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Structural relaxation of amorphous silicon during thermal and CW laser annealing

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Abstract

Different amorphous silicon thin films were prepared by high energy ion bombardment of crystalline silicon (a-Si) and by magnetron sputtering deposition (a-Si:H and a-$Si_{1-x}C_x$:H). All samples were laser annealed and a-Si sample was thermally annealed. Structural changes were monitored by bandwidth and position of transverse optical (TO)-like vibrational band in Raman spectrum of amorphous silicon. They were compared with changes of broad background signal, recently interpreted as 'boson peak'. Correlation of structural and boson peak changes was explained by a fractal model.

Keywords: Amorphous silicon; Boson peak; Fractal model

1. Introduction

Amorphous silicon, studied in recent years, still has a structure and properties that are not yet fully understood. The amorphous silicon belongs to the class of tetrahedral amorphous semiconductors (TAS) that differs from other amorphous and glassy solids. For example, contrary to other disordered solids, the structure and the vibrational density of states (VDOS) of TAS are well explained in the frame of a continuous random network (CRN) model. Also, the boson peak, a general property that appears in the vibrational spectra of other disordered solids, is not observed in TAS.

Recently, we have shown that, in addition to the transversal acoustical (TA), transversal optical (TO), longitudinal acoustical (LA) and longitudinal optical (LO) phonon-like vibrational bands that are well described by the CRN model, a broad background signal (BBS) exists in Raman spectra of a-Si:H and a-GaAs [1–7]. Since the spectral shape, boson-like character, depolarization ratio, etc., of this signal is similar to the boson peak in other disordered solids, we have suggested that it corresponds to the boson peak in TAS. There are several different explanations of the boson peak nature: blobs or cohesive domains with disorder in force constants [8], clusters [9], fractals [10], but none of them succeeds in explaining all features. We have used the fractal model to explain the boson peak in Raman spectra of a-Si, a-GaAs and a-Si_xC_{1-x}:H. The unusual high frequency tail of the boson peak that extends to ~ 2000 cm^{-1} in a-Si:H and to ~ 1000 cm^{-1} in a-GaAs is in accordance with the fractal model where the boson peak is interpreted in terms of

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strained nanometer blobs or clusters of host atoms whose overcoordination is relaxed through bond percolation (for more details see Ref. [1]). For the frequencies above these values, the information about the boson peak is undetermined due to contribution from a luminescence and a constant electronic background scattering. Another interpretation of the BBS is by the model of multiphonon Raman scattering [11], but our recent results on a-Si_xC_{1-x}:H and on high energy ion implanted GaAs [4–6] show the systematic behavior of the BBS that is in accordance with the model of strained nanometer regions embedded in the continuous random network. Following this line, here we present the investigation of the broad background signal in dependence on thermal and CW laser annealing. We apply the fractal model to fit the spectral form of the boson peak and to interpret the boson peak by strained nanometer blobs (domains) embedded in the continuous random network.

2. Experiment

Amorphous silicon thin layers (a-Si:H and a-$Si_{0.8}C_{0.2}$:H) were prepared by the magnetron sputtering method and by ion bombardment of a pure Si crystalline target (a-Si). Raman spectra were recorded by a triple spectrometer (DILOR Z-24). The excitation light $\lambda = 514.5$ nm of a Ar-ion laser (COHERENT INOVA 100) was used. The laser light was focused on an elliptical spot with dimensions of 100×200 μm. The spectra were recorded in the spectral interval of 20 to 2500 cm^{-1} by photon counting detection. The signal accumulation time was 3 s and the spectral step was 4 cm^{-1}. During thermal and laser annealing and spectra recording, the samples were evacuated to 0.07 Pa.

In cw-laser annealing process, the laser power was gradually increased in an interval from 0.1 to 6 W. The exposure time was 10 min with 50 min during the spectrum recording. The laser spot was always 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 performed on a sample obtained by ion bombardment in the temperature interval from 150 to 600°C and 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 temperature reduced by the boson occupation factor [7].

