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Structural disturbances of near-surface areas in silicon solar cell modified by P^+ ion implantation and thermal treatment

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Structural changes of ⟨001⟩-oriented Si-single crystal platelets after P^+ ion implantation and subsequent thermal treatment were analysed by means of diffraction methods using the synchrotron radiation with energy of 8 keV. Ion implantation was preceded by P and B diffusion processes to generate n–p junction and BSF (back surface field). The results obtained for such monocrystalline Si with a buried amorphised layer permitted to estimate the structural changes caused by the process of the layer formation. Analysis of the diffraction line profiles as well as of the pole figures showed that the crystal regions in the near-surface layer experienced certain misorientations. Both the effective depth of a strongly defected region, and the stress distribution in the sub-surface area were determined. The evaluation of the diffraction patterns allowed estimating the widths of the amorphised layer and of the transition zone between the amorphised region and the bulk. Moreover, the static Debye-Waller coefficient L and the diffusion loss parameter d were calculated. The above structure parameters are compared with those for conventional Si solar cells (without structural modification).

Keywords: ion implantation, buried amorphised layer, structural modification, stress distribution.

1. Introduction

Point defects are generated in the crystal lattice by accelerated ions as well as by phenomena of internal ionisation and implantation of foreign atoms in the crystal. The nuclear collisions are accompanied by large losses of the energy of the ions and changes in its motion direction. This leads to a distortion of the target structure and creates some depletion areas (clusters) on the track of the implantation ion. The clusters, with a diameter of 10 nm or more, are characterised by high concentration of point defects (Fig. 1). Clusters merged in a dense stream of implanted ions, form a continuous layer. Then the structure defects are the result of interaction of the primary point defects with the other ones and with the crystal impurities. At the same time the dislocation loops appear on the wedges of displacement or in areas where the implanted ions are stopped. These combined effects have a strong influence on the properties of the irradiated materials [1].

Because a significant part of the interstitial atoms of the defected areas become electrically active, it is possible to distinguish the conditions of ionic implantation and arising

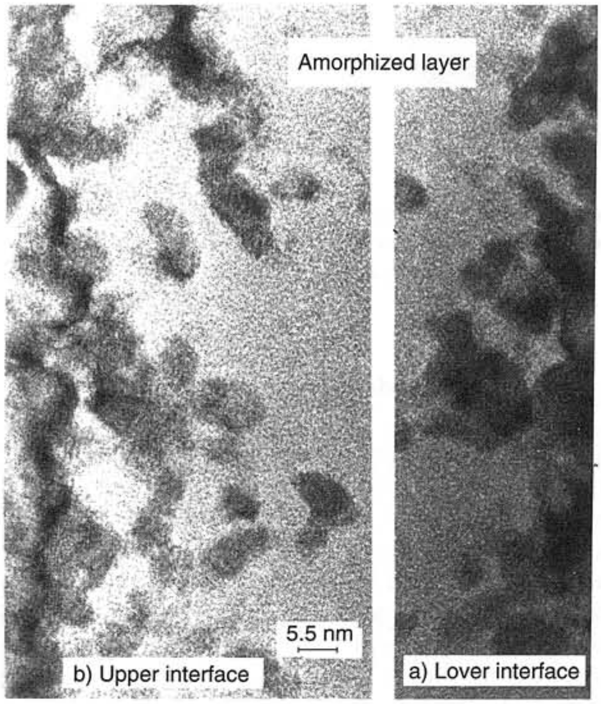

Fig. 1. HREM image of Si crystal implanted by P^+ ions. Visible irregular clusters near the sample surface (left side) and more defected (amorphous) areas (central part of the picture).

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of annealing defects [2,3]. The energy spectrum of the infrared region of solar radiation, which can induce the photoelectric conversion in the amorphous silicon has a greater absorption coefficient (10^2 cm^{-1}) when compared to that of monocrystalline silicon. The new, perspective solution leads to increasing the efficiency of photoelectric conversion of solar spectrum energy, consisting in the structure overlapping of the amorphous and the crystalline phases in one optoelectronic device [3–5].

