

**TRANSIENT STRUCTURAL RELAXATION OF AMORPHOUS SILICON**W. SINKE<sup>1</sup>, T. WARABISAKO, M. MIYAO and T. TOKUYAMA<sup>2</sup>*Central Research Laboratory, Hitachi Ltd., PO Box 2, Kokubunji, Tokyo 185, Japan*

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Transient structural relaxation of ion-implanted and vacuum-evaporated amorphous silicon has been studied over a wide range of times and temperatures using Raman spectroscopy. For ultra-fast, pulsed-laser induced heating at  $\geq 1000^\circ\text{C}$  relaxation occurs on a nanosecond time-scale. Thermal annealing at  $200\text{--}600^\circ\text{C}$  induces relaxation within seconds to hours. For heating at a certain temperature, the degree of relaxation (as defined by the bond-angle distortion) initially increases roughly logarithmically with time. Subsequently a pseudo-saturation level is reached which is temperature-dependent. The activation energy associated with the very first part of the relaxation is  $\approx 0.5$  eV for ion-implanted amorphous silicon and thermal annealing. Relaxation is enhanced in the case of pulsed-laser induced heating, which may be related to the formation of a high density of electrons and holes and the resulting network softening. It is suggested that the melting temperature of a-Si is influenced by the state of relaxation and that it varies with the heating procedure used. The initial state of relaxation of a-Si formed by vacuum evaporation is found to be strongly dependent on preparation conditions. Upon further annealing the films relax to a saturation level which is only slightly dependent on the initial conditions.

**1. Introduction**

In spite of the fact that amorphous silicon has been studied extensively in recent years, its structure and properties are not yet fully understood [1]. Moreover, they are known to be dependent on the thermal history of the material. In this respect the temperature at which deposition or formation took place as well as the temperature of a subsequent annealing are of importance. Already in 1970 Brodsky and coworkers [2] reported that optical-, electrical- and spin properties of deposited a-Si films change when heat treatment is applied after deposition. Depending on preparation conditions deposited a-Si appears to be porous [3], so that considerable amounts of

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impurities may diffuse into the films upon exposure to air. It is a well-known experimental fact that the indiffusion of impurities can be suppressed by annealing before exposure. This treatment is usually referred to as 'densification'. Although the reduction of porosity and indiffusion occurs along with the observed changes in film properties a simple relation can be excluded. This has been suggested by Thomas et al. [4] for vacuum-evaporated a-Si on the basis of in situ spin measurements and is in agreement with the fact that ion-implanted a-Si, which is not porous, also exhibits clear changes upon heating [5].

The results mentioned before only reflect in an indirect way the structural changes that occur in that a-Si network. More direct information on an atomic level can be obtained from Raman spectroscopy [6]. This method has been used by Tsu et al. [7–9] and has the additional advantage that it is insensitive to impurities. Using Raman spectroscopy it is possible to determine the average bond-angle distortion (from the ideal tetrahedral value) in the a-Si network [6]. The available data indicate that annealing of deposited a-Si in the temperature range 200–600 °C results in a decrease of the average bond-angle distortion [8,9]. This release of strain energy is called structural relaxation. For each temperature relaxation saturates at a specific level.

Until now only furnace annealing has been used to study relaxation. Because this is intrinsically a slow heating method one has never been able to study the transient behaviour of relaxation. In this paper we report the first data on the time-dependence of structural relaxation, as obtained from Raman scattering experiments. Relaxation has been induced by pulsed-laser annealing, rapid thermal annealing and furnace annealing, over a wide range of times (nanoseconds to hours) and temperatures (200 to  $\approx 1000$  °C). Experiments were performed on ion-implanted a-Si and on a-Si prepared by ultra-high vacuum evaporation under various conditions.

## 2. Experimental

a-Si layers have been prepared using two different techniques. First, a layer of a-Si was formed by dual P<sup>+</sup> implantation into Si(100). The energies and doses were 50 keV/10<sup>16</sup> cm<sup>-2</sup> and 170 keV/2 × 10<sup>16</sup> cm<sup>-2</sup>, respectively. The layer thickness, as determined by cross-sectional transmission electron microscopy, was 370 nm. Second, 500 nm a-Si layers were formed by evaporation in ultra-high vacuum onto quartz substrates, using an electron-beam evaporator. The total pressure during deposition was  $\approx 10^{-7}$  Pa. The evaporation rate was kept constant at 0.3 nm/s for all samples. Depositions were made at various substrate temperatures and after deposition, annealing for 30 min at various low temperatures (densification) was performed in the vacuum chamber prior to exposure to air. This densification was applied to vary the porosity of the samples and thus the indiffusion of impurities upon exposure to air. Indicating the different samples by their substrate temperature ( $T_{\text{sub}}$ ) and their densification temperature ( $T_{\text{dens}}$ ) in °C the following samples were prepared:

$T_{\text{sub}}/T_{\text{dens}} = \text{RT}/-, 100/100, 100/250, 100/400$  and  $250/-$ . For reference one sample was prepared at a deposition rate of  $\approx 4 \text{ nm/s}$  and  $T_{\text{sub}}/T_{\text{dens}} = 100/100$ . The pressure during this deposition was  $\approx 10^{-5} \text{ Pa}$ .