3. Results

In our experiment, we induced structural changes in amorphous silicon samples with thermal and laser annealing. To analyze structural changes during annealing of the samples, we fitted a theoretical curve consisting of four Gaussians, representing the TO, TA, LO and LA vibrational bands, and a boson peak

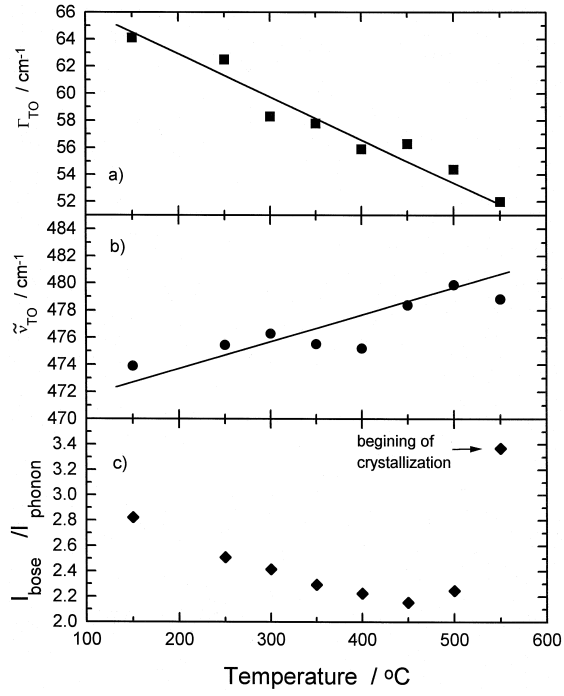

Fig. 1. Temperature dependent changes of (a) TO bandwidth Γ_{TO}, (b) TO peak position ν_{TO} and (c) ratio of boson peak integral intensity and integral intensity of all amorphous bands (TA, LA, LO, TO) for thermally annealed sample (a-Si). Straight lines were added as a visual aid.

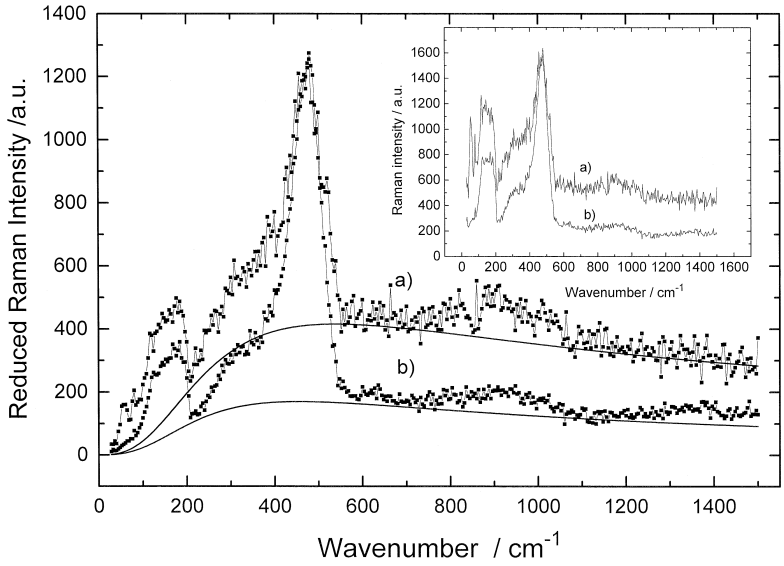

Fig. 2. Raman spectra and boson peak for thermally annealed sample: (a) at 150°C and (b) at 450°C. Insert shows Raman spectra before reduction by the boson occupation factor.

in the reduced Raman spectrum. The boson peak is, according to the fractal model, given by equation:

$$I^{\mathrm{R}} = A\tilde{\nu}^3\left(\tilde{\nu}^2 + \tilde{\nu}_{\mathrm{col}}^2\right)\left[\frac{\tilde{d}}{D}(\sigma + d - D) - \frac{5}{2}\right], \qquad (1)$$

where A is amplitude, $\tilde{\nu}_{\mathrm{col}}$ is the crossover wavenumber from the phonon to fracton scattering regime, $\tilde{d}$ the spectral dimension, D fractal dimension, d space dimension, and σ the scaling index describing the modulation of density in the embedding space by vibration [12]. The fitting results are shown in Figs. 1 and 3.

