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Investigations on the effect of high pressure on the annealing behavior of oxygen related defects in silicon

C. A. Londos[1], M. S. Potsidi[1], A. Misiuk[2], J. Bak – Misiuk[3], A. Shalimov[3], V. V. Emtsev[4]

[1] University of Athens, Physics Department, Solid State Section, Panepistimiopolis, Zografos, Athens 157 84, Greece, hlontos@cc.uoa.gr

[2] Institute of Electron Technology, Al. Lotnikow 32/46, 02-668 Warsaw, Poland, misiuk@ite.waw.pl

[3] Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 46, 02-668 Warsaw, Poland, bakmi@ifpan.edu.pl

[4] Ioffe Physicotechnical Institute of the Russian Academy of Sciences, Polytechnicheskaya ul. 26 194021 St. Petersburg, Russia, emtsev@pop.ioffe.rsii.ru

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Abstract. Infrared and x-ray studies are reported on the effect of high pressure (HP) treatments on the annealing behavior of oxygen-related defects, particularly the VO defect, formed in neutron-irradiated Cz-Si. Upon annealing at 300 ^{o}C, the VO defect begins to convert to the VO_2 defect. The main purpose of this paper is the study of the effect of pressure on the conversion of the VO to the VO_2 defect. To this end, isothermal treatments of 45 min duration at a time, were performed at temperatures T_1=325 ^{o}C and T_2=350 ^{o}C with and without the application of hydrostatic pressure of 10.5 kbar. The analysis of the IR results indicates that the application of pressure enhances the growth of the VO_2 defect and also the growth of the various V_nO_m complexes, which give rise to satellite bands in the region of the VO band. X-Ray reciprocal space maps and rocking curves received at the end of the annealing sequence reveal the presence of point-like defects, which are more numerous in the stressed samples. These defects could be considered to act as nucleation sites for the oxygen impurity precipitation.

Introduction

The main oxygen-related defect in irradiated Cz-grown Si is the oxygen-vacancy complex, the well-known A-center the neutral charge state of which gives rise to a LVM band at ~ 828 cm^{-1}. Upon annealing at ~300 ^{o}C the defect becomes mobile and being captured by an oxygen interstitial atom it leads to the formation of the VO_2 defect [1] detected in the IR spectra by the 885 cm^{-1} LVM band. Other defects formed at these temperatures are the V_2O, V_2O_2, V_3O_2, giving rise [2] to IR bands at 839, 824, and 833 cm^{-1}, respectively. They are weak bands, which appear in the spectra in the frequency range of the A-center band. For this reason they are called satellite bands.

Pressure dependent optical and electrical measurements have been proved particularly useful [3-6] in providing information for microscopic defect characterization. Furthermore, the annealing behavior of various defects is expected to be affected [7,8] by the application of pressure since the positions of the surrounding atoms change. It is known that in the annealing process of the VO center, more than one mechanisms are involved [9]. Pressure is expected to affect differently each one of the above mechanisms. In that case we hope to be able to discriminate among the various

mechanisms and their particular contributions to the annealing process of the VO center. This is one of the purposes of the present paper. Another purpose is to study the effect of pressure on the formation process of the VO_2 defect and that of the satellite bands of the A-center.

Experimental details

Four Cz-Si samples of 2mm thickness, mechanically polished in both sides, were irradiated with 5 MeV fast neutrons, at a fluence of 10^{17} n/cm^2, at room temperature. Two of the samples, named as S_3 and S_5 were subjected to isothermal heat treatments, of 45 min duration at a time, at the temperature of T_1=325 ^{o}C. The sample S_3 was annealed under high pressure of ~ 10.5 kbar and the sample S_5 under atmospheric pressure (1 bar). The other two samples, named as S_4 and S_8 were subjected to the same procedure but at temperature T_2=350 ^{o}C, the sample S_4 under high pressure and the sample S_8 at atmospheric pressure. After each treatment the IR spectra were taken at room temperature and the intensities of the 828 cm^{-1} and 885 cm^{-1} LVM bands of the VO and the VO_2 defects respectively were recorded with a JASCO-700 IR spectrometer of dispersive kind. X-ray investigations were carried out in the double and triple axis configurations using a high–resolution MRD-PHILIPS diffractometer. Measurements of the FWHM (Full Width at Half Maximum) of the symmetrical 111 and 333 rocking curves as well as reciprocal space mapping (RSM) for the 111 and 333 reflections were performed. Simultaneously, diffuse scattering intensity measurements were made and the sizes of process-induced defects were calculated.