Annealing of the a-Si layers to induce structural relaxation was performed in three ways. First, ultrafast heating to very high temperatures was achieved using pulsed-laser irradiation at energy densities just below the threshold for surface melting of the material, which is  $\approx 0.1 \text{ J/cm}^2$ . The laser used was a homogenized Q-switched ruby laser (pulselength 32 ns, wavelength 694 nm). The estimated heating time at the peak temperature is in the order of 10 ns. To extend the duration, multiple-pulse irradiation was employed: 10, 100 and 1000 pulses. Laser irradiations were performed in air. The second heating method was rapid thermal annealing (RTA) in the time range from 5 to 10 min, at temperatures of 400 and 600°C. The system used was the AG Associates Heatpulse 610, which is based on halogen lamp heating. The temperature was monitored using a thermocouple attached to the Si wafer used as a susceptor. Annealing was carried out under flowing nitrogen. The third heating method was conventional furnace annealing (FA) at temperatures of 200, 400 and 600°C, in the time range from 10 min to 3 h, under flowing nitrogen. The shortest annealing time for FA is the same as the longest for RTA, which enables matching of the time ranges covered by both methods.

Characterization of the a-Si layers and monitoring of structural relaxation was performed using Raman spectroscopy. Spectra were taken in a backscattering geometry (see fig. 1) using a Cary 82 triple-grating monochromator with photon counting system. The 531 nm line of a krypton laser was used as a light source. The diameter of the beam on the sample surface was  $\approx 100 \mu\text{m}$  and the total power was  $\approx 150 \text{ mW}$ . Measurements were performed with a slit width of  $5\text{--}10 \text{ cm}^{-1}$ . In the case of vacuum-evaporated samples the

#### RAMAN SPECTROMETER

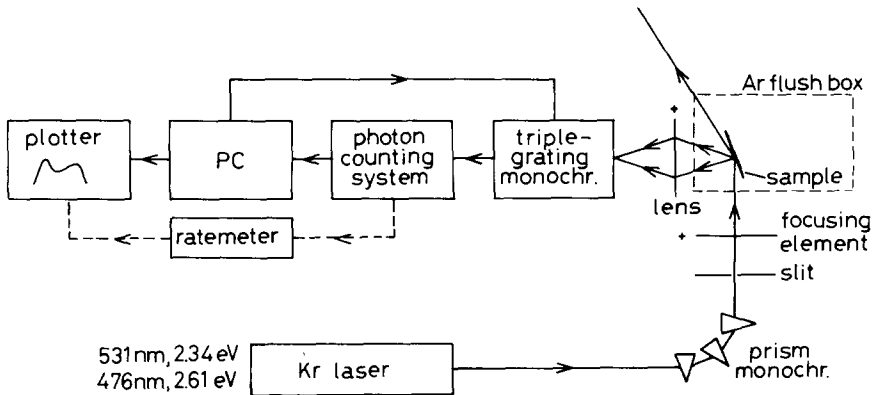


Fig. 1. Experimental set-up for Raman measurements.

impurity content after exposure to air was determined using secondary ion mass spectrometry (SIMS).

### 3. Results and discussion

#### 3.1. General

Figure 2 shows a typical example of a Raman spectrum of a-Si (in this case formed by vacuum evaporation onto a quartz substrate held at room temperature) in comparison with the spectrum of the same sample after annealing for 1 h at 600 °C in a nitrogen ambient. After annealing the following changes can be observed. First, the ratio of the height of the TO (transverse optic) and the TA (transverse acoustic) peaks increases upon annealing. Second, the position of the TO peak shifts towards higher wavenumbers and third, the width of the TO peak (indicated by the arrow) decreases. All these changes are indicative of structural relaxation of the a-Si network [6–9]. The narrowing of the TO peak directly reflects a narrowing of the distribution of stretching vibrational frequencies and can be related quantitatively to the relaxation process via the bond-angle distortion [16]:

$$\Gamma/2 \cong 7.5 + 3\Delta\theta_b, \quad (1)$$

in which  $\Gamma/2$  is the half width of the TO peak measured at the high-wavenumber side (to avoid influences of the nearby LO = longitudinal optic peak) and  $\Delta\theta_b$  is the root-mean-square bond-angle distortion.  $\Gamma/2$  is in  $\text{cm}^{-1}$ ,  $\Delta\theta_b$  is in degrees.

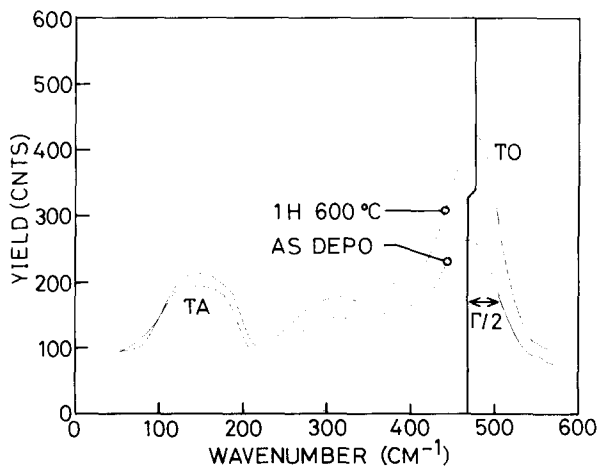


Fig. 2. Raman spectra of vacuum evaporated a-Si before and after thermal annealing.

