Comparison of structural changes in amorphous silicon induced by thermal and cw laser annealing

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Abstract

Thermal and photo-induced annealing was performed on different samples of amorphous silicon. The structural changes were monitored by Raman spectroscopy by means of the frequency shift and change in width of the TO-like phonon band of a-Si. While thermal annealing leads to the expected increase of structural order with temperature, photo-induced annealing shows anomalous behaviour: an increase of disorder with light soaking. This effect is discussed in terms of structural rearrangements of atoms caused by photo-induced electronic transitions. © 1997 Elsevier Science B.V.

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1. Introduction

Many experiments demonstrate a close connection between the structural and optoelectronic properties of amorphous silicon. Therefore, an understanding of structural changes induced by thermal and/or cw-laser annealing of amorphous silicon is very important for its industrial application. As a result of disorder in amorphous solids, the selection rules in the Raman scattering process break down, allowing all vibrational modes to be Raman active. This enables Raman spectroscopy to be an useful method for monitoring structural changes in annealing processes.

Here, we compare the structural changes in amorphous silicon introduced by cw-laser annealing with those obtained by thermal annealing. Experimental results show that different structural changes are induced in amorphous silicon by these two different annealing methods. While thermal annealing induces structural ordering, cw-laser annealing has the opposite effect, manifested by a decrease of structural order.

2. Experimental

Thin layers of amorphous silicon (a-Si:H and a-Si1.8C0.2:H) were prepared by the magnetron sputtering method described in [1] and by ion bombardment of a pure Si crystalline target (a-Si). Implantation was achieved with two energies of 30Si+ (75 and 150 keV) in order to ensure that the surface layer was completely amorphized from the surface to a depth of 300 nm. Raman spectra were recorded by a DILOR Z-24 triple spectrometer. The excitation light was the
green line, $\lambda = 514.5$ nm, of a Coherent Inova 100 Ar- ion laser. The laser light was focused on an elliptical spot with dimensions of $100 \times 200 \mu$m. The spectra were recorded in the spectral interval of 20–2500 cm$^{-1}$ by photon counting detection. The signal accumulation time was 3 s and the spectral step was 4 cm$^{-1}$. During spectra recording and laser annealing, the samples were evacuated to 0.07 Pa.

In the cw-laser annealing process, the laser power was gradually increased in intervals from 0.1 to 6 W. The exposed time was 10 min plus 50 min during spectrum recording. The laser spot was always focused on the same position of the sample. The mean temperature of the exposed part of the sample was determined from the Stokes/anti-Stokes ratio of the Raman scattering intensity. Thermal annealing was carried out on a sample obtained by ion bombardment in the temperature interval from 150 to 550°C and for 30 min of annealing time. The temperature step was 50°C. For this sample the laser excitation power for Raman scattering was 0.6 W. The Raman spectra were corrected for the spectrometer throughput and the temperature reduced by the boson occupation factor [2].

3. Results and discussion

In Raman spectra, the structural changes of amorphous silicon can be monitored by two parameters: position and width of the TO-like phonon band at $\sim 480$ cm$^{-1}$, $\tilde{\nu}_{TO}$ and $\Gamma_{TO}$ respectively. $\tilde{\nu}_{TO}$ depends on the Si–Si bond length, where longer bonds give a lower energy peak position [3]. $\Gamma_{TO}$ depends on the rms bond-angle distortion $\Delta \Theta$ according to the relation $\Gamma'_\Theta = \Gamma'_0 + a \Delta \Theta$, where $\Gamma'_0 = 32$ cm$^{-1}$ and $\Gamma'_\Theta$ is the bond-width contribution associated with bond angle distortion $\Gamma'_\Theta = a \Delta \Theta$, $a$ being a constant [4]. Tsu [5]

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Fig. 1. Correlation of $\tilde{\nu}_{TO}$ and $\Gamma_{\Theta}$ for thermally annealed a-Si (●) and a-Si:H (∆) with different hydrogen concentrations.
has found a correlation between $\tilde{\nu}_{TO}$ and $\Gamma_\Theta$ expressed by 
$$\tilde{\nu}_{TO} = \tilde{\nu}_0 + k\Gamma_\Theta^2$$ 
where $\tilde{\nu}_0$ and $k$ are constants.