Experimental results and discussion

A. Infrared results

Fig. 1 presents the IR spectra, between 800 and 900 cm^{-1}, after successive anneals of 45 min duration, at T_1=325 ^{o}C under hydrostatic pressure of 10.5 kbars (sample S_3) and at atmospheric pressure (sample S_5). Using Lorentzian profiles, we have also distinguished in the region of A-center band the presence of the previous mentioned satellite bands at 839, 824 and 833 cm^{-1} attributed [2,10] to the V_2O, V_2O_2, V_3O_2 complexes respectively.

Fig. 2 presents the time evolution of all the detected bands, at T_1=325 ^{o}C. By studying the figures, we immediately observe the following: i) the decay of the VO defect is clearly faster under pressure. In a previous preliminary study [11] we have tentatively attributed the phenomenon to the reduction of the energy barrier ΔE associated with the process. The effect of pressure on the pre-exponential factor r_o is found [8] to be negligible for Si and can be neglected. ii) the growth of the VO_2 defect under pressure is much larger than the expected growth from the corresponding decay of the VO defect. This is a strong indication for the activation of additional mechanisms in the production of the VO_2 defect. Actually, besides the usual reaction $VO+O_i \rightarrow VO_2$, considered for the formation of the VO_2 defect, there are also suggestions [12] for the reaction $V+O_2 \rightarrow VO_2$, where the idea of fast diffusing oxygen dimers has been employed. Another mechanism [8] is through the production of additional vacancies during the anneals under pressure. Sources of these vacancies are multivacancy defects, as for example the pentavacancy center, which anneal at this temperature range emitting vacancies. iii) the production of the V_2O defect is more enhanced under pressure especially after the first 45 min anneal. The presence of the V_2O_2 defect is more profound in the spectra under pressure. Fig. 2 shows that the V_2O_2 defect appears after the first anneal under pressure, although in the case of anneal at atmospheric pressure it appears after the second 45 min anneal. The V_3O_2 defect appears only in the sample treated under pressure. Since the formation of all of the above centers requires the presence of vacancies and since their presence is stronger in the sample treated under pressure it can be argued that the mechanism [8] involving the additional production of vacancies is more probable to prevail.

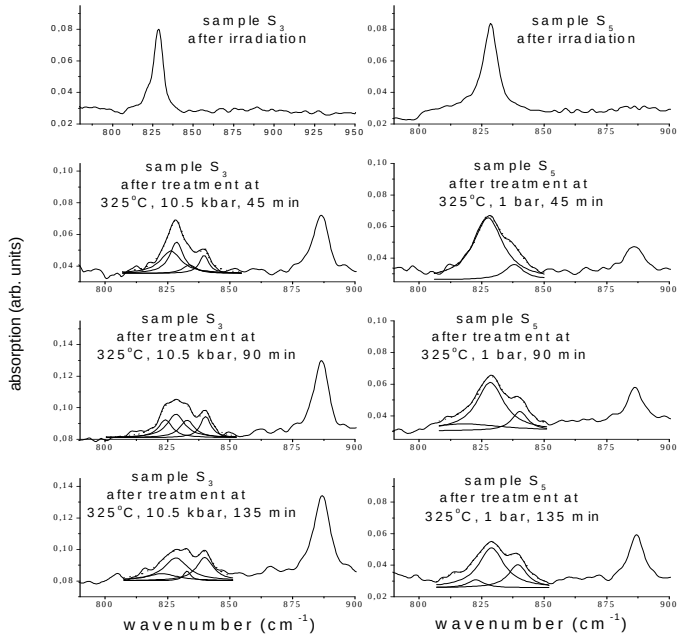

Fig. 1 IR spectra of the samples S_3 and S_5 respectively after successive isothermal anneals of 45 min duration at T_1=325 ^oC.

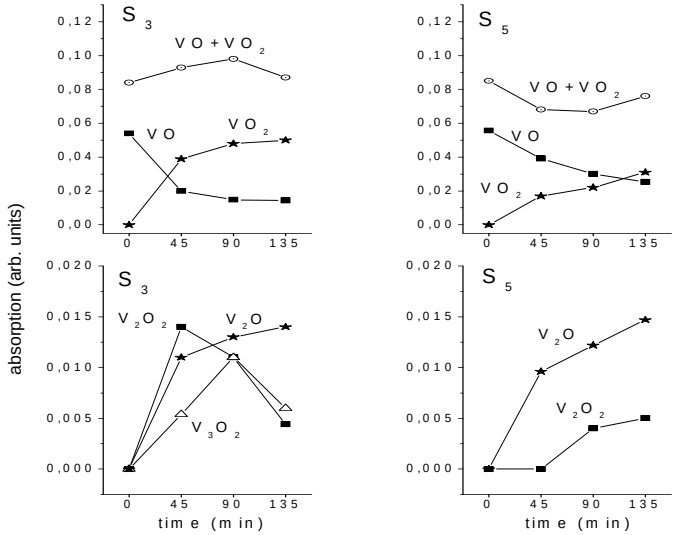

Fig. 2 The evolution with time of the VO, VO_2 and the satellite defects V_2O, V_2O_2 and V_3O_2 for the samples S_3 and S_5 respectively.