Figure 2 shows that annealing at 600 °C for 1 h does not induce crystallization to any measurable extent. Traces of crystalline material in the order of a percent or less can easily be detected by the appearance of a strong peak in the Raman spectrum around 520  $\text{cm}^{-1}$  [9].

It is worth noting that model-building experience has shown that it is impossible to construct any (continuous) random network for a-Si with  $0^\circ \leq \Delta\theta_b \leq 6.6^\circ$  [6]. This indicates the fundamental separation between a-Si and crystalline Si (c-Si) and shows that crystallization is a discontinuous transition from one state of Si to another.

In the following, the relaxation process is characterized by the position and half width of the TO peak. In order to measure these quantities in an accurate way Raman spectra were taken in the wavenumber range of 440 to 600  $\text{cm}^{-1}$ . The measuring time was chosen such that statistics allowed a determination of the peak position with an accuracy of  $\pm 0.5 \text{ cm}^{-1}$  and of the peak half width of  $\pm 1 \text{ cm}^{-1}$ .

### 3.2. Ion-implanted amorphous silicon

#### 3.2.1. Heating by pulsed-laser irradiation

Figure 3 shows the TO peak position for an ion-implanted a-Si sample as a function of the number of laser pulses used to induce ultrashort-time heating. If we assume the effective heating time for one pulse to be  $\approx 10 \text{ ns}$ , the horizontal axis may be interpreted as a time axis, ranging from 10 ns to 10  $\mu\text{s}$ .

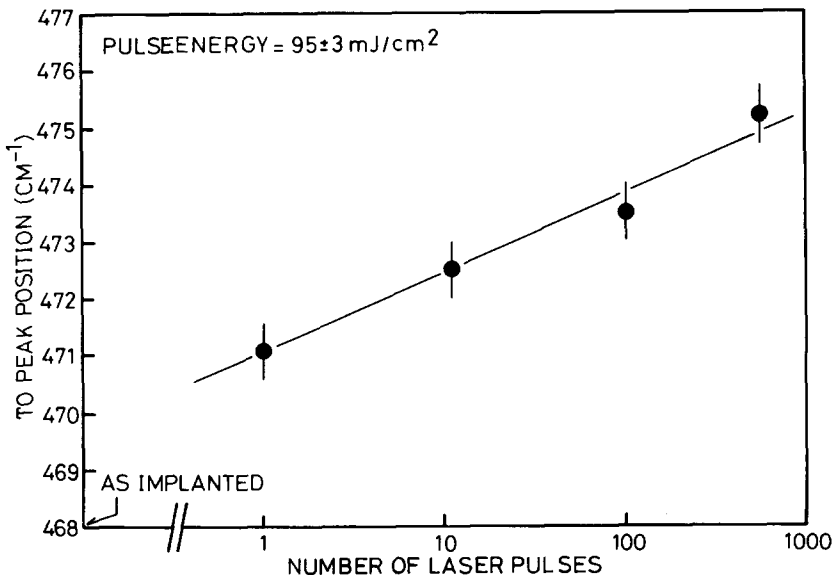


Fig. 3. TO peak position of ion-implanted a-Si as a function of the number of laser pulses used for irradiation.

As the laser energy density in this experiment was just below the threshold value to melt the a-Si (melting temperature  $\approx 1200^\circ\text{C}$  [10]) the estimated peak temperature is  $\geq 1000^\circ\text{C}$ . The figure shows that one laser pulse results in a peak shift of  $\approx 3\text{ cm}^{-1}$ . When multiple-pulse irradiation is used the shift is found to increase logarithmically with the number of larger pulses.

A similar effect is found for the peak width, as is indicated in fig. 4. However, the ratio between the magnitude of the initial change induced by one pulse and the magnitude of the additional changes induced by multiple-pulse irradiation is different between fig. 3 and 4. Upon irradiation with one laser pulse the bond-angle distortion in the a-Si network is found to decrease from  $\approx 12.2^\circ$  to  $\approx 10.5^\circ$ . Irradiation with  $\approx 1000$  pulses causes a further decrease to  $9.8^\circ$ . According to refs. [8,9], the energy stored in the a-Si network due to the bond-angle distortions is given by

$$U_\theta \cong 6(1/2)k_\theta(r_b\Delta\theta_b)^2, \quad (2)$$

in which  $U_\theta$  is the stored energy,  $k_\theta$  is a force constant equal to  $9.2\text{ N/m}$ ,  $r_b$  is the Si-Si bond length ( $0.235\text{ nm}$ ) and  $\Delta\theta_b$  is the average bond-angle distortion.

For the as-implanted a-Si  $U_\theta \cong 42\text{ kJ/mol}$ . Upon irradiation with one pulse this energy decreases to  $\approx 31\text{ kJ/mol}$ . After 1000 pulses the energy has decreased to  $\approx 27\text{ kJ/mol}$ .

