to our results, the values measured by Zink *et al.*[11] on an evaporated film and those of Mertig *et al.*[12] In contrast to our present results, the film of Zink has a positive excess specific heat. Although the origin of this discrepancy cannot be known, we should remark that the film was not annealed and, consequently, it could be far from the relaxed state. Since we have not measured Δc_p below 100 K, we can take the values of Zink *et al.* as reference for an upper bound to Δc_p for relaxed a-Si. We consider that the dashed line in Fig. 3 is a reasonable upper bound. Furthermore, the two samples we measured are not defect-free. Although they have enthalpies that exceed $\Delta H_{ac}^{df}(T_0)$ by 4 and 1.7 kJ/mol (samples A and B, respectively), their Δc_p values are very close to zero. So, we will consider that this upper bound is valid for defect-free a-Si as well as for a-Si containing structural defects.

Measurement of Δc_p allows determination of the temperature variation of ΔH_{ac} and ΔS_{ac} through the application of Eqs. (1) and (2). According to the upper bound established above, variation of these magnitudes can only take place below 100 K. In the case of ΔH_{ac}, Eq. (1) delivers a negligible maximum variation of 0.02 kJ/mol, whereas the variation of ΔS_{ac} between 0 and 100 K, $\delta\Delta S_{ac}$, is more substantial but below 0.4 J/K/mol (see inset of Fig. 3).

The ΔS_{ac} and ΔH_{ac} values calculated so far will serve to determine the Gibbs free energy of relaxed a-Si (Eq. (3)). The results have been plotted in Fig. 4 together with the free energy of liquid Si, ΔG_{lc}. The intersection of the ΔG_{lc} and ΔG_{ac} curves delivers the melting point, T_{al}, of the various states of relaxed a-Si. Defect-free a-Si melts at a temperature quite close to c-Si, T_{cl}-T_{al} = 70–95 K. On the other hand, structural defects have a very pronounced effect on the melting temperature that can be 350 K below T_{cl}.

The only experimental determination of the melting point of a-Si [T_{al}(exp)-T_{cl} = 200 ± 50 K] was carried out on Si amorphized by ion implantation,[16] and both experiment[21] and theory[22] indicate that the film relaxed before melting. So, this value can be compared with our predictions in Fig. 4. This comparison indicates that, although this film was relaxed, it contained a density of defects high enough to have a significant effect on the melting point.

Finally, we must say that in the literature the melting point of a-Si has been only analyzed in terms of structural relaxation. Experiments have shown that unrelaxed a-Si melts at 115 K below relaxed a-Si.[21] The present work shows that the density of defects is an additional structural parameter that has to be taken into account. By taking it into account, we have predicted that T_{al} spans over a range of

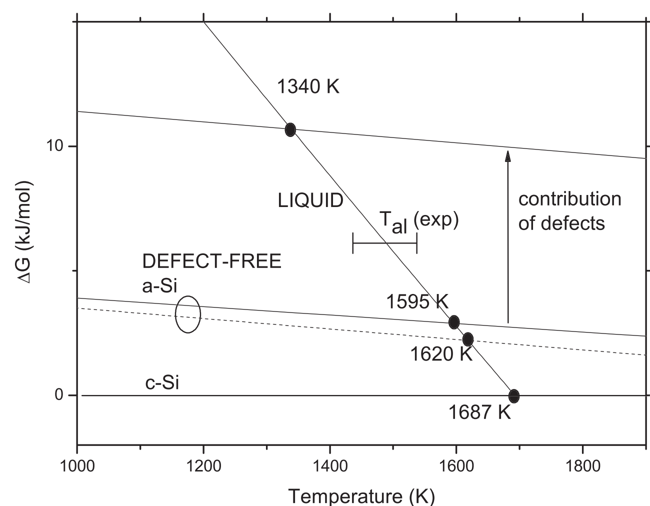

FIG. 4. Excess Gibbs free energy of relaxed a-Si. The dotted line takes into account the maximum contribution of Δc_p. The upper curve is the free energy for the a-Si with maximum crystallization enthalpy (maximum density of structural defects) reported so far.[4] Intersection with the curve of liquid Si delivers the expected melting points of a-Si that can be compared to the melting point of c-Si (1687 K). The horizontal bar is the only experimental determination of T_{al}.

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280 K, meaning that the density of defects has a stronger influence on T_{al} than the degree of relaxation.

CONCLUSIONS

The measurements of the excess specific heat of a-Si with respect to c-Si, Δc_p, reported here, led us to conclude that above 100 K, Δc_p becomes negligible when samples have been previously dehydrogenated (and relaxed). This conclusion does not depend on the density of structural defects (i.e., it is independent of the sample crystallization enthalpy). Below 100 K, an upper bound to Δc_p has been established that limits the maximum variation of the enthalpy and entropy with temperature. These results, together with previous measurements of the crystallization enthalpy,[4] make clear that, from the thermodynamic point of view, relaxed a-Si is much closer to c-Si than was previously thought. Finally, the melting point of a-Si has been predicted and found to be very close to that of c-Si for defect-free relaxed material. Furthermore, it is concluded that the density of defects has a more pronounced effect on the melting temperature than the degree of relaxation does.

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