Optical-absorption study of structural relaxation of ion-implanted *a*-Si

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The structural relaxation process occurring in ion-implanted *a*-Si is investigated through optical-absorption measurements. The strain reduction associated with the relaxation process leads to an increase in the band gap of the material and to sharpening of the band edge. Changes occurring in the sub-gap region of the absorption spectra point in the previously suggested direction of point-defect annihilation being associated with the relaxation phenomenon.

The structure of amorphous Si (*a*-Si) is generally considered to be a continuous random network with the Si atoms being fourfold coordinated and covalently bonded.[1] The change occurring in its physical properties upon annealing, referred to as "structural relaxation," has been viewed as a process to which every atom in the network contributes, giving rise to continuous variations of the average network parameters, such as the average tetrahedral bond-angle distortion. In the case of *a*-Si produced via a highly nonequilibrium process, such as ion implantation, it can be expected that the network contains a large number of structural defects, similar to the ones observed in ion-implanted crystalline Si. This has been confirmed by the presence of vacancies and vacancy-impurity complexes in ion-implanted *a*-Si, detected by Mössbauer spectroscopy.[2] In this frame it is reasonable to expect that structural relaxation in such material could also be related to the process of defects annihilation which, in turn, would lead to concommitant bond-angle rearrangement and, therefore, to a variation of the average strain in the material.

The investigation of the above-mentioned aspects has drawn considerable interest around the structural-relaxation process in ion-implanted *a*-Si as shown by the extensive experimental work recently carried out by a variety of techniques which, besides Mössbauer spectroscopy, included Raman spectroscopy,[3,4] infrared reflectivity,[5] x-ray diffraction,[6] calorimetry,[4,7,8] electrical measurements,[9,10] and metal diffusion.[11] They have provided strong indications that, in ion-implanted *a*-Si, structural relaxation is intimately related to mutual annihilation of point defects and point-defect complexes,[4,11] with consequent reduction of the average tetrahedral bond-angle distortion in the material.[4,2] A technique that is sensitive both to the average strain in the material and to the presence of point defects is the one based on optical-absorption measurements. In the sub-gap region of semiconductors, in fact, the absorption depends on the presence of defects and it has been widely used for investigation in *a*-Si:H (Refs. 12 and 13) as well as in ion-implanted semiconductors.[14,15] In the region at and above the fundamental band-edge region, on the other hand, the exponential band tail and optical band gap depend on the average strain in the material as observed in *a*-Si:H.[16] In this paper we, therefore, present a study of the structural-relaxation process in ion-implanted *a*-Si performed by optical-absorption measurements carried out from energies greater than the band gap down to energies well within the sub-gap region, in order to provide further elements as to the mechanisms occurring during the process. The results we have obtained also point in the direction of the relaxation process being associated with point-defect evolution and annihilation accompanied by strain reduction in the material.

The optical-absorption spectra of ion-implanted *a*-Si we report start at about 2.5 eV and range down to 0.48 eV, an energy far into the sub-gap region of *a*-Si. This has been accomplished thanks to photothermal deflection spectroscopy (PDS),[12] a highly sensitive technique which enables detection of low levels of absorption, typical of the sub-gap spectral region of semiconductors, even in layers as thin as the ion-implanted ones. In order to also obtain absorption data in the spectral region above the fundamental band edge, measurements have been performed on 800-nm-thick Si on sapphire samples which were single crystalline before implantation. The versus (vs) wavelength interference oscillations effect has been eliminated according to a procedure, based on simultaneous transmission and PDS measurements,[17] which does not require a detailed knowledge of the wavelength dependence of the refractive index. Absolute absorption values were obtained by normalizing the PDS spectra with respect to values obtained in the spectral region where the samples were optically opaque.[18] The samples were implanted at 80 K with Si ions with a total dose 8.4×10^{14} cm^{-2} at 150 and 300 keV (dose ratio 0.4:1, respectively) so as to obtain a 500-nm fairly uniform amorphous film. The implanted film depth distribution of damage was verified by Rutherford backscattering measurements (not shown) and the amorphous structure of the films was detected and monitored after each annealing by reflection high-energy electron diffraction (not shown).

Figure 1 shows the spectra relative to the as-implanted sample and to the sample after having undergone 15-min

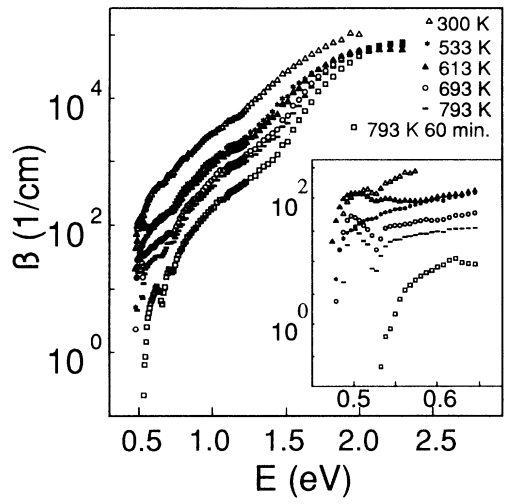

FIG. 1. Absorption spectra of ion-implanted a-Si annealed successively under increasing temperatures and durations. Details of the low-energy region are shown in the inset.