The aim of the present study is the analysis of structural disturbances of near-surface areas in a crystalline silicon solar cell modified by P^+ ion implantation and thermal treatment (Fig. 2). First of all, the authors attention has been concentrated on the possibility of evaluating certain parameters of the structure provided by the analysis of the registered diffraction signal. Among such parameters there can be numbered the crystallographic orientation of the subareas, the static Debye-Waller coefficient L, and the diffusion loss parameter μ_d. The above structure parameters are compared with those for conventional Si solar cells (without structural modification). These parameters were estimated on the basis of the measurements of the diffraction effects, realised by the technique of high resolution X-ray diffraction, using a beam of synchrotronic radiation.

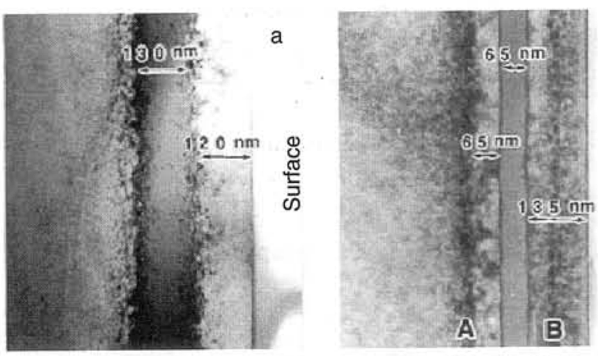

Fig. 2. HREM images of the buried amorphised substructure formed by impurity implantation (after Ref. 5): as implanted (a), after adequate thermal treatment (b). The geometrical dimensions are visualised in the figure.

2. Experimental details

The subject of the structural investigation was a monocrystalline Si solar cell before and after modification by P^+ ion implantation and subsequent thermal treatment. The sample was a plate of monocrystalline Si type p, with a surface 25×30 mm and a thickness of 250 μm having the main elements of a solar cell is the junction n–p and BSF. Both junctions were produced in one technological cycle as a result of the diffusion of phosphorous from $POCl_3$ source and the diffusion from boron-emulsion. In the process of ion implantation of phosphorous at the energy 180 keV and a dose of the range of 10^{15} cm^{-2} and subsequent heating in nitrogen atmosphere at the temperature 500°C for 21 min, an amorphised buried layer was produced in the cell emitter. During ionic implantation half of the sample surface was screened. Thus in the performed investigations the authors had to their disposal a sample whose one half represented the starting solar cell, and the other is a cell with a modified emitter.

For the modified sample, the (001) back-reflection pole figure for 0÷3°/0.3° range of the pole angle α and for 0÷360°/20° range of azimuthal angle β was registered based on its 4th order of 004 reflection, using 8 keV energy of synchrotron radiation[1]. Each point of the figure presents the line profile of the 004 Si reflection. The registration was carried-out by means of modified Rigaku-Denki X-ray goniometer, equipped with an appropriate slit system, and operated with PC remote control panel. For the both stages of the sample, high-resolution diffraction patterns by means of the Philips-MPD goniometer[2], as a reference data were registered, too. The results of the measurement and observations are presented in Figs. 3–5.

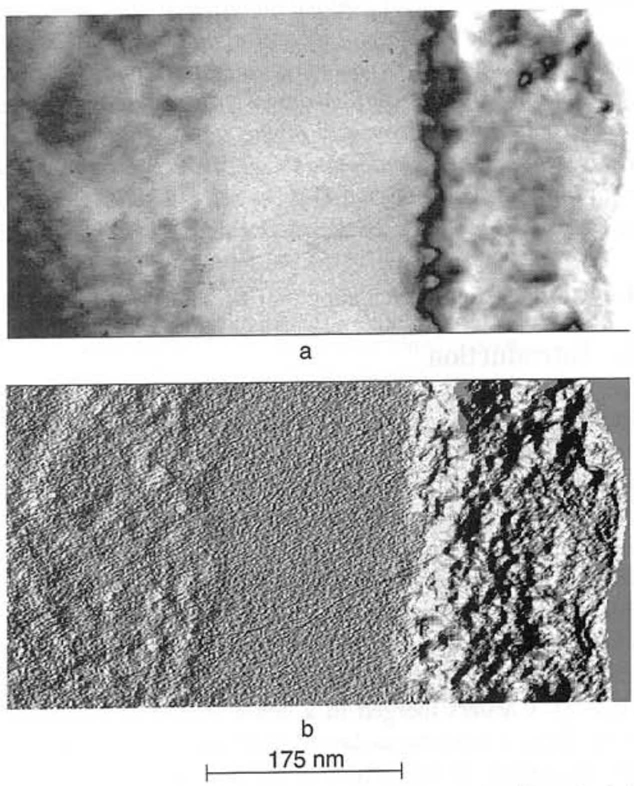

Fig. 3. TEM micrograph of the single Si crystal with a buried amorphous-like layer formed by P^+ ion implantation and the thermal treatment.

