STRUCTURAL RELAXATION OF AMORPHOUS SILICON INDUCED BY HIGH TEMPERATURE ANNEALING

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Structural relaxation of amorphous Si is studied in the temperature range 500-850 °C using Raman spectroscopy. The minumum value for the Raman peakwidth that can be obtained is inversely proportional to the anneal temperature. The relaxation process is basically the same in a-Si prepared by ion implantation and by vacuum evaporation.

Introduction

The optical,[1] vibrational,[2] and thermodynamic[3] properties of amorphous silicon (a-Si) vary strongly with the way of preparation and other treatments. This is related to the atomic structure of a-Si which is thought to be a covalently bonded and 4-fold coordinated continuous random network.[4] Variations in a-Si properties, including the free energy, have been attributed[5] mainly to non-equilibrium defects such as di- and tri- vacancies, dangling and floating bonds,[6,7] and other types of defects. A high concentration of such defects results in a large average bond angle distortion ($\Delta\theta$).[5] Removal of defects leads to a state of lower free energy and is known as structural relaxation. One way to induce relaxation of a-Si is by thermal annealing.

Structural relaxation of a-Si can be examined by Raman spectroscopy.[2,8] The Raman spectrum of a-Si reflects the full vibrational density of states[9,10] and changes in the spectrum upon annealing can be related to changes in $\Delta\theta$.[2,11–13] As the a-Si relaxes, the first order transverse-optic-like (TO) peak decreases in width and shifts in position. Relaxation has previously been studied for temperatures up to 600 °C. During the first seconds to minutes structural relaxation takes place until a temperature dependent, pseudo saturation level is reached.[2,9] Higher temperatures lead to a more relaxed state. For temperatures above 600 °C relaxation has not yet been studied because at these temperatures a-Si crystallizes but it has been suggested that at 600 °C a-Si is fully relaxed and that no further changes are expected when higher temperatures are used.[2]

In this paper we present data on a-Si annealed to high temperatures (500-850 °C). By using thick a-Si on crystal or a-Si on SiO_2 substrates the crystallization was delayed so we could probe the higher temperature regime. Raman spectroscopy shows that structural relaxation does continue to these higher temperatures. This has implications for models of defects in a-Si.

Experiment

Three methods were used for preparing the a-Si samples: (I) Chemical vapor deposited polycrystalline Si (0.5 μm) on thermally oxidized Si was fully amorphized by ion implantation of 5×10^{15} cm^{-2} ^{28}Si^{+} at 100 and 300 keV. (II) Thick a-Si on a c-Si substrate was made by implants of 5×10^{15} cm^{-2} ^{28}Si^{+} at 0.5, 1, and 2 MeV. (III) A 200 nm thick a-Si layer was evaporated onto a thermal oxide layer in a vacuum chamber (basepressure 1×10^{-8} mbar) with a deposition rate of 1 Ås^{-1}. After deposition the material was densified by heating for one hour at 220 °C in the vacuum chamber prior to exposure to air.[14]

Most of the thermal treatments were done with a rapid thermal annealer. The samples were placed between two Si wafers. The temperature was monitored with a thermocouple mounted next to the sample and with a pyrometer. Anneals were carried out under flowing nitrogen (5 litres/min). Some anneals were done in a vacuum oven. Temperatures ranged from 500 to 800 °C with times from 1 sec to 1 hr. Another set of samples was annealed on a heated stage[15,16]. By means of reflectivity measurements the temperature was determined. The anneal time is defined as the interval at the target temperature and not the total duration of the heating cycle. Additionally, one sample has been laser heated for ≈ 80 msec to a temperature of 850 °C, as was estimated from the solid phase epitaxial regrowth rate of a reference sample.[15,16] Heat up and cool down time are very different for the different heating methods, therefore the anneal times have to be interpreted with some reserve.

Raman measurements were performed using the 514.5 nm line of an argon ion laser. The spectra were taken using a Spex triple-grating monochromator. The dimensions of the beam were 50 μm by 200 μm and the total power on target < 150 mW. The half-width-at-half-maximum of the TO peak ($\Gamma/2$) was determined at the high energy side of the peak after background subtraction. In order to determine this width accurately the spectrum was decomposed into gaussians. The instrumental resolution, including broadening effects due to finite entrance slits was ≈ 3.5 cm^{-1}. Since the features in the a-Si spectrum were very broad this had little influence on the determination of $\Gamma/2$.

Results

Fig. 1 shows part of the Raman spectra of two evaporated a-Si samples, one after an RTA anneal of 1.5 sec at 800 °C, and one after 1 hr vacuum anneal. The fits give a smaller value for the width at 800 °C than for 500 °C, which means that a short anneal at high temperature leads to a more relaxed state than can be obtained by prolonged heating at 500 °C. In the inset a complete spectrum is shown.

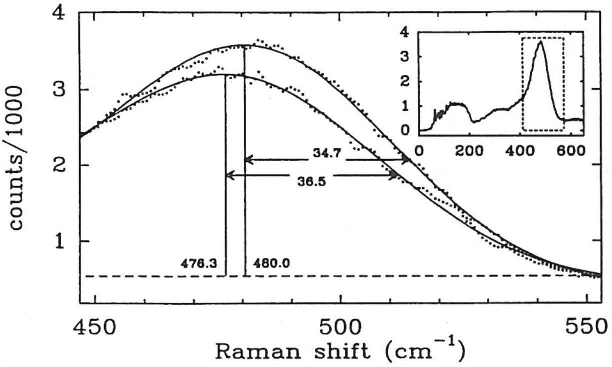

Fig 1 Raman spectra of evaporated a-Si annealed for 1.5 sec at 800°C and for 1 hr at 500 °C. In the inset a complete spectrum is shown.