Although the temperature during laser irradiation is far above the normal crystallization temperature of a-Si there is no indication from Raman that

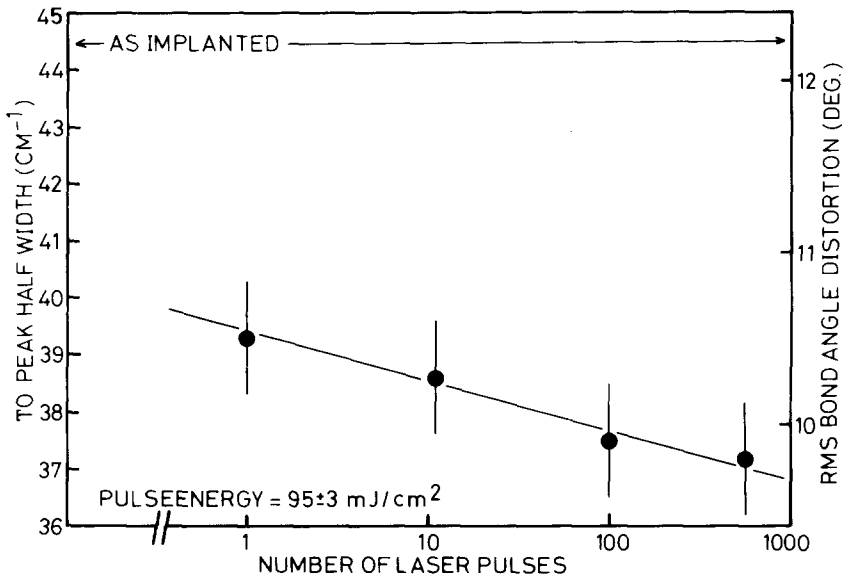


Fig. 4. TO peak half width as well as average bond-angle distortion of ion-implanted a-Si as a function of the number of laser pulses used for irradiation.

crystallization has occurred. Therefore either the nucleation rate is too low to form a substantial number of crystallites or the growth of nuclei is such that they remain too small to be observed. In any case the volume fraction of crystalline material should be smaller than  $\approx 1\%$  [9].

### 3.2.2. Rapid thermal annealing and furnace annealing

Analogous to fig. 3, fig. 5 shows the position of the TO peak of ion-implanted a-Si as a function of heating time. Heating was performed using RTA and FA. Whereas fig. 3 showed relaxation on a nanosecond timescale at a temperature of  $\approx 1000^\circ\text{C}$ , fig. 5 shows relaxation on a timescale of seconds at temperatures up to  $600^\circ\text{C}$ . For heating at  $400^\circ\text{C}$  the position of the TO peak initially shifts towards higher wavenumbers. Subsequently, saturation is reached and the peak position stays constant within the measuring accuracy upon further heating. When heating is performed at  $200^\circ\text{C}$ , a very slow upward shift is observed but a saturation level cannot be found within the maximum annealing time used here. For heating at  $600^\circ\text{C}$  a very fast upward shift of the TO peak position is observed which is shielded for annealing times over 20 s by the epitaxial regrowth (single-crystallization) of the a-Si layer on the substrate. In the figure the upper limit of the TO peak position ( $480\text{ cm}^{-1}$  [11]) for a-Si is indicated. Extrapolation of the observed shift at  $600^\circ\text{C}$  shows it is very likely that the TO peak position would saturate close to this fundamental limit if epitaxy would be prevented.

Figure 6 shows the TO peak width as well as the corresponding bond-angle distortion as a function of annealing time for the same set of samples used in

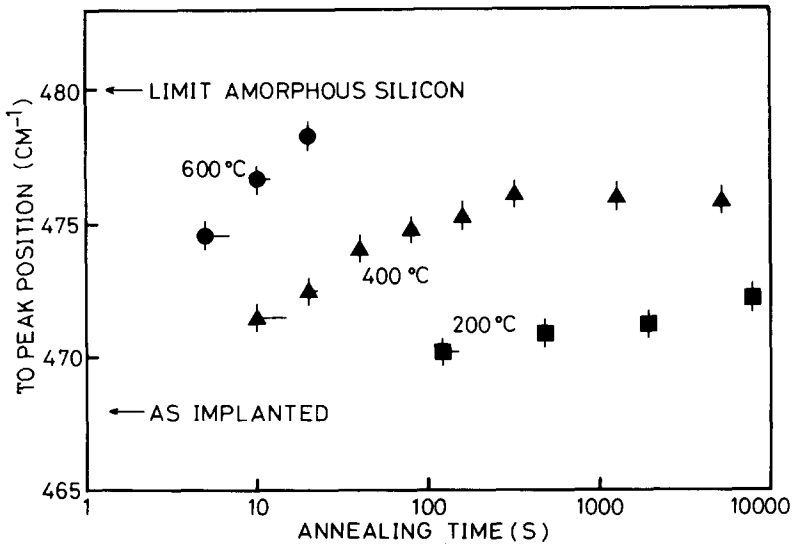


Fig. 5. TO peak position of ion-implanted a-Si as a function of annealing time at various temperatures.