isochronal heat treatments, subsequently carried out at increasing temperatures, up to a maximum value of 793 K. Also shown is the spectrum relative to an additional annealing at 793 K for 1 h. Annealing for a total of 2 h at 793 K did not produce any further changes in the spectrum which is, therefore, not reported. We note that, with the progressive increase in heat treatment, the absorption values decrease all over the investigated spectral region, while the absorption edge progressively shifts to larger energies and sharpens, as shown in greater detail in Figs. 2 and 3 where the changes in the band-edge slopes and in the Tauc plots are reported, respectively. In Fig. 2 the lines correspond to the exponential fits carried out in the band-edge regions of the spectra. The structural-relaxation phenomenon thus leads to a continuous increase in the optical gap E_G of the material and to a decrease in the inverse logarithmic slope E_0 which characterizes the band-edge exponential dependence of the absorption coefficient $[\beta=\beta_0 \exp(E/E_0)]$. The vs temperature and time evolutions of the two parameters are reported in Fig. 4 which shows that the 1-h annealing at 793 K leads to a saturation of their values.

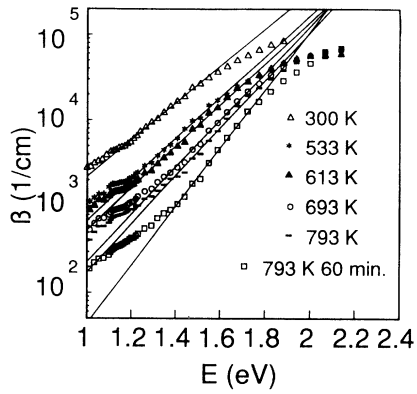

FIG. 3. Tauc plots (see text) of data of Fig. 1.

The progressive sharpening of the band edge, which is observed with increasing heat treatments, is to be ascribed to the progressive reduction of strain in the material that is known to affect the exponential absorption edge in semiconductors.[16] A reduction in strain, during the structural-relaxation process in ion-implanted a-Si, has in fact been detected by Raman-spectroscopy measurements[3,4] and has also been related to the relaxation enthalpy detected by calorimetric measurements.[4] The progressive increase in E_G is also associated to occurring strain reduction as reported for structural-disorder-associated results in a-Si:H (Ref. 16) where it has been observed that a reduction in thermally or structurally induced disorder in the material also leads to an increase of E_G and a decrease of E_0. Moreover, the authors find that the observed variations in E_0 and E_G are linearly dependent which, as shown later on, is also the result we find for implanted a-Si. In particular, the authors in Ref. 16 describe both E_0 and E_G in terms of the mean square of the thermally and disorder-induced displacement of the atoms from their equilibrium positions. They eventually obtain a linear dependence between the two parameters supported by their experimental data and governed by the equation

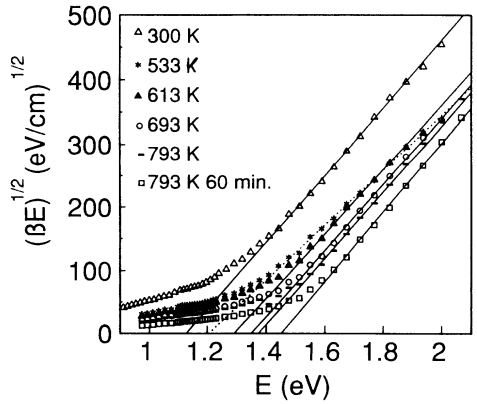

FIG. 2. Exponential fits of the band-edge tails for the data of Fig. 1.

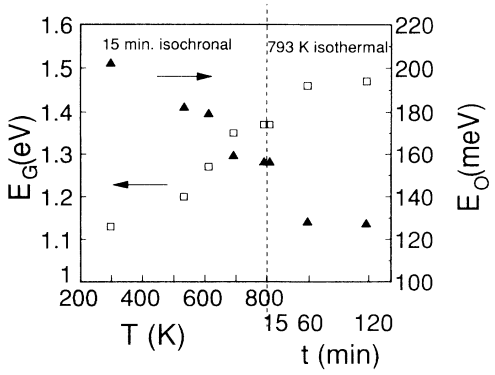

FIG. 4. E_G and E_0 (see text) as a function of annealing conditions for implanted a-Si.

$$E_G(T,X)=E_G(0,0)-\langle U^2\rangle_0 D\left[\frac{E_0(T,X)}{E_0(0,0)}-1\right],$$

where T is the temperature, X is a parameter describing structural disorder, $\langle U^2\rangle_0$ is the mean square of the zero-point uncertainty in the atomic position, and D is a second-order deformation potential. A linear fit to their E_G vs E_0 data yielded a slope of ~ 6.2 and, by using a value 0.08 Å for $\langle U^2\rangle_0^{1/2}$ and of 17 meV for $E_0(0,0)$ (Ref. 16) the authors finally obtain $D=16$ eV/Å^2 (Ref. 19) a value of the same order of magnitude as similar deformation potential obtained in crystalline Ge (4–5 eV/Å^2) (Ref. 20) which confirms the validity of their approach. Finally, a value of 2.0 eV was obtained for $E_G(0,0)$ which should represent the upper limit for the band gap of a-SiH$_x$ family of materials.