In Fig. 1a, we plotted changes of the TO vibrational band width in dependence of annealing temperature. It is obvious that the TO vibrational band becomes narrower as the annealing temperature was raised. At the same time, the peak position $\tilde{\nu}_{\mathrm{TO}}$ is moving to the higher wave numbers (Fig. 1b). These changes are characteristic for structural relaxation of an amorphous network [13]. Stolk et al. [14] showed, by measuring carrier life time τ, that it is possible to relate the concentration of defects in a-Si to the change of dihedral bond angle $\Delta\Theta$. The change of dihedral bond angle is related to TO bandwidth Γ_{TO}

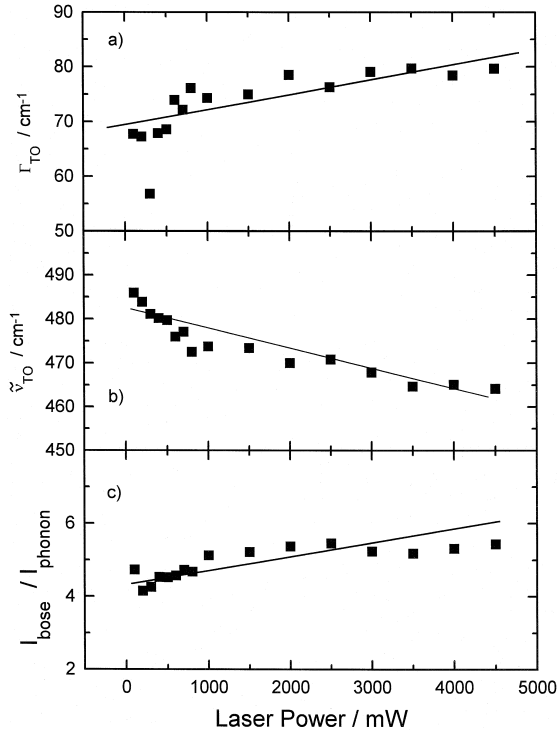

Fig. 3. Laser power dependence of (a) TO bandwidth Γ_{TO}, (b) TO peak position ν_{TO} and (c) ratio of boson peak integral intensity and integral intensity of all amorphous bands (TA, LA, LO, TO) for cw laser annealed sample (a-$Si_{1-x}C_x$:H). Straight lines were added as a visual aid.

by the equation: $\Gamma_{\mathrm{TO}}^2 = \Gamma_o + c\Delta\Theta^2$. If the concentration of defects is changed by a factor 10 during the relaxation of the a-Si, the Γ_{TO} will be decreased by about 10 cm^{-1} (see Ref. [14]). In our experiment the change of Γ_{TO} during the relaxation of the sample was about 12 cm^{-1} so we can also expect decrease in the defect concentration for at least a factor of 10.

In Fig. 1c, we plotted the ratio $(I_{\mathrm{bose}}/I_{\mathrm{phonon}})$ of integral intensity of the boson peak to the integral intensity of all amorphous phase bands (TO, TA, LO, LA) in dependence on annealing temperature. We can see that the relative intensity of the boson peak is decreasing as the sample is relaxing. Change of the boson peak in the Raman spectra during thermal annealing is presented in Fig. 2.

Experimental results for the laser-annealed a-$Si_{1-x}C_x$:H sample, corrected for the temperature effects and plotted in Fig. 3, show the opposite behavior than the thermally annealed sample. The increase of Γ_{TO} and decrease of $\tilde{\nu}_{\mathrm{TO}}$, shown in Fig. 3a and b, respectively, during laser illumination shows that cw laser annealing produces an increase of disorder in the amorphous silicon network. From the increase of Γ_{TO}, we can assume, according to Stolk et al. [14], that the number of point defects increased. The decrease of $\tilde{\nu}_{\mathrm{TO}}$ shows the increase of strain in the sample.

4. Discussion

The sample used in the thermal annealing experiment was obtained by amorphisation of a crystalline silicon (c-Si) wafer with high-energy (Si^+) ion bombardment. The amorphous layer is generated when the concentration of point defects, interstitials and vacancies, implanted by the high energy ions, reach critical concentration [13]. The resulting structure agrees with the continuous random network (CRN) model for a-Si[10]. Simple point defects, like single vacancies and interstitials or small clusters of defects, can easily be imagined in a perfect, fully connected CRN, as in a perfect crystal lattice [13]. The possible existence of stable single vacancies and small vacancy clusters in fourfold covalently bonded CRN has been predicted from calculations based on the Keating potential [15]. Experiments showed that the main mechanism for structural relaxation of a-Si is the annihilation of point defects, and the fact that the density of a-Si remains unchanged upon relaxation suggests mutual annihilation of low and high density defects [13]. The simplest example of such a process is vacancy-interstitial recombination.

In the fractal model, the origin of the boson peak in amorphous material is discussed in terms of strained nanometer clusters inside the overconstrained amorphous network. Amorphous solids are considered overconstrained when the average coordination number $\langle r \rangle$ exceeds $r_{\mathrm{p}} \approx 2.4$. The network then consists of floppy and rigid regions. In these rigid regions, there is a large gradient of strain from the surface towards the center of the cluster. This behavior is expected for a self-similar fractal connectivity. Thus, the assumption of the fractal model is that overconstrained amorphous solids relax through bond percolation of nanometer-sized fractal blobs [1].