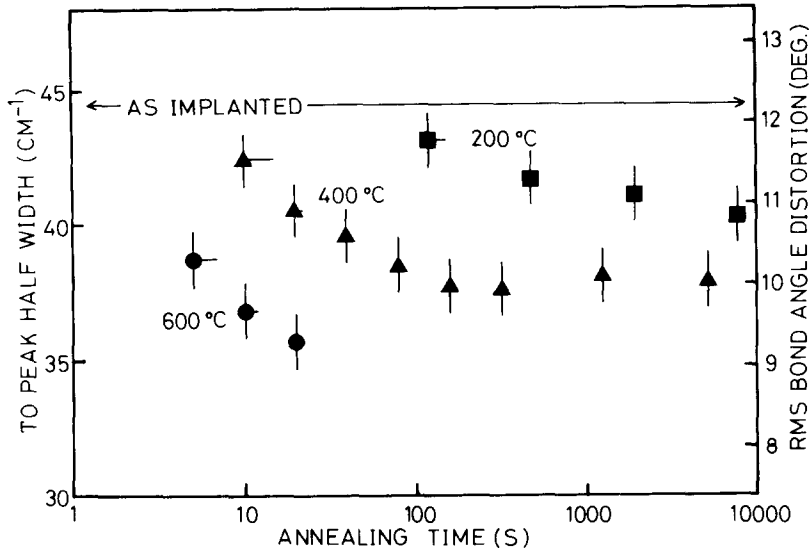


Fig. 6. TO peak half width as well as average bond-angle distortion of ion-implanted a-Si as a function of annealing time at various temperatures.

fig. 5. It is clear that the trends observed here are very much like those in fig. 5. The maximum network relaxation which can be obtained before epitaxy occurs, is from a bond-angle distortion of  $\approx 12.2^\circ$  to  $\approx 9.2^\circ$  for annealing at  $600^\circ\text{C}$ . According to formula (2) these values correspond to stored energies of 42 and 24 kJ/mol, respectively.

The present results indicate that the a-Si network relaxes to a state which is dependent on the annealing temperature. This is in contrast to ref. [5], in which one particular metastable state (in terms of optical properties and spin density) is found for a whole range of annealing temperatures ( $400\text{--}600^\circ\text{C}$ ). This suggests that there is no simple correlation between those film properties and the state of relaxation in terms of bond-angle distortion.

### 3.2.3. Relaxation rate and activation energy

Now that the transient behaviour of structural relaxation has been determined the question remains how this can be explained in terms of fundamental parameters like activation energy. The results shown in figs. 5 and 6 indicate that the relaxation initially increases logarithmically with annealing time and subsequently saturates. Both the slope of the initial part and the saturation level increase with annealing temperature. These observations suggest the following model. In the as-implanted a-Si various processes can contribute to the initial part of the relaxation. Each process is characterized by its own activation energy. However, the number of available transitions at each activation energy is limited. Upon annealing at a certain temperature, first the transitions with low activation energy are depleted, giving rise to the



first part of the relaxation. Subsequently, transitions with higher activation energies have to be used to obtain further relaxation until these are depleted too. Finally, all transitions which can occur within reasonable time at that specific temperature are depleted and the relaxation reaches a pseudo saturation (in practice, relaxation will proceed very slowly until the fundamental limit is reached or crystallization occurs). This model explains why both the relaxation rate and the pseudo saturation level increase with temperature.

To obtain an estimate of the activation energy associated with the first part of the relaxation, a relaxation 'velocity' is defined as the reverse annealing time required to obtain a decrease of the TO peak half width of  $1 \text{ cm}^{-1}$ . This time can be estimated by extrapolation of the data in fig. 6. The results are shown in fig. 7. The effective activation energy is  $\approx 0.5 \text{ eV}$ . This value could reflect the average energy needed to break highly strained bonds in the as-implanted a-Si network.

Note that the activation energy for structural relaxation deduced from our measurements differs from that obtained by Tsu et al. [8,9] ( $\approx 0.2 \text{ eV}$ ). However, in the present case the activation energy is related to the initial stage of the transient relaxation, while Tsu et al. assigned an activation energy to the pseudo plateau in the relaxation. The authors did not find any time dependence of the relaxation within the range studied (15–150 min). In view of the dependence shown in figs. 5 and 6, it is concluded that their measurements have been performed in the pseudo saturation region.

If we apply the procedure discussed before to obtain the velocity of laser-induced relaxation in fig. 4, the value is much higher than would be expected on the basis of the temperature difference (see fig. 7). This is attributed to non-thermal effects in the relaxation under high-power laser irradiation. During the irradiation a very high density of electron-hole pairs is formed, which may soften the a-Si network and enhance relaxation.

### 3.2.4. *Melting temperature of amorphous silicon*

For several years there has been a controversy concerning the melting temperature of a-Si [12–14]. In summary, results from experiments concerning nanosecond pulsed-laser induced melting indicate that the melting temperature of a-Si is  $\approx 200 \text{ K}$  below that of c-Si. On the other hand, experiments concerning solid-phase epitaxial regrowth of a-Si using cw laser irradiation show that the material can be heated to temperatures very close to the melting point of c-Si without melting. Recently, Olson and coworkers [15] have used microsecond laser pulses to induce solid-phase epitaxy of a-Si and found that for thin ( $\leq 100 \text{ nm}$ ) films melting of a-Si does not occur at temperatures well above  $1300^\circ\text{C}$ , while for thick (260 nm) films the a-Si melts at a temperature of  $\approx 1190^\circ\text{C}$ . In this context the observation of relaxation enhancement under laser irradiation might have interesting implications.