[1]The measurement was conducted on SAXS (5.2 L) beamline at ELETTRA Laboratory in Trieste (May 1999), according to the research proposal "Structural Investigation of Near Surface Layers in Silicon Plates for Solar Cells".

[2]The registration of diffraction profile by means of high resolution X-ray diffraction technique was performed in the Philips Analytical X-Ray Lab. in Almelo, Netherlands

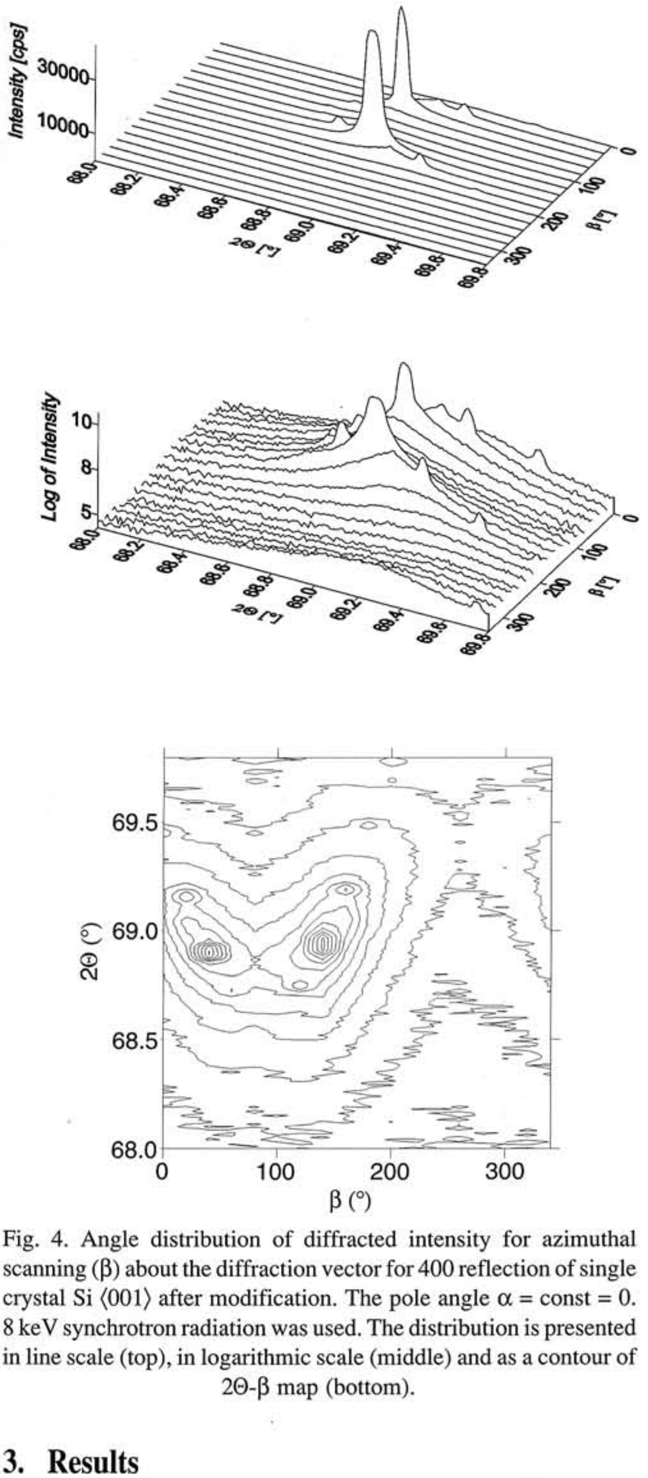

Fig. 4. Angle distribution of diffracted intensity for azimuthal scanning (β) about the diffraction vector for 400 reflection of single crystal Si ⟨001⟩ after modification. The pole angle α = const = 0. 8 keV synchrotron radiation was used. The distribution is presented in line scale (top), in logarithmic scale (middle) and as a contour of 2Θ-β map (bottom).