Fig. 2 and 3 show the half width (Γ/2) as function of the nominal anneal time at various temperatures for evaporated and implanteda-Si respectively. Each point represents the average value of at least 3 measurements. The standard deviation was determined to be 0.3 cm^{-1}. It is again seen that higher temperatures give smaller peakwidths. This indicates that relaxation is neither saturated at 600 °C nor at 700 nor at 800 °C although the differences are quite small. The data suggest that at each temperature a pseudo saturation level is reached, and that this level is reached in shorter times for higher temperatures. This is in agreement with previous results at lower temperatures.[2,9] It cannot be excluded that prolonged annealing in the lower temperature range (500-600 °C) could lead to similar relaxation as observed for high temperature (750-850 °C) annealing. However we were not able to observe this because the samples crystallized.

From a comparison of the data for a-Si prepared by evaporation (fig 2) and by implantion (fig 3) it seems that both kinetics and quasi-saturation level are the same for the two different materials. The evaporated material could however be annealed somewhat longer at high temperature before crystallization occured than the implanted material. Fig 3 also shows the result for the laser annealed sample. The value for the width is larger than the value for 800 °C at 1 sec. This would indicate that the annealing time is too short and the sample has not yet reached its pseudo saturation level. In addition to the short anneal time, heat up and cool down timesfor this sample were significiantly faster than for the RTA samples.

In figure 4 the minumum peak width which can be obtained is shown as a function of the annealing temperature. Some reference data for lower aneal temperatures are also shown .[8] The peakwidth is inversely proportional to the annealing temperature. The physical meaning of this phenomenological relation is not clear.

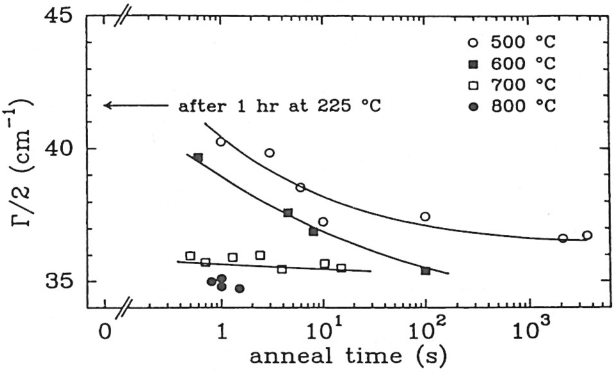

Fig 2 Raman peak half width as a function of anneal time for different temperatures for evaporated a-Si.

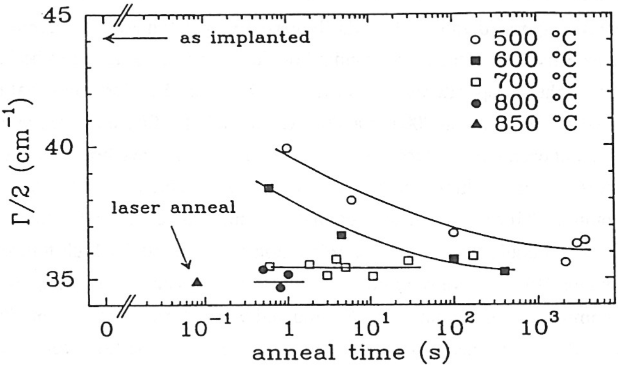

Fig 3 Raman peak half width as a function of anneal time for different temperatures for implanted a-Si.

Defects and relaxation

Recent experiments suggest that structural relaxation is fully controlled by annihilation of point defects.[5] At high temperature annealing (750-850 °C) a-Si reaches a more relaxed state which would indicate that more defects can be annealed than can be obtained by prolonged heating at lower temperatures. This is similar in c-Si where some complex defects can only be annealed out using higher temperatures.[17]

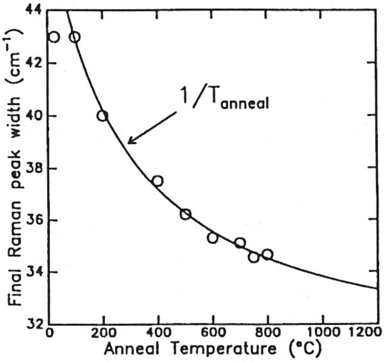

Fig 4 The minimum peak width as a function of annealing temperature. Reference data for lower temperatures are also shown.8

An interesting question is whether relaxation will still continue and to what peak width value, at temperatures > 800 °C. We can estimate the minimum width from the 1/T curve in figure 4. By extrapolation, the peak width after annealing at the melting temperature of a-Si, 1185 °C is found to be 33.5 cm^{-1}. This suggest that further annealing above 800 °C only results in an additional narrowing of the peak width of at most 1.5 cm^{-1}.

Summary and conclusions

We have studied structural relaxation at high temperature of both ion implanted and evaporated a-Si using Raman spectroscopy. The minimum value for the width of the main peak, which is an indicator for the state of relaxation of a-Si, is inversely proportional to the annealing temperature. At higher temperatures, the temperature depedent pseudo saturation level is reached in shorter times.

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