According to ref. [12] the difference in Gibbs free energy between a-Si and c-Si is of the order of  $10 \text{ kJ/mol}$ . Using calculated values for the free energy of liquid Si (l-Si) as a function of temperature, this difference in free energy is

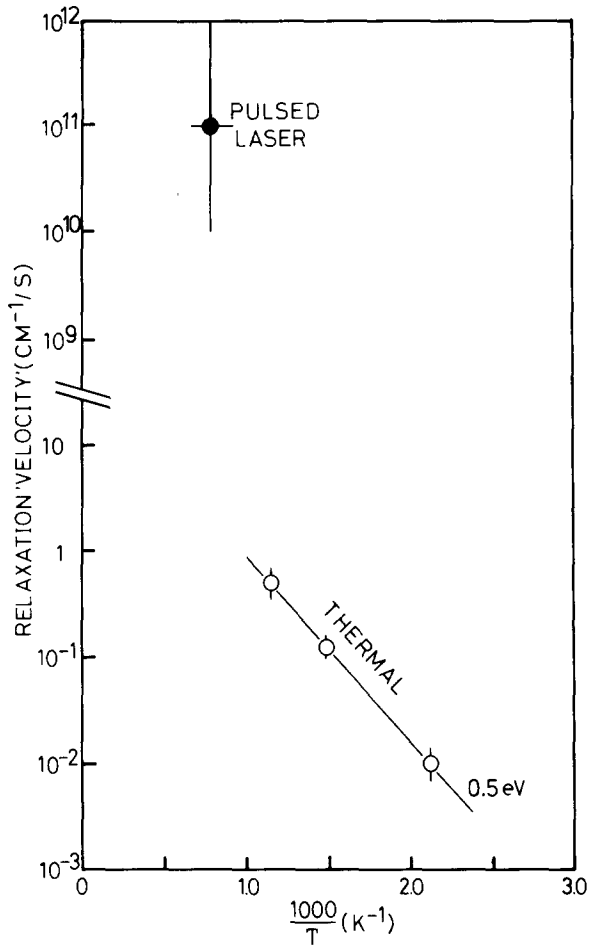


Fig. 7. Relaxation 'velocity' (see text) of ion-implanted a-Si as a function of annealing temperature.

predicted to result in a difference in melting temperature between a-Si and c-Si of several hundred degrees. As has been pointed out earlier, the energy stored in the a-Si network due to bond-angle distortions can be as high as  $\approx 40$  kJ/mol for as-implanted a-Si. The estimated minimum energy for any a-Si network (assuming  $\Delta\Theta_b = 6.6^\circ$  [6]) is  $\approx 12$  kJ/mol, comparable to the difference in free energy between a-Si and c-Si given in refs. [12,13]. This value could be interpreted as the energy stored in a fully relaxed a-Si network. Our results indicate that this state of full relaxation cannot be reached for all types of a-Si and, more important, under all heating conditions. In some cases the a-Si is transferred into c-Si before the relaxation saturates (see figs. 5 and 6). In other cases the a-Si might be melted before full relaxation is reached. This

is supported by the observation that heating by a single laser pulse at an energy density just below the threshold for melting still does not induce full relaxation. In such cases, when a-Si melts from a state with higher energy content, the transition temperature is expected to be lower than for fully relaxed a-Si. The energy release upon relaxation, as inferred from the present Raman results, is anywhere between 0 and  $\approx 20$  kJ/mol. In view of the prediction that a difference in free energy between a-Si and c-Si of  $\approx 10$  kJ/mol would give rise to a difference in melting temperature of several hundreds of degrees [12,13] it is clear that the state of relaxation cannot be neglected in the considerations of the melting temperature. These findings are in contrast with those from calorimetric studies in ref. [13], in which the authors state that either relaxation does not occur during temperature ramping (40 K/min) or that the energy release upon relaxation is negligible. Our results indicate that neither is the case for the samples used in this study.

In the experiments by Olson et al. [15] mentioned before, thin a-Si films could be heated to temperatures  $> 1300^\circ\text{C}$  while thick films appeared to melt at  $1190^\circ\text{C}$ . Heating was performed using a microsecond pulsed dye laser operated at a wavelength of 590 nm. At this wavelength the absorption depth in a-Si is  $\approx 100$  nm [16], which is equal to the thickness of the thin film. Consequently, in the case of the thin film all material is heated in the presence of a high density of photons, while in the case of the thick film deeper regions are heated by thermal diffusion only. As has been shown in a previous section (see fig. 7), relaxation is enhanced for pulsed-laser irradiation (note that the Raman laser probes an a-Si region within the absorption depth of the pulsed laser). Therefore the thin film is expected to relax further during heating than the (deeper regions of the) thick film and melting in the thin film is expected to occur at a higher temperature than in the thick film, as observed.

### 3.3. Vacuum evaporated amorphous silicon

Figures 8 and 9 show measurements of the TO peak position and the TO peak width as a function of annealing time for a-Si samples prepared by vacuum evaporation. The annealing temperature used was  $600^\circ\text{C}$ . In the figures are indicated the substrate temperature during deposition ( $T_{\text{sub}}$ ) and the temperature of the densification annealing ( $T_{\text{dens}}$ ), which was performed in vacuum before exposure to air, for the various samples. SIMS measurements have shown that the RT/- sample contains a high concentration of impurities (mainly oxygen). These impurities have diffused into the film upon exposure to air and indicate that the film is porous. On the other hand, the 100/400 sample shows a very low impurity content, indicating that the film has been sufficiently closed against indiffusion. The 100/100 film is intermediate in this respect. No data are available for the 100/250 film and the 250/- film. However, the latter one is expected to be completely closed while the former one is expected to be comparable to the 100/100 film (this will be discussed later).

