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THE EFFECT OF HYDROGEN ON DISLOCATION PHOTOLUMINESCENCE IN SILICON

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Résumé - On a étudié l'influence des conditions de déformation plastique sur l'intensité de différentes lignes des spectres de luminescence du silicium produites par les dislocations. Par comparaison avec les résultats des signaux de résonance de spin, on montre que la partie courte longueur d'onde du spectre est liée aux dislocations fraîches, tandis que la partie grande longueur d'onde correspond à des transitions électriques mettant en jeu des dislocations ou bien reconstruites ou bien décorées. On discute dans le cadre de ce modèle le changement du spectre de luminescence par hydrogénation.

Abstract - The influence of deformation conditions on intensity different lines of dislocation luminescence spectra in silicon has been discovered. Comparison of these data with the results on the annealing ESR signal shows that short wavelength part of the spectrum is connected with fresh dislocations, while long wavelength part is corresponded to electron transitions with participation of either reconstructed or decorated dislocations. In this model the change of luminescence spectrum under hydrogenation is discussed.

A great interest in the effect of hydrogen on the behaviour of amorphous materials has arisen from the possibility to control electrical properties of hydrogenated amorphous silicon (a-Si) /1/. However, the changes produced by hydrogen in structure of amorphous materials remain obscure to the present day. Hydrogen is considered, among other things, to saturate dangling bonds which are found to be one of the principal defects in amorphous semiconductors of the IV group. Nearly complete disappearance of the ESR signal in hydrogenated a-Si /2/ is direct and effective evidence that dangling bonds are neutralized at the cost of covalent interaction with hydrogen atoms. It is of interest, in this connection, to examine the effect of hydrogen on dislocation properties in crystalline silicon (c-Si), which were known to contain a great amount of dangling bonds.

In the present paper dislocation properties were observed with the help of the dislocation luminescence spectrum discovered earlier /3/. It should be noted, however, that the dislocation luminescence spectrum is found to display a considerably more complex structure than it has been reported in /3/, and it's nature is greatly dependent on the conditions of introducing dislocations, which eventually determine the dislocation structure /4/. The first part of the paper is devoted to the description of the luminescence technique, hydro-
genation procedures of plastically deformed samples and conditions for plastic deformation. The second part deals with the dependence of photoluminescence spectra of specimens on the conditions of plastic deformation and subsequent heat treatment, with luminescence spectra of hydrogenated samples and the discussion of the experimental date obtained.

EXPERIMENTAL

Initial samples were cut out in the form of bars measuring $3 \times 3 \times 8 \text{ mm}^3$ with the edge orientation of $\langle 111 \rangle$, $\langle 112 \rangle$, $\langle 110 \rangle$ and plastically deformed either by compression along the $\langle 110 \rangle$ axis in the creep regime or bending around the $\langle 110 \rangle$ axis. In the latter case samples were cut out in the form of bars measuring $3 \times 3 \times 25 \text{ mm}^3$ and the edge orientation $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 110 \rangle$. The deformation temperature of the samples might range from 600 to 800°C. To observe photoluminescence spectra plates $3 \times 3 \times 0.5 \text{ mm}^3$ in size were cut out of the deformed samples and polished chemically in the solution HF:HNO$_3=1:7$. Luminescence was excited by an argon laser with a wavelength of 514 nm. The samples were placed in an optical cryostat enabling the measurement temperature to be maintained in the range of 2-150 K. The luminescence spectra were recorded using a high-transmission grating monochromator with an aperture of 1:3.5. The samples were hydrogenated by proton implantation with an energy of 180 kev and dose up to $10^{18} \text{ cm}^{-2}$ and then annealed at 200-350°C, hydrogen diffusing deep into the samples. In addition, the method of hydrogenation samples in a glow discharge was applied there to prevent the surface layer from being heavily destroyed. The samples were dehydrogenated by annealing at 600-650°C.

EXPERIMENTAL RESULTS AND DISCUSSION

The shape and intensity of individual luminescence bands proved to be dependent on the plastic deformation temperature of the sample. Fig.1 exhibits luminescence spectra of the samples containing approximately an equal number of dislocations but deformed at different temperatures. The bottom curve demonstrates the spectrum of a sample after annealing at 800°C. It is well seen that the elevated temperature of deformation is responsible for a decrease in a relative intensity of a short wavelength side of the spectrum. At the same time one can observe a narrowing of separate spectrum lines, which shows up most vividly after annealing. All the samples produced by such deformation can conditionally be divided into two groups: the samples deformed at temperatures above and below 700°C. The former display, as a rule, two intensive distinct lines with maxima at energies of 0.80 ev and 0.87 ev and a weakly pronounced short wavelength part of the spectrum in the range of 0.88-1.0 ev. In the latter one finds a greater integral intensity in the short-wave spectrum part. Under some deformation conditions there are resolved separate lines, the
principal of which possess maxima at the energies of 0.93 ev and 0.98 ev. It is worth noting that such a difference may be due to a considerable rearrangement in both the dislocation structure and impurity surroundings of dislocations in the temperature range about 700°C. A similar "threshold" dependence of the behaviour of plastically deformed crystals is also disclosed by other methods /5-7/.