As shown in Fig. 1, in the thermally annealing process $\tilde{\nu}_{TO}$ increases and $\Gamma_\Theta^2$ decreases with increase of temperature. These changes are characteristic of structural relaxation of an amorphous network [6]. Similar behaviour is observed for the samples with different hydrogen concentrations [1]. Since hydrogen relaxes the strain in an amorphous network, one expects structural ordering also with an increase of hydrogen content [1]. We also observed this effect (Fig. 1) on samples with hydrogen content between 9% and 15% obtained under the same deposited conditions. The dashed line in Fig. 1 was proposed by Tsu for a-Si:H films deposited by sputtering. The solid lines were drawn by means of linear regression on our experimental data. The shift of our lines from Tsu's value [5] could be due to different deposition conditions such as substrate temperature, content of working gas in the magnetron chamber, etc.

Fig. 2 shows changes in $\tilde{\nu}_{TO}$ and $\Gamma_\Theta^2$ induced by laser annealing. The arrow indicates the direction of increasing laser power. The thermal contribution caused by laser heating was subtracted from the data presented. The mean temperature of the exposed part of the sample was calculated by the ratio of Stokes to anti-Stokes Raman scattering intensity. The temperature range was between 150 and 700°C, similar to the temperature range for thermal annealing. The decrease of $\tilde{\nu}_{TO}$ and increase of $\Gamma_\Theta$ during laser illumination, shown in Fig. 2, shows that cw-laser annealing produces an increase of disorder in the amorphous silicon network. We assume that changes of observed parameters cannot be explained by thermal expansion because this produces a compressive stress on the illuminated spot and the effect is known to cause a $\tilde{\nu}_{TO}$ shift in the opposite direction (blue shift) [3].

Fig. 2. Correlation of $\tilde{\nu}_{TO}$ and $\Gamma_\Theta^2$ for cw-laser annealed samples: a-Si (□), a-Si:H (●), a-Si$_{0.5}$C$_{0.2}$H (○).
The dashed line represents experimental results provided by Tsu for molecular beam deposited a-Si. This line is parallel to those obtained by linear regression on our sets of data (full lines in Fig. 2), so one can conclude that the structural disorder created in all laser-annealed samples has a similar character to that in a-Si obtained by molecular beam deposition.

The following processes may be responsible for the photo-induced structural disordering of amorphous silicon:

1. With absorption of laser light, more electrons are excited to the conduction band, causing changes in the Si–Si bond strength. The resulting decrease of this bond strength causes lower $\tilde{v}_{TO}$ and larger bond angle distortion [3].

2. The structure of covalent amorphous silicon was shown to exhibit various possible metastable states [7]. According to a model proposed by Abdulhalim et al. [7], energy absorbed in amorphous silicon produces hot mobile electrons. These electrons can interact with single atoms or with groups of atoms, causing structural rearrangement that can be considered as transitions between different metastable states. Within this model, our results would imply that the hot electrons pump material from one to another, more disordered, metastable state.

From the present results, the second mechanism seems more probable since compressive stress would not allow the expansion of Si–Si bonds as assumed in the first model. For more direct verification, experiments are planned in which laser treatment and measurements will be performed at series of high temperatures, which will enable direct comparison of thermal and optical effects.

4. Conclusion

We have carried out thermal and photo-induced annealing of amorphous silicon. While thermal annealing leads to the expected increase of structural order with temperature, photo-induced annealing shows an anomalous behaviour, namely an increase of disorder during light soaking. This effect has been discussed as being the result of structural rearrangements of atoms caused by electronic transitions.

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References