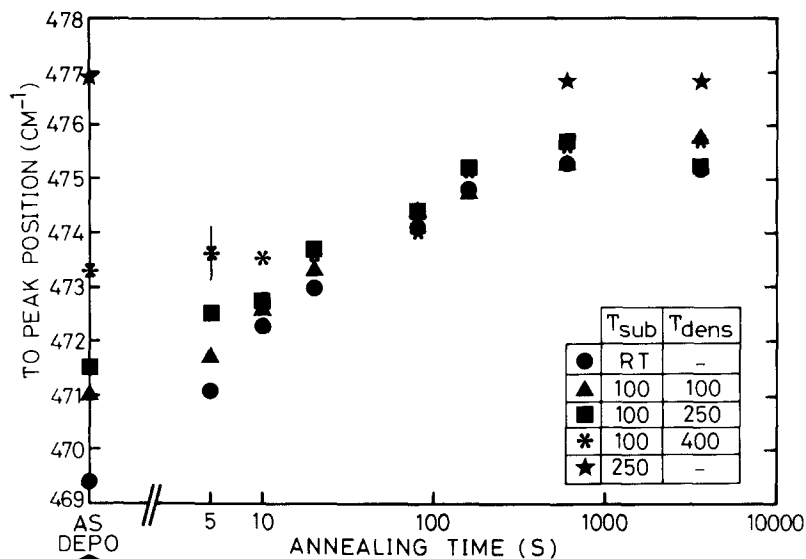


Fig. 8. TO peak position of vacuum evaporated a-Si as a function of annealing time at 600 °C. Indicated are the preparation conditions for the various samples (see text).

At this point we note that the 100/100 film which was deposited at a very high deposition rate of  $\approx 4$  nm/s was found to be identical to the 100/100 film of the above series in terms of Raman spectroscopy. Apparently, the deposition rate is not a critical parameter in determining the film atomic structure for a substrate temperature of 100 °C. For that reason this sample will not be discussed separately.

The initial position of the TO peaks, as is shown in fig. 8, is strongly dependent on the preparation conditions of the a-Si film. It varies from  $\approx 469$   $\text{cm}^{-1}$  for the RT/- film to  $\approx 477$   $\text{cm}^{-1}$  for the 250/- film. If we tentatively relate these values to the observed properties concerning impurity indiffusion, then a film can be considered to be sufficiently densified if the TO peak is positioned at or beyond  $\approx 473$   $\text{cm}^{-1}$  (in this specific case). Therefore the 100/250 film, which lies close to the 100/100 film, is expected to be somewhat porous, while the 250/100 film is expected to be fully closed. Upon annealing the position of the TO peak for the various films shifts towards higher wavenumbers and the distribution narrows. For annealing times  $\geq 20$  s the differences between the peak positions of the various films (except the 250/-film) are very small. However, the films with the highest position in the as-deposited state tend to maintain the highest position upon annealing. The position of the TO peak of 250/-film does not show any change upon annealing, indicating the as-deposited film is fully relaxed. The relaxation of the other films saturates after annealing for about 500 s but still then the TO peak of the 250/-film is located significantly above those of the other films.

Figure 9 shows that also the width of the TO peak depends strongly on preparation conditions. Analogous to fig. 8, the criterion for film densification would now be a peak half width of  $\approx 37 \text{ cm}^{-1}$  or less. Upon annealing the width of the various TO peaks decreases while again the distribution narrows. In contrast to fig. 8, the 250/-film is not clearly separated from the other films after annealing. We suggest that the separation in fig. 8 is related to stress in the 250/-film due to the deposition on a heated substrate. Similar to fig. 8, the films which show strong relaxation in the as-deposited state tend to relax more than others upon annealing. Although the effect is rather small it indicates that the relaxation process is independent on the initial structure and/or the impurity content of the film. In the case of a porous film, the initial (void) structure could be stabilized by impurities which prevent the film from becoming a homogeneous closed network.

A comparison of the data in figs. 5 and 6 and those in figs. 8 and 9 shows that at the same temperature, relaxation is considerably faster in the case of ion-implanted a-Si than in the case of evaporated a-Si. This difference can be related to the presence of phosphorus in the ion-implanted a-Si (phosphorus is also known to influence nucleation and crystallization [17]) or to a difference in structure between the two kinds of a-Si. It has been shown that the epitaxial growth rate of porous a-Si is considerably smaller than that of ion-implanted a-Si [18], which illustrates the possible influence of the network structure on atomic rearrangement processes.

