Interaction of dislocations with hydrogen and oxygen in silicon

Yu. A. Osip'yan, A. M. Rtishchev, É. A. Shteĭnman, E. B. Yakimov, and N. A. Yarykin

Institute of Solid State Physics, USSR Academy of Sciences

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The change in the electric properties and dislocation photoluminescence spectra of silicon single crystals saturated with hydrogen following subsequent dehydrogenation is investigated. Hydrogen is found to compensate for the acceptor action of the dislocation and to reduce sharply the intensity of the dislocation luminescence. In contrast to hydrogen, oxygen alters only one line (0.81 eV) of the dislocation luminescence spectrum. Some peculiarities in the temperature dependence of the intensity of some lines of the dislocation spectrum are observed. The results are explained by assuming that atomic hydrogen saturates the broken dislocation bonds.

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Investigations of the effect of hydrogen on properties of amorphous and crystalline silicon has attracted tremendous interest in recent years, in connection with the possibility of substantially improving the solar energy converters produced on their basis. The increase of the carrier lifetime when silicon is hydrated is attributed[1] to saturation of the broken bonds by hydrogen atoms. On the other hand, it is usually assumed that the electric properties of the dislocations in semiconducting crystals are determined by a considerable degree by the existence of dangling bonds in their nuclei. In the case of silicon, thorough studies were made of the energy spectrum connected with the dislocations[2] and of the effect of dislocations on the electric properties of the crystals,[3–5] and characteristic dislocation luminescence was observed.[6] There are also data on the influence of the broken dislocation bonds on the nonradiative recombination time.[7] All this has raised hopes of being able to register sufficiently reliably the interaction of hydrogen with the dangling bonds of the dislocations, by measuring the corresponding changes of the electric and optical properties of plastically deformed crystals.

In the present study we have investigated the changes of the electric properties and of the dislocation luminescence of plastically deformed single crystals of silicon saturated with atomic hydrogen.

At the same time, we have investigated the influence of oxygen on the spectrum of the dislocation luminescence, since it is known[5,8] that oxygen is effectively captured by dislocations, especially at relatively high temperatures of the deformation or of the subsequent annealing, and the hydrogenation and dehydrogenation processes that were accompanied in our experiments by suitable heat treatment.

It was observed that hydrogen influences substantially the entire spectrum of dislocation luminescence and the electrical properties of plastically deformed silicon. The oxygen captured by the dislocations during the heat treatment compensates, just as hydrogen, for the acceptor action of the dislocations. In this case, however, a change in the intensity of only one line, 0.81 eV, is observed in the dislocation-luminescence spectrum. The results are explained under the assumption that the hydrogen interacts directly with the dangling bonds, whereas the oxygen is captured by the dislocations but does not enter into a chemical bond with the atoms on the edge of the extra half-plane.

PROCEDURE

The investigations were performed on *n*-Si samples with phosphorus density $N_d = 4 \cdot 10^{13}$ cm^{-3}. The crystals were deformed by three-point bending at 850 °C or by four-point bending at 620 °C about the ⟨110⟩ axis. The geometry and the deformation conditions were similar to those used in Refs. 3 and 5. In the former case, the plastically deformed region with dislocation density 10^8–10^{10} cm^{-2} was localized under the central support–wedge-shaped sapphire rod–and penetrated through the entire crystal in the form of a column ~1 mm wide. In the second case, samples 400 m thick, with a broad face parallel to {100} were cut from the deformed crystals. The samples contained 60° dislocations whose density was determined from the etch pits and was varied in the interval $5 \cdot 10^5$–$5 \cdot 10^7$ cm^{-2} by changing the duration of the formation and the applied stress. When the silicon is plastically deformed by three-point bending, a region with *p*-type conductivity appears in the region of the maximum dislocation density, i.e., a dislocation *n-p-n* structure is produced. To investigate the changes of the electric properties of the crystal when it is hydrated, it was found convenient to measure the resistance of the *n-p-n* junction, which changed much more than the resistance of the uniformly deformed crystal.

The hydrogen was introduced into the silicon crystals by implantation of protons of energy 180 keV with a dose up to 10^{18} cm^{-2}. The crystals were then annealed at 200–350 °C, so that the hydrogen diffused in the interior of the crystal, as was manifest by a change in the properties of the investigated samples. The samples were dehydrated by annealing at 600–650 °C for 1–3 h.

The luminescence was excited with an argon laser of wavelength 5145 Å, focused on the surface of the sample. The samples were placed in a helium cryostat

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that made it possible to vary their temperature between 2 and 150 K. The luminescence spectrum was analyzed with an SM monochromator and a germanium photoresistor as a detector. Prior to the measurements the samples were chemically polished in a standard $HF : HNO_3 = 1 : 7$ solution. In all the cases, the heat treatment of the control undeformed samples did not change their properties. To investigate the influence of the oxygen we used crystals grown by the Czochralski method, whose relative oxygen content was estimated from the effect of the "donor action of the dislocations" (Ref. 5). The control oxygen-free crystals were grown by crucibleless zone melting in which the oxygen density was $N_O \leq 10^{16}$ cm^{-3}.