Fig. 3 shows the IR spectra, in the same frequency range as that of the Fig. 1, after successive anneals of 45 min duration, at T_2=350 ^oC under hydrostatic pressure of 10.5 kbars (sample S_4) and at atmospheric pressure (sample S_8).

Fig. 4 depicts the time evolution of all the detected bands, at T_2=350 ^oC. Concerning the decay of the VO band and the growth of the VO_2 band, similar observations to those made by studying Fig. 1, hold in this case. Concerning the evolution of V_2O, V_2O_2 and V_3O_2 cm^{-1} bands, the picture seems to be significantly different. All the satellite bands appear after the first 45 min annealing step, both in the sample treated at high pressure and in the sample treated at atmospheric pressure. This means that at this temperature, the effect of pressure on the production of additional vacancies is not so significant as in the case of the anneals at T_1=325 ^oC. In other words, the temperature of

350 ^{o}C, is itself sufficient for the activation of the mechanism of the production of vacancies after the first 45 min anneal.

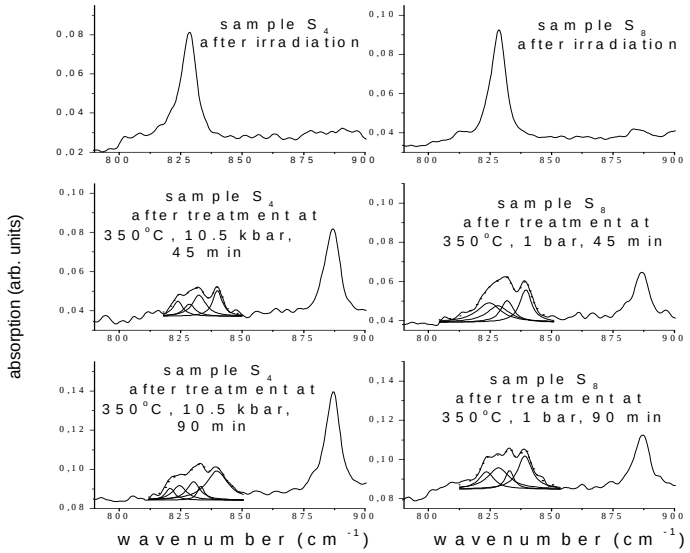

Fig. 3 IR spectra of the samples S_4 and S_8 respectively after successive isothermal anneals of 45 min duration at T_1=350 ^{o}C.

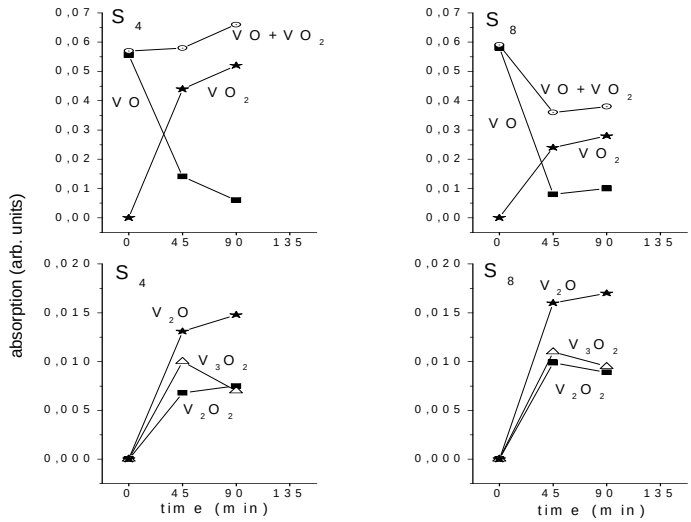

Fig. 4 The evolution with time of the VO, VO_2 and the satellite defects V_2O, V_2O_2 and V_3O_2 for the samples S_4 and S_8 respectively.

B. X-Ray results

The effect of annealing conditions with and without pressure on the diffuse scattering intensity is presented in Fig. 5, depicting the reciprocal space maps of the samples, and Fig. 6 depicting the rocking curves, correspondingly. No changes of the FWHM were found for the investigated samples. However, as it is visible from reciprocal space maps and rocking curves the influence of high pressure on the diffuse scattering intensity depends on the temperature of the treatment. For the lower temperature treatment (325 ^{o}C), high pressure results in an increased diffuse scattering. The opposite is detected for the higher temperature treatment (350 ^{o}C) (see Fig.5 and Fig 6). The effects

observed for the 333 reflections are the same as for the 111 reflections.

