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Synchrotron topographic and photoluminescence investigations of porous layer in HT - HP treated silicon implanted with deuterium ions

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The 001 oriented Cz-Si samples were implanted at room temperature with 200 keV deuterium ions to the dose 1.7×10^{17} cm^{-2} and treated at up to 950 °C under hydrostatic Ar pressure (HP) up to 11 kbar for up to 10 h. The sample properties were studied by means of monochromatic synchrotron X-ray diffraction topography as well as by rocking curve (RC) and photoluminescence (PL) measurements. The thermal annealing caused rapid disappearance of interference effects in RCs and topographs. This process was significantly moderated by HP providing the layers with spongy like structure owing the presence of deuterium - filled inclusions. In the last case the most significant contribution of the PL peaks attributed to dislocations was observed.

1 Introduction

It is well established that implantation of silicon with high doses of gaseous elements can lead, in effect of annealing at sufficiently high temperature (HT), to the formation of gaseous inclusions of nanometric dimensions forming a porous - like structure. This process is to some extent parallel to the process of exfoliation of the shot-through layer and its mechanism is still not well known. The formation of gaseous agglomerate is usually activated by thermal annealing and can be significantly modified by applied high hydrostatic pressure (HP).

In the present work we studied HT-HP treated Czochralski grown silicon (Cz-Si) implanted with 200 keV deuterium ions (Si:D) at room temperature to a dose 1.7×10^{17} cm^{-2}. The samples were examined with monochromatic beam and white beam topography realized with the use of synchrotron source of X-Ray radiation as well as by photoluminescence (PL) spectroscopy. The transmission electron microscopic (TEM) studies were also performed for some samples. Some former results for analogously treated samples were reported elsewhere [1].

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2 Experimental

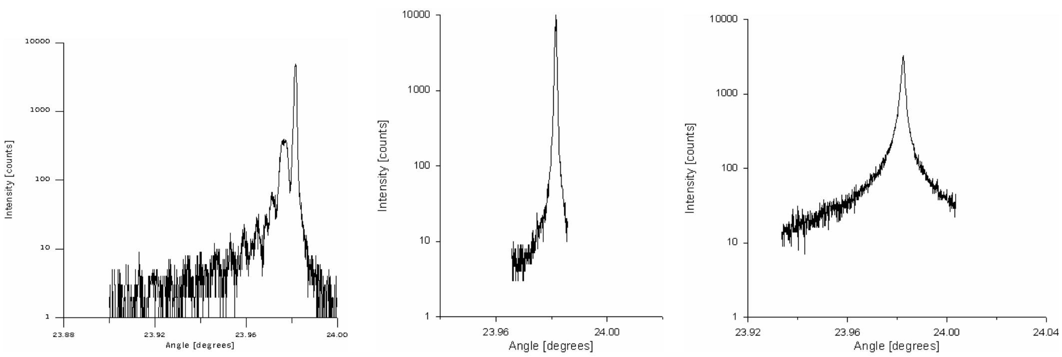
In the present work we studied silicon implanted with 200 keV deuterium ions at room temperature to a dose 1.7x10^{17} /cm^2 provided by the Institute of Physics RAS in Novosibirsk. The Si:D samples were studied just after D$^+$ implantation and after thermal annealing for up to 10 h at 450 °C, 650 °C and 950 °C under 1 bar and under HP = 11 kbar exerted by ambient argon atmosphere.

The samples were examined in HASYLAB at the monochromatic beam station E2 by taking rocking curves and plane wave topographs in symmetrical 400 reflection of the wavelength of 0.115 nm selected by piezoelectronically stabilized monochromator with two silicon crystals. The rocking curves were recorded with a probe beam limited to a very small size close to 50×50 μm^2 enabling significant reduction of the effects caused by bending of the samples. The TEM studies were additionally performed in selected samples.

The PL spectra were obtained using the 488 nm Ar laser line. The emission from a sample was analysed by Jobin-Yvon HR460 grating monochromator and detected by Hamamatsu 5509-72 photomultiplier using lock-in technique. Special precautions were taken to obtain highly reproducible PL. To be able to compare the PL intensities from various samples all PL spectra were normalized to the intensity of transverse optical (TO) phonon-assisted free exciton emission (FE$_{TO}$). In respective below presented figures the PL spectra were vertically shifted for clarity. The label e.g. x 0.1 means that the intensity of presented PL spectrum was increased 10 times.

3 Results and discussion

The rocking curves for as implanted samples exhibited a series of characteristic maxima located at low angle side with period increasing for lower angles. The analysis of the rocking curve based on fitting of numerically simulated curves points the existence of the strain minimum located at average ion range and relatively small lattice parameter change in the near-surface shot-through layer. The representative rocking curves for the as implanted state and after two annealing processes at 450 °C under 1 bar and 10.7 kbar are shown, respectively, in Figs. 1 a-c.