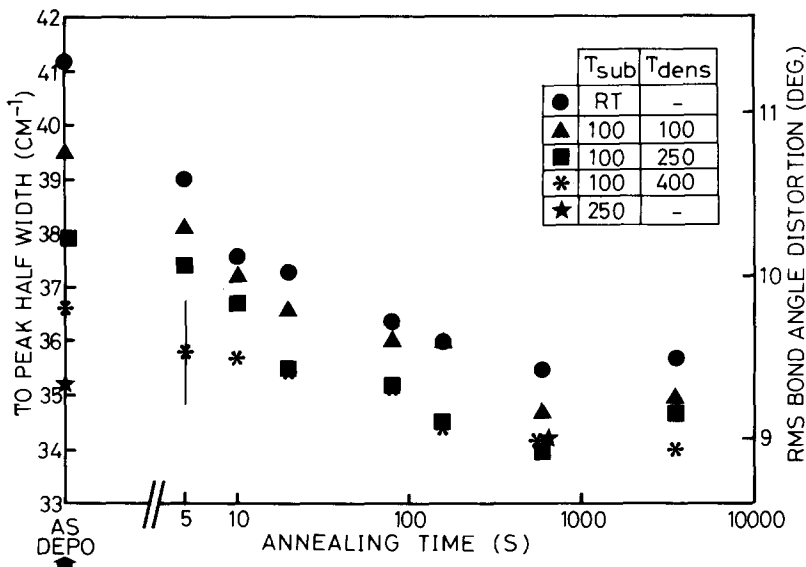


Fig. 9. TO peak half width as well as average bond-angle distortion of vacuum evaporated a-Si as a function of annealing time at  $600^\circ\text{C}$ . Indicated are the preparation conditions for the different samples (see text).

#### 4. Conclusions

Structural relaxation of a-Si induced by annealing has been investigated over a wide range of times and temperatures.

For a-Si formed by ion implantation into Si(100), relaxation is found to occur on a nanosecond timescale when the material is heated to  $\approx 1000^\circ\text{C}$  using pulsed-laser irradiation. Although this temperature is far beyond the normal crystallization temperature of a-Si there is no indication from Raman spectroscopy that the relaxation is accompanied by the formation of crystallites. Heating in the range of  $200$  to  $600^\circ\text{C}$  induces relaxation within seconds to hours. The results indicate that relaxation saturates at a level which is dependent on the annealing temperature. The activation energy associated with the first part of the transient relaxation is estimated to be  $\approx 0.5$  eV for heating by RTA and FA. Relaxation is enhanced in the case of heating by pulsed-laser irradiation, which may be related to the formation of a high density of electrons and holes and the resulting network softening. It is suggested that the melting temperature of a-Si is influenced by the state of relaxation. Therefore the actual melting temperature may vary by more than  $100^\circ\text{C}$  from one experiment to another, depending on the heating method and -rate.

a-Si formed by vacuum evaporation behaves in a way comparable to that of ion-implanted a-Si, that is, relaxation initially increases with annealing time and subsequently saturates. The saturation level is slightly dependent on the initial state of the material, which suggests that the structure of the as-deposited film and/or the impurity content influence the relaxation process.

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#### Note added in proof

In this paper we use expressions for the bond-angle distortion vs. Raman peak half-width ( $\Gamma/2 \approx 7.5 + 3\Delta\Theta_b$ ; formula 1) and for the distortion energy vs. bond-angle distortion ( $U_\Theta = 6(1/2)k_\Theta(r_b\Delta\Theta_b)^2$ , with  $k_\Theta = 9.2$  N/m; formula 2) as given by Beeman et al. [6] and Tsu et al. [8,9]. These expressions are partly based on experimental data provided by Cerdeira et al. [a] and on calculations by Martin [b], in which a modified Keating potential is used to describe bending- and stretching forces in the Si lattice. Application to our

results yields network distortion energies of up to 40 kJ/mol for  $\Delta\Theta_b \approx 12^\circ$ . The absolute minimum distortion energy (for  $\Delta\Theta_b = 6.6^\circ$ ) calculated in that way is  $\approx 12$  kJ/mol.

Wong and Lucovsky [c] use a Born potential and a Bethe lattice structure to evaluate the relation between the degree of distortion and the Raman spectrum. Linear interpolation of their numbers yields the following relation:  $\Gamma/2 \approx 5\Delta\Theta_b - 5$ . The full range of bond-angle distortions according to their estimates is  $7^\circ$  to  $10^\circ$ . In addition, according to Saito et al. [d], the distortion energy is given by  $U_\theta = 6(1/3)\beta(r_b\Delta\Theta_b)^2$ , in which  $\beta = 9.7$  N/m. Application of the latter two expressions to our results yields distortion energies of up to 19 kJ/mol for  $\Delta\Theta_b \approx 10^\circ$  and an absolute minimum of 10 kJ/mol for  $\Delta\theta_b \approx 7^\circ$ .

The differences between the expressions for the bond-angle distortion vs. Raman peak half-width illustrate a rather fundamental uncertainty concerning the relation between the degree of disorder in the a-Si network and features in the Raman spectrum. The differences between the expressions for the distortion energy are due to different estimates of the ratio  $\beta/\alpha$  (bond-bending force constant/bond-stretching constant) as they appear in Keating's potential [b]. Tsu et al. use  $\beta/\alpha \approx 0.29$  whereas Saito et al. use  $\beta/\alpha \approx 0.20$ .

At present it is not possible to decide which set of expressions for  $\Delta\Theta_b$  and  $U_\theta$  is most reliable. However, we feel that the absolute numbers of the strain energy calculated using Tsu's expressions are rather high, which suggests that the range of bond-angle distortions and the value of  $\beta/\alpha$  are overestimated.

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