In recent experiments [4–6], it was discovered that the intensity of the boson peak is dependent on the disorder level inside amorphous material, as determined by Rutherford backscattering (RBS). Independent of whether disorder is increased by higher dose, higher dose rate, or lower implant T, the boson peak will increase faster than bands characteristic of the amorphous phase [1,4–6]. Also, the intensity of the boson peak increased as the concentration of carbon atoms in the a-Si sample increased [1]. For concentrations to 30 at.%, carbon incorporation is mainly substitutional [16]. Due to its ionic diameter, a C atom, placed substitutionally, causes a local strain and deformation of the network. In the frame of the fractal model, we expect a nucleation of fractal blobs at locations of carbon bonding. The fact that the boson peak increases faster than the amorphous phase in those experiments confirms the hypothesis of amorphous solids being composites of amorphous and fractal phase [1,4–6].

As we showed above, the relaxation is connected with the concentration of point defects, so we can assume that the intensity of the boson peak is connected with the concentration of point defects. Comparing our results with similar results for samples with different carbon concentration [1], we assumed that the number of nanometer fractal blobs is dependent on point-defect concentration and, in our case,

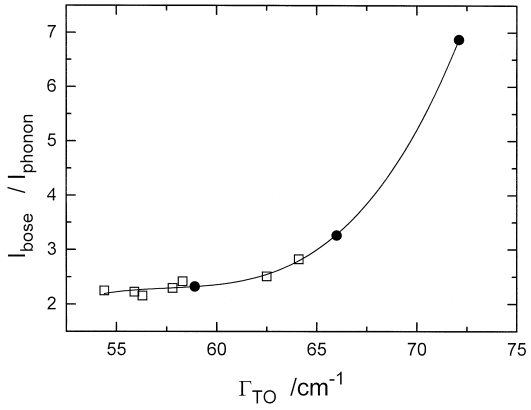

Fig. 4. Correlation between Γ_{TO} and I_{bose}/I_{phonon} ratio for thermally annealed samples (hallow squares) and a-$Si_{1-x}C_x$:H samples with different carbon concentrations (full circles). The curve was added as a visual aid.

their nucleation begins around point defects. With relaxation of the material, the number of point defects and relative intensity of the boson peak decrease.

Correlation between Γ_{TO} and the I_{bose}/I_{phonon} ratio, shown in Fig. 4 supports our conclusion. For thermally annealed samples (hollow squares) and for a-$Si_{1-x}C_x$:H samples with different carbon concentrations from another experiment [1] (full circles) the relative intensity of the boson peak increases as Γ_{TO} increases.

The increase of the boson peak for annealing temperature of 550°C (Fig. 1c) can be explained with the beginning of crystallization. The sample was completely crystallized at temperature of 600°C, so it is reasonable to assume that at 550°C a small concentration of crystals is already formed inside the a-Si layer. Crystalline silicon has a smaller volume than the surrounding amorphous silicon [13], and that generates local strain in the amorphous matrix. These points could be, similar to point defects, nucleation centers for new nanometer-sized fractal blobs. This hypothesis has to be confirmed with further experiments.

We showed in Figs. 1 and 3 that amorphous silicon responds differently to thermal and laser annealing. While thermal annealing causes relaxation, laser annealed samples do not relax as expected for increased disorder and internal strain, the $\tilde{\nu}_{TO}$ increases while Γ_{TO} decreases. Photo-induced disorder could be caused by change in the point-defect concentration, probably due to transitions between different metastable states or by increase of Si–Si bond length caused by electron excitations [17,18]. At the same time, the relative boson peak intensity increased with applied laser power (Fig. 3c). The behavior of the boson peak confirms the hypothesis that the generation of the nanometer fractal blobs is connected with relaxation of local strain caused by point defects. Similar behavior during laser annealing is observed in an a-Si:H sample.

5. Conclusion

We showed that a connection between structural changes and boson peak intensity can be established. We inferred that the boson peak intensity is connected with the concentration of point defects inside the amorphous matrix. In addition, we showed that the fractal model is a good alternative for explanation of the origin of the boson peak in our samples. We found that besides the expected behavior of increased structural order by thermal annealing, the photo-induced process increased disorder.

Acknowledgements

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