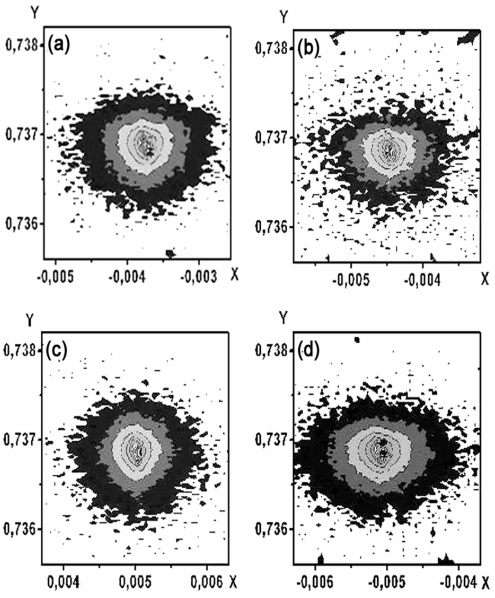

Fig. 5 333 reciprocal space maps of the S_3 - (a), S_5 - (b), S_4 - (c) and S_8 - (d) samples. The axes are marked in λ/2d units (λ - wavelength, d – interplanar distance).

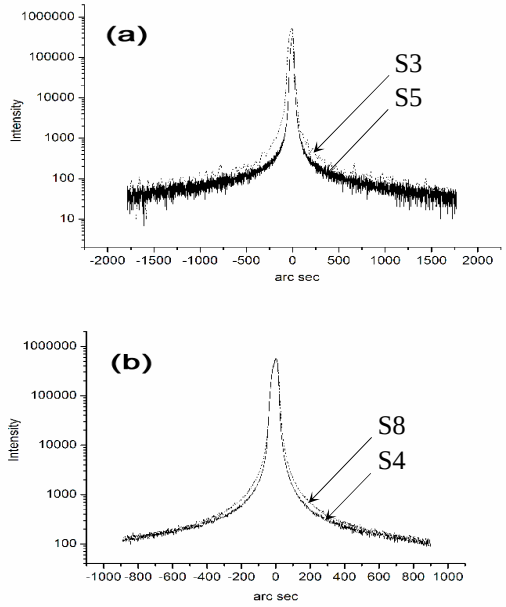

Fig. 6 333 Rocking curves of samples annealed under high pressure (S_3, S_4) as compared with those from the samples annealed at atmospheric pressure (S_5, S_8).

X-ray diffuse scattering has been observed in the investigated Cz-Si crystals due to the presence of treatment-induced defects. It is known that diffuse scattering observed close to the Bragg peak arises from the long- range displacement fields associated with various defects. This diffuse scattering has been used for the estimation of the average defect size by a method described in the literature e.g by Patel [13]. The defect sizes are presented in Table 1.

Sample	Defect size $[\mu m]$
S_3	0.57
S_5	1.74
S_4	0.88
S_8	1.43

Table 1 Size of defects determined from diffuse scattering intensity

The defect size is smaller for the samples annealed under high pressure as compared to the samples annealed under atmospheric pressure. Because the diffuse scattering increases with the increasing size of the defects and their number [13], we can conclude that the defect concentration is increased in the case of sample S_3, as compared with the sample S_5. This is because the diffuse scattering intensity increases and the defect size decreases, for the sample S_3, as can be seen from Fig. 5a and Fig. 5b and Table 1. In the case of samples S_4 and S_8, as can be seen from Fig. 5c and

Fig. 5d and Table 1 the diffuse scattering intensity increases for the sample S_8 with the increase of the defect size, indicating a less marked increase of the defect concentration. Decreased defect dimensions with HP can be related to a higher number of nucleation centers for oxygen precipitation at HT-HP treated samples and therefore to a larger concentration of smaller defects created at such conditions. Notice, that the VO_2 defects could also act [16] as nuclei for oxygen precipitation.

At this point it is important to note that estimations from X-ray data result in a larger precipitate size as compared to those obtained by other methods, e.g electron microscopy, since the diffuse scattering measurements are more sensitive to the strain fields that surround the precipitates, rather than to observing the precipitate itself.

Summary

The effect of high hydrostatic pressure on the evolution of VO, VO_2, V_2O, V_2O_2 and V_3O_2 defects in neutron-irradiated Cz-Si have been studied for two temperatures: T_1=325 ^oC and T_2=350 ^oC. The analysis of the IR data indicates a faster decay of the VO defect. The larger than expected growth of VO_2 defect is attributed to a pressure-stimulated production of vacancies in the samples. The x-ray results indicate the presence of point-like defects, which are smaller but more numerous in the samples treated under pressure. These point-like defects could be considered as nuclei for oxygen precipitation, which is known to be enhanced under hydrostatic pressure.

Acknowledgements

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