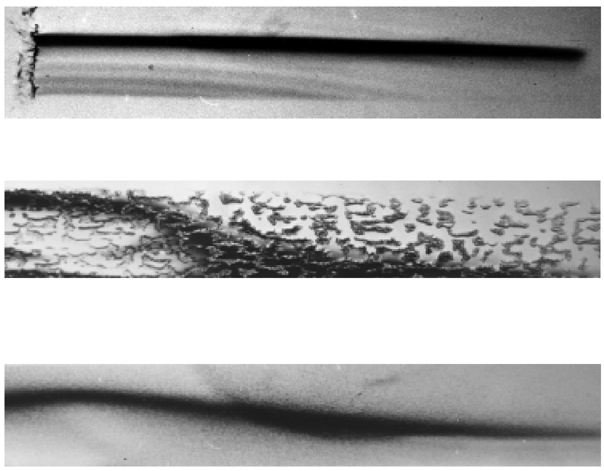


a) b) c)

Fig. 1 The synchrotron RCs of Si samples implanted with 200 keV deuterium ions in 004 reflection of 0.115 nm: a) as-implanted, b) after 1 h annealing at 450 °C under 1 bar, c) after 1 h annealing at 450 °C under HP = 10.7 kbar.

The monochromatic beam topograph of the as implanted sample shown in Fig. 2a reveals, thanks to a considerable bending, the interference fringes corresponding to the fringes in RC shown in Fig. 1a. The topograph of the sample annealed under 1 bar (shown in Fig. 2b) reproduced only fragments of the not exfoliated pieces of the top Si layer. The rocking curves were similar to those of the perfect (non-implanted) silicon. The non-exfoliated fragments were much smaller in the case of treatment at 650 °C than of that one done at 450 °C. The situation was different when the treatment was performed under 10.7 kbar. In this case the topographs revealed “grain like” contrast indicating the presence of small gaseous inclusions (Fig. 2c). The RCs exhibited some tails of enhanced intensity on both sides of the rocking curve.

The representative TEM picture of the sample with the structure similar as for that treated at 920 K – 10.7 kbar for 10 h is presented in Fig. 3.



a.

b.

c.

Fig. 2 The synchrotron plane wave topographs of Si:D samples in 400 reflection of 0.115 nm: a) as-implanted sample; b) the sample after 1 h annealing at 450 °C under 1 bar (the same as in case of Fig. 1b); c) the sample after 1 h annealing at 450 °C under 10.7 kbar (the same as in case of Fig. 1c).

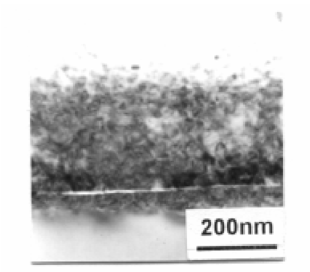
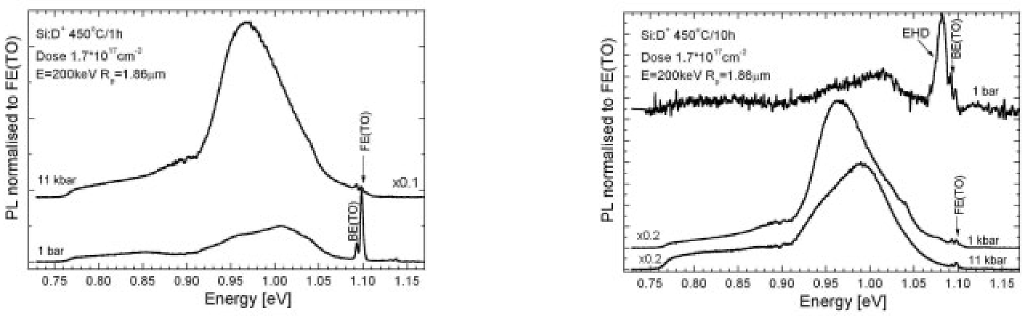


Fig. 3 TEM image of Si:D treated at 920 K – 10.7 kbar for 10 h.

The representative PL spectra of some characteristic samples are shown in Figs. 4 and 5. In these spectra the PL lines at about 1.09 eV are related to the transverse optical (TO) phonon-assisted recombination of bound (BE(TO)) and free (FE(TO)) excitons. Below 1.09 eV some defect-related PL emission is observed.