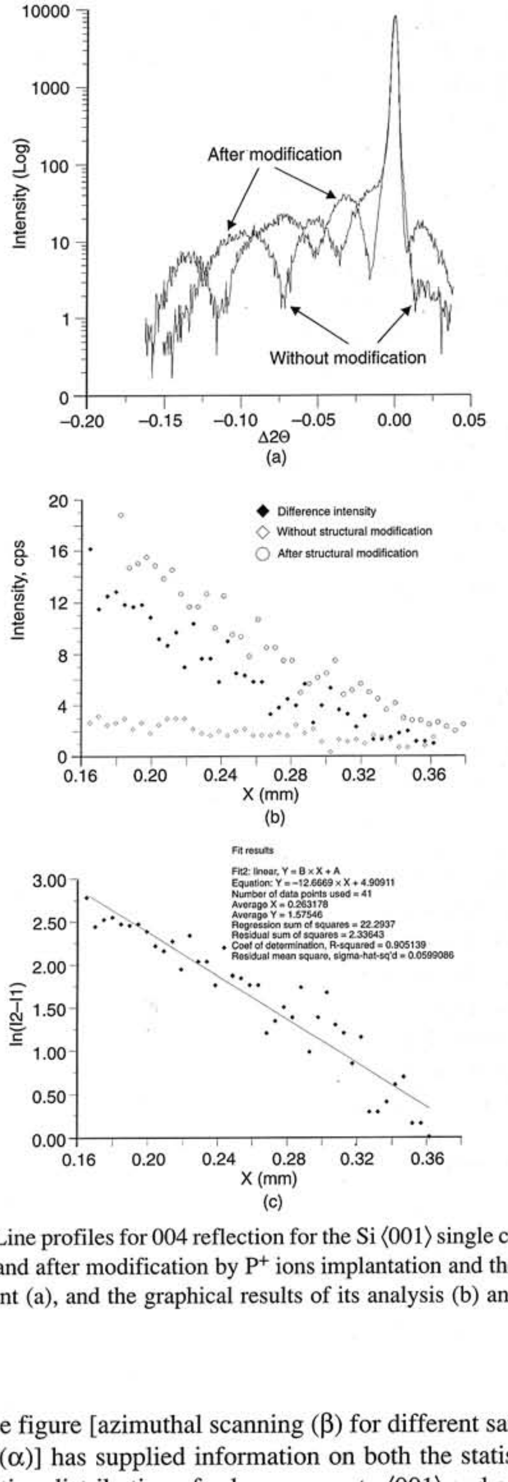

Fig. 5. Line profiles for 004 reflection for the Si ⟨001⟩ single crystal before and after modification by P^+ ions implantation and thermal treatment (a), and the graphical results of its analysis (b) and (c).

3. Results

Figure 3 shown the microstructure of the examined samples made by means of an transmission electron microscope (TEM). For better visualisation of the defected surface of areas adjoining the amorphised buried layer in Fig. 3(b), the TEM micrograph has been presented as a "shaded relief". Unfortunately, the applied thermal treatment was not complete (i.e. it did not result in the formation of a planar substructure with sharp interfaces), which is evidenced by the result of microscopic investigations, shown in Fig. 3, [compare with Fig. 2(b)].

Pole figure [azimuthal scanning (β) for different sample tilting (α)] has supplied information on both the statistical orientation distribution of subareas near to ⟨001⟩ and on the character of structure distortion in the near-surface layer of the examined sample. The profile of the diffraction line was analysed at each point (α, β) of the measured pole figure.

Figure 4 shows an illustrative distribution of profiles for a constant angle $\alpha = 0$. From the analysis of a part of the profiles of lines coupled with the main maximum, the structure parameters were estimated. Basing on the parameters of the strongest maximum in the distribution of β scan, the mean disorientation equal to 0.76 was estimated.