RESULTS

Plastic deformation produces in the photoluminescence spectrum of silicon crystals new lines in the region 0.7–1.0 eV. Some of these lines are observed also in the original crystals, if the density of the growth dislocations in them exceed 10^4 cm^{-2}. With increasing density of the introduced dislocations, the intensity of the dislocation spectrum increases monotonically, and the intensity of the exciton part of the spectrum decreases simultaneously and falls below the sensitivity limit of our procedure at a dislocation density ~10^7 cm^{-2}. It turned out that the character of the dislocation spectrum depends substantially on the deformation temperature and on the subsequent heat treatment. In particular, if the deformation took place at $T = 800$ °C, the obtained spectra agreed well with those published in Ref. 6. Lowering the deformation temperature changed both the width and the relative intensity of the individual lines; in particular, the short-wave part of the spectrum became much more intense. Since it is known that the EPR spectrum due to the broken dislocation bonds is observed only in crystals deformed at temperature ≤700 °C (Ref. 9), we investigated mainly just such crystals.

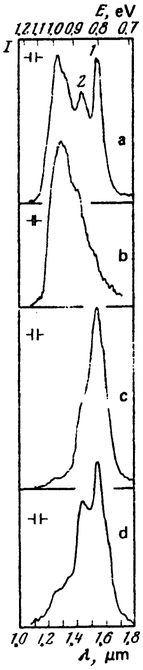

FIG. 1. Dislocation-luminescence spectrum of plastically deformed silicon after deformation at 620 °C (a), implentation with hydrogen, and subsequent annealing at 350 °C (b), annealing for 1 h (c) and 2 h (d) at 650 °C.

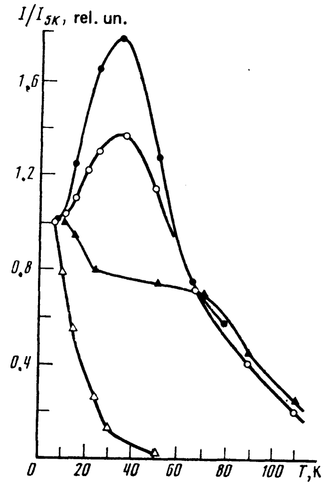

FIG. 2. Temperature dependences of the intensity I of individual lines of the photoluminescence spectrum: ●) of the H line in the initial sample; ○) of the H line in the deformed sample; ▲) of the line 1 (0.81 eV); △) of the short-wave region of the spectrum.

A typical spectrum of the dislocation luminescence of silicon deformed at $T = 620$ °C is shown in Fig. 1a. Two intense lines can be distinguished, line 1 at 0.81 eV and line 2 at 0.87 eV, as well as a number of lines in the region 0.88–1 eV. The foregoing subdivision is based on the difference in the temperature dependences of the radiation intensity. Figure 2 shows the temperature dependence of the intensities of certain dislocation-spectrum lines. It is seen that the intensity of the short-wave part of the spectrum depends on the temperature much more strongly than the intensity of the 0.81 eV line. The dependences of the intensity of line 2 on the temperature are now shown in this figure, inasmuch as at low intensities they could not be separated from the wing of line 1. It can be stated, however, that the intensity of line 2 decreased with increasing temperature at first in the same manner as the intensity of the lines in the region 0.88–1 eV, but starting with approximately 20 K the decrease slowed down and with further rise of temperature line 2 behaves just like line 1.

Annealing at $T < 700$ °C hardly changes the character of the spectrum. On the other hand, raising the annealing or plastic-deformation temperature to above 700 °C leads to a noticeable decrease of the line intensity in the region 0.88–1 eV and to a relative change in the intensities of lines 1 and 2 (Fig. 3). The behavior of line 1 depends essentially on the content of the oxygen in the initial crystal. Thus, in crystals grown by crucibleless zone melting the intensity of line 1, while increasing with rising annealing temperature, does not exceed as a rule the intensity of line 2 (Fig. 3b). In crystals with oxygen content $N_O > 10^{17}$ cm^{-3}, the intensity of line 1 immediately after plastic deformation at 620 °C is high-

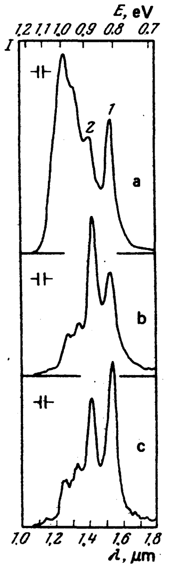

FIG. 3. Influence of annealing at 750°C on the dislocation-luminescence spectrum in crystal with a small (b) and large (c) content of oxygen: a) spectrum after deformation at 620°C.

er than in the oxygen-poor crystal, and increases rapidly upon annealing (Fig. 3c). It should be noted that in Ref. 10 a broadening of this line was observed in oxygen-containing crystals following high-temperature annealing, but nothing was reported concerning the change of its intensity.