A broad PL band between 0.5–0.9 eV was already observed after the 1 h treatment in the Si:D samples HT-HP treated at 450 °C. Its large full width at half maximum (FWHM) and asymmetric character suggests that the band is a superposition of a variety of the different levels. Similar band has been observed in He^+ implanted silicon and has been explained as due to He bubbles of large size variety [2]. In Si:D one can also expect that the process of the accumulation of D^+ ions will take place during the HT-HP treatment and that the clusters of different size will be created in the implanted region. In such case the defects related to these clusters should generate a variety of closely separated energetic levels. It will lead to the appearance of a broad PL maximum in the case of defects being the radiative recombination centres. One can notice that the creation of these defects is strongly stimulated under HP. The intensity of the band at around 0.97 eV is about 20 times higher in the sample treated under 11 bar for 1 h than in that one annealed under 1 bar (see Fig. 4a). Lower FWHM of this emission maximum may be interpreted as due to the fact that the sample structure is better ordered with less pronounced diversity in the energy of the levels.

The more prolonged HT-HP treatment (for 10 h) results in a changed character of the PL emission depending on the applied pressure (Fig. 4b). The emission at 1.081 eV is related to multiexciton complex recombination creating so-called condensed phase. The so-called electron-hole droplet (EHD) was detected for the samples treated under atmospheric pressure with a simultaneous significant decrease of the defect-related emission. The EHD emission appears in the PL spectrum at high excitation level, but the role of impurities, defects and dislocations in the creation of this condensed phase of excitons in silicon [3] has been also confirmed. There are two possibilities that can lead to the appearance of the EHD emission. The first one is a creation of a surface layer of silicon separated from the bulk by energetic barrier that limits a diffusion of the exited carriers in the depth of the implanted region. It is equivalent to the higher excitation level in the near surface region and appearing of EHD emission. Still high concentration of the deuterium was indicated by the secondary ion mass spectrometry (SIMS) [1]. The second possibility can be a redistribution (caused by partial out-diffusion) of deuterium through the sample that retards creation of the large dimension defects acting as the radiative recombination centres. In this case the exited carriers can recombine either through the non-radiative transitions or through the exciton recombination processes. At relatively high excitation level the condensed phase of multiexcitons will be created and the EHD emission will be observed in the PL spectrum.



a. b.

Fig. 4 The PL spectra of HT-HP treated Si:D samples treated at 450 °C for a) 1 h and b) 10 h, under 1 bar and HP.

A low intensity of PL signal (low signal to noise ratio - see Fig. 4b) indicates that the non-radiative recombination centres should be really created during treatment under atmospheric pressure.

Prolonged annealing under 11 kbar (10 h) at 650 °C leads to an appearance of the broad PL line at ~ 0.8 eV (Fig. 5) known as the D1 line [4] and related to the presence of dislocations. Its FWHM is relatively wide; it can mean the presence of some disturbances in the dislocation structure leading to some spread of the energy levels related to the dislocations. The creation of the dislocation structure in the implanted region is strongly enhanced in effect of the HT-HP treatment (see Fig. 5). A short time annealing at 650 °C under atmospheric pressure creates a similar structure as described above for the annealing at 450 °C under 1 bar for 10 h.

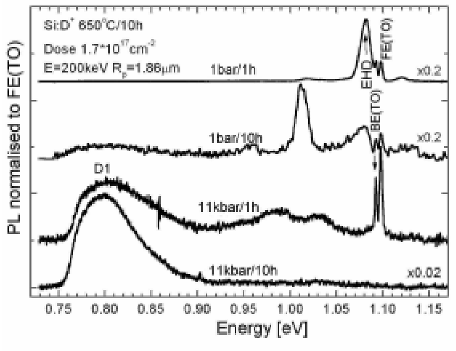


Fig. 5 The PL spectra for Si:D, HT-HP treated at 650 °C.

After prolonged annealing at 450 °C under 1 bar a weak D1 emission and the strong PL band with maximum at 1.01 eV were observed. The FWHM of the 1.01 eV PL band suggests a wide spread of the energy levels related to the defects responsible for this emission. This band overlaps the spectral range, where the emission related to a defect composed of silicon self-interstitials has been reported (the so called W line [5]). Emission at this region has been also assigned to bivacancies [2].

4 Conclusion

Comparing the X-ray diffraction measurements and PL studies it may be noted that the highest intensity of the PL spectra attributed to the dislocation-related lines concerns the samples subjected to the treatment under the highest pressure resulting in retardation of exfoliation and in the creation of spongy like structure (compare TEM results). For annealing at atmospheric pressure we observe much smaller amount of dislocation attributed features, which may also be well explained by extended exfoliation with lost of the considerable part of the top layer, as confirmed by a practical identity of the rocking curves with those observed for the non-implanted silicon.

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