It is seen from Fig. 1 b,c that a decrease in the short wavelength lines intensity is accompanied by a corresponding rise in the intensity of bands 0.80 and 0.87 ev. At such deformation the amount of dangling bonds contributing to the ESR signal is known to decrease below the sensitivity limit /5,8/. If a reduction in the number of unsaturated bonds points to the rearrangement in the spin system then by means of low-temperature deformation we introduce dislocations having the highest number of unpaired spins, and a corresponding growth of the short wavelength spectrum part takes account of the relationship between the observed bands and unsatisfied bonds. On the other hand, the results in /9/ show that lowering the deformation temperature permits one to introduce dislocations surrounded by a less dense impurity atmosphere than at high-temperature deformation. Elevated deformation temperatures or a subsequent high-temperature annealing of the samples deformed at low temperatures may encourage the formation of impurity atmospheres. In /4/ we have reported on some correlation between the intensity of the line 0.80 ev and oxygen content in the starting samples. Yet the deformed samples heavily doped with other impurities such as copper, aluminium, zinc demonstrated no marked change in the dislocation spectrum. In this connection we believe the lines observed in the photoluminescence to be, seemingly, due to electron transitions onto dislocation energy levels. From this point of view, two states of dislocation structure therewith may be distinguished in the crystals: fresh dislocations introduced at the lowest temperatures, relaxed dislocations introduced at a temperature above 700°C and those annealed in this temperature range. The first structure conforms to the luminescence spectrum with the intensive short wavelength side 0.88-1 ev (fig.1a), the second does to the spectrum, in which only the long-wave length side 0.8-0.88 ev with more intensive lines of 0.80 ev and 0.87 ev is practically found to occur (Fig.1c). In this case the dislocations from the second state can be transferred to the first one using a short deformation attending the thermal impact during the quenching of the samples. This leads to simultaneous transformation of the spectrum from the c- or d-type to the a-type in Fig.1. Similar quenching of the initial samples fails to bring about the occurrence of any lines in this spectrum range.

The date on hydrogenation of samples with dislocations are shown in Fig.2. The luminescence spectrum of the hydrogenated samples has a wide band (H) (Fig.2b) with a maximum of about 0.95 ev. Nothing definite can be said about the short wavelength side of the initial spectrum as an intensive luminescence band is left at this place. As to long wavelength lines, their intensity is well seen to drop sharply.

The temperature dependence of the intensity of the new luminescence line differs significantly from that of the initial spectrum lines (Fig.3), the maximum position of the new line is found underfinite. With using temperatures the maximum line value shifts first to the short wavelength side and then back to the long wavelength side, coinciding with the initial spectrum line 0.93 ev. The temperature dependence of the initial spectrum lines is likely to be caused by the action of a certain mechanism of nonradiative recombination which is initiated by temperature. The activation energy in this case is very low and ranges from about 0.003 to 0.006 ev. A markedly
Fig. 2 - The dislocation luminescence spectra of plastically deformed silicon after deformation at 620°C (a), hydrogen implantation and subsequent annealing at 350°C (b), annealing for 1 h (c) and 2 h (d) at 650°C.

different temperature dependence of the line H has enabled one to assume that it differs from the initial spectrum lines in nature /4/. Nevertheless, the studies into the effect of the deformation method (temperature and rates of loading) on the kinetics of the temperature drop in the initial spectrum lines 0.93 ev and 0.98 ev have revealed great changes in the activation energy of this drop. Again, hydrogenation of the samples in the glow discharge has demonstrated that in the luminescence spectrum remain initial short-wave lines, the temperature dependence of which resembles the behaviour of the line H. Both hydrogenation methods lead to increased quantum luminescence yield that agrees with conclusions in /10/ on blocking of non-radiative recombination channels with hydrogen. Annealing of hydrogenated samples at the temperatures of 600 to 650°C causes reduction in the initial spectrum except for some annealing of the short-wavelength spectrum part, Fig. 2 (c,d). Thus hydrogenation of deformed silicon samples results in a marked quenching of the long wave-

Fig. 3 - The temperature dependence of the intensity of individual lines of the dislocation spectra normalized to the intensity of the corresponding lines at 5 K. * denotes the temperature dependence of the line H in the initial sample, O - in the plastically deformed sample; ▲ - of the line 0.80 ev, △ - of the short wavelength spectrum side of unhydrogenated sample.

length spectrum part related with the rearranged dislocation structure. The possibility of such an influence of hydrogen is confirmed by the experiments on neutralization of localized paramagnetic centers in a-Si for which the number of introduced hydrogen atoms should be much greater than that of the unpaired spins there /11/. The same ratio was found on producing hydrogenated germanium /12/. Evidently, it points to the fact that in amorphous materials exist and may chemically react with atomic hydrogen other nonparamagnetic defects similar to paired dangling bonds /13/. The same type of pairing can also be expected on relaxed dislocations on which no ESR signal is found to occur but lines in the luminescence spectrum are observable. The breaking of such bonds with hydrogen could result in quenching of appropriate luminescence lines.
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