As a result of the analysis of the obtained spatial distribution profiles of a diffracted beam and theoretical modelling [6] the value of the Debye-Waller static factor

$$L_{av} = \frac{2\pi^2}{d_{hkl}^2}\overline{U^2}$$

where $U = \Delta d \, L_{av} \cong 5.7\times10^{-2}$ was calculated (see Fig. 5).

In Fig. 5(b), for the 004 reflection, there have been shown the tails of the dependence I(x) (where $x = r\Delta\varphi/\sin2\theta_B$, $\Delta\varphi$ is the small angular rotation in the surrounding of $2\theta_B$, r is the distance of the entry slit of the detector from the goniometer axis), measured for both of the examined sample (i.e., the area with and without modifications). In the chosen range of variation of x for the modified area, the increase of intensity of the diffracted beams is very well visible, which is evidence of increased level of diffusive dispersion, induced by the introduced structural changes. Analysis of the dependence of the logarithm of the difference in the intensity I(x) for both profiles allowed to determine the value of the additional parameter of the crystal structure $\mu_D = 1.2$ cm^{-1} is the coefficient of the additional energy losses on the imperfections of the crystal structure [6–10] [see Fig. 5(b) and 5(c)]. The knowledge of the value of the both parameters L_{av} and μ_D allowed to evaluate the mean dimensions of the disturbed areas-clusters (r ≅ 10–20nm) and of the concentration of the dislocation loops ($c_{av} \cong 10^{11} - 10^{12}$ cm^{-2}) occurring as a result of the structural modification of the emitter.

To observe the changes in the optoelectronic properties of the solar cell, induced by the structural modification of its emitter, from the spectral response there has been determined the internal quantum efficiency (IQE) for both cells. In the case of a cell with a modified emitter, a general decrease of IQE value was observed almost in the whole range of the wavelengths (400–1200 nm). This is particularly violent in the short wave range of the spectrum.

3. Conclusions

The given study contains a preliminary analysis of the results of X-ray investigations of the structural changes occurring in a Si-emitter of a solar cell, induced by the formation of the so-called amorphised buried layer. The investigations were carried out on a platelet of Si single crystal, type p, with the surface 25×30 mm and a thickness of 250 μm, having the main elements of a solar cell – n–p junction and BSF. Both junctions were produced in one technological process (phosphorous diffusion from a $POCl_3$ source and the diffusion from boron-emulsion). The amorphised buried layer, about 180 nm thick, was produced at a depth of about 180 nm under the sample surface in the process of ionic implantation of phosphorous at the energy 180 keV and the dose of the order of 10^{15} cm^{-2} and the following thermal treatment, in nitrogen atmosphere, at the temperature 500°C. The duration of the thermal treatment was 21 min. X-ray structural investigations were accompanied by measurements conducted by TEM. To determine the changes in the optoelectronic properties of the solar cell, induced by the structural modification of the emitter, there were carried out measurements of the spectral response and reflection.

The results of these measurements were used to determination the internal quantum efficiency of both cells, the initial cell and the cell with a modified emitter. X-ray analysis of the experimental data allowed estimating the values of the parameters characterising the degree of structural perfection of the near-surface areas of the examined semi-conducting structure. The determined value of Debye-Waller parameter L_{av} is 5.7×10^{-2}, and the parameter of diffusion losses $\mu_D = 1.2$ cm^{-1} which is equivalent to the presence in the emitter area of clusters with the dimensions r ≅ 10–20 nm, at the concentration of dislocation loops $c_{av} \cong 10^{11}–10^{12}$ cm^{-2}.

From the obtained measurement results it is evident that the performed thermal treatment was not complete. Both the upper and the lower crystalline layer did not recover ("recrystallise") in a sufficient degree and remained further on strongly defected, which was manifested in the determination of the electronic properties of the modified solar cell.

The presented investigation results of the diffraction effects have the character of a preliminary analysis only. The authors have at their disposal a rather large base of measurement data obtained in an experiment utilising the synchrotron beam, i.e., nearly 200 measured profiles of the diffraction lines. Utilising of the synchrotron beam in the performed investigations guarantees optimal conditions of a thorough analysis of the introduced structural changes in the near-surface areas of the cell and a computer simulation of the diffraction effects deriving from the model structures. The study is continued and the results will be presented in the nearest future.

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