In Fig. 5, we report the E_G vs E_0 plot we obtain in the case of ion-implanted a-Si. The results clearly indicate a linear dependence between the parameters even in the case of implanted a-Si and the value of the slope of the linear fit curve, 4.5, yields $D=13$ eV/Å^2 which is close to the one reported for a-Si:H. Even the value we obtain for $E_G(0,0)$, 1.9 eV, is consistent with the a-Si:H value. The strain dependence behavior of both E_0 and E_G we find in implanted a-Si is, therefore, in close agreement with the results reported for a-Si:H. It should nevertheless be mentioned that both the as-implanted value (1.15 eV) and the annealing dependence we obtain for E_G is in strong contradiction with other results reported for ion-implanted a-Si films[21] where an annealing independent value of 1.4–1.5 eV was reported. However, some indetermination may arise in such a case due to the fact that, unlike the present case, elimination of the vs. wavelength interference oscillations from the transmission spectra should involve a regression procedure which requires a detailed knowledge of the wavelength dependence of the refractive index.[22] As a matter of fact, the results we obtain concerning E_G are also similar to the ones reported during structural relaxation of a-Si films obtained by vacuum evaporation on a substrate at room temperature and then annealed for 2 h at 773 K.[23] Upon annealing, E_G changed from 1.26 to about 1.5 eV, a value that is very close to the one we obtain for the fully relaxed implanted a-Si (1.46 eV). The similarity in the strain associated behaviors of E_G during the structural relaxation of a-Si films obtained by implantation and by evaporation is consistent with the similarity that is also observed in the results of calorimetric measurements performed during the relaxation of such kinds of films,[4] bearing in mind that, as stated earlier on, the calorimetric results have also been related to the strain reduction in the films. The results we have obtained at and above the band-edge region of ion-implanted a-Si thus confirm the occurrence of strain reduction during the structural-relaxation process.

Regarding the sub-gap region of the spectra, as mentioned earlier on, the absorption in such a region depends on the defects present in the material. In a-Si:H the excess sub-gap absorption with respect to the exponential band tail, β_{ex}, has enabled the determination of the absolute concentration of dangling bonds over a range of three orders of magnitude.[12] According to an optical sum rule such concentration is proportional to the integral of β_{ex} over the sub-gap energy region and $\beta_{ex}=\beta-\beta_0\exp(E/E_0)$. We have performed such integrals for the as-implanted and the fully relaxed samples using the β_0 and E_0 obtained earlier on through a fit of the absorption data in the respective band-edge regions. We have found a reduction of nearly a factor of 5 in the integral calculated for the fully relaxed sample with respect to the one relative to the as-implanted sample. The reduction is, therefore, greater than the factor of 2 reported for the decrease in concentration of dangling bonds alone in relaxed ion-implanted a-Si as determined by electron paramagnetic resonance[4,5] and almost the same as the one reported for the reduction of point-defects concentration in relaxed material (a factor of ~ 5) as determined by metal diffusion and solubility measurements.[4,11] The results we have obtained, therefore, point in the same direction as earlier suggestions, that is, that the structural-relaxation process in ion-implanted a-Si is accompanied by point-defect annihilation. In this respect it is also interesting to point out that some peak structures appear in the sub-gap absorption spectra near 0.5 eV (see inset of Fig. 1) at the annealing temperature of 613 K, gradually decrease for larger temperatures, and are no longer detectable when the sample becomes fully relaxed. Such an evolution may be compatible with the formation of some secondary defect complexes during the intermediate stages of the relaxation process. The determination of the nature of such eventual complexes requires further investigations.

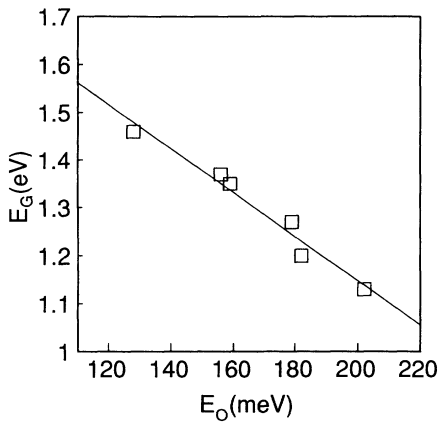

FIG. 5. E_G vs E_0 plot for annealed implanted a-Si.

In conclusion, we have presented an optical-absorption study of the structural-relaxation process in ion-implanted a-Si. It has been observed that, in agreement with earlier observations, the relaxation process is associated with strain reduction in the material that has led to a progressive sharpening of the band edge and an increase of the optical gap of the material until a value of ~ 1.5 eV is reached, consistent with values obtained in relaxed evaporated a-Si and in hydrogenated a-Si. Moreover, changes occurring upon relaxation of the material

in the sub-gap region of the spectra are consistent with earlier evidence that the relaxation process is accompanied by point defects and point-defect complexes evolution and annihilation.

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