Proton implanation by itself produces practically no change in either the electric properties or the luminescence of the plastically deformed crystal. The subsequent annealing, however, which stimulates the diffusion of hydrogen into the interior of the crystal, influences substantially both the electric conductivity and the luminescence spectrum. Figure 4 shows the dependence of the resistance of an *n-p-n* structure whose *p*-region is produced by plastic deformation ($N_D \sim 10^9$ cm^{-2}) on a 60-minute isochronous annealing. The hydrogen diffusion restores the *n*-type conductivity, and consequently short circuits the *p-n* junctions, and decreases strongly the resistance of the structure. At 350 °C the effect reaches saturation. It was observed by layer-by-layer chemical polishing after 10 h of annealing at 350 °C the hydrogen restores the *n*-type of conductivity at a depth of the order of 20 μm. A similar annealing leads to a noticeable decrease of the intensities of line 1 and 2 in the luminescence spectrum and to the appearance of a new intense wide band with a unresolved structure, with a maximum near 0.95 eV (Fig. 1b), which we shall call hereafter the *H* band.

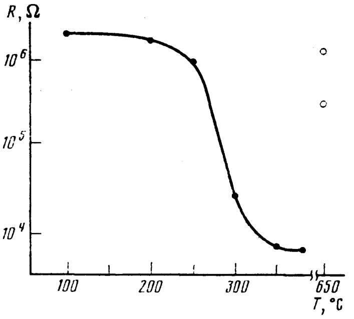

FIG. 4. Influence of implantation with protons and subsequent isochronous annealing on the resistance of a dislocation *n-p-n* structure. The light circles show the resistance after annealing at 650 °C for 1 h (lower point) and 2 h (upper).

Annealing at 650 °C leads to a vanishing of the *H* band and to a gradual restoration of the initial spectrum (Figs. 1c and 1d). The electric properties are also gradually restored by this annealing. The points of Fig. 4 show the gradual restoration of the resistance of an *n-p-n* junction after successive one-hour annealings at 650 °C. It is seen that even a two-hour annealing at 650 °C did not restore fully either the luminescence spectrum or the electric properties.

DISCUSSION OF RESULTS

It follows from our results that hydrogen, just as oxygen,[5] cancels the acceptor action of the dislocations. However, their influence on the dislocation luminescence spectra differs substantially, thus indicating different mechanisms of the interaction between these impurities and the dislocations. Saturation of the crystal with hydrogen led to an almost complete extinction of the dislocation luminescence. Lines 1 and 2 remained visible in the spectrum in the form of weak inflections on the long-wave wing of the *H* line. The short-wave part of the spectrum also vanished, for otherwise its contribution would be noticeable on the temperature dependence of the intensity of the *H* line (Fig. 2). If it is assumed that broken dislocation bonds participate in the formation of the dislocation spectrum, the saturation of these bonds by hydrogen would actually manifest itself in a simultaneous extinction of all the dislocation lines, as was in fact observed in experiment. The possibility of such a saturation is indirectly indicated in Ref. 11. In addition, the photoluminescence spectrum of amorphous silicon saturated with hydrogen revealed[1] a wide band with a maximum near 0.9 eV, which we attribute to the action of hydrogen that saturated the broken bonds. It should be noted that in our study the hydrogenation and the dehydrogenation were carried out at temperatures below 700 °C, i.e., the observed changes cannot be attributed only to heat treatment (see above). On the other hand, the influence of oxygen when gathered by the dislocations in the annealing at 700 °C is revealed by an increase of the intensity of only one line, 0.81 eV.

In principle, the acceptor action of dislocations can be cancelled either by producing a sufficient number of donor centers, or by saturating the dangling bonds, meaning by making them electrically inactive. It is known that donor centers are produced near dislocations in crystals with oxygen.[5,8] It appears that the 0.81 eV line does indeed correspond to an electronic transition with participation of such a donor center. The hydrogen, on the other hand, probably interacts directly with the dangling bonds, although it is not excluded that it participated also in the production of a certain number of donor centers in the course of the heat treatment.

It should be noted that we have observed in this study certain peculiarities of the dislocation-luminescence spectrum, not observed in the preceding investigations.[6,10] Thus, the long-wave part of the dislocation luminescence (0.87–1 eV) turned out to be sensitive both to the deformation temperature and to the subsequent annealing. With increasing temperature, the intensity of the short-wave component decreases. It should be noted here that the spectrum is observed only in crystals with dislocations and does not vanish even after annealing above 1000 °C. This indicates that the spectrum is due only to dislocations, since all the known point defects are reliably annealed out at these temperatures. On the other hand, the dependence of the intensities of the individual lines of the spectrum on the temperature is substantially different (Fig. 2), thus indicating a different character of the electronic transitions that cause the individual spectral lines. It was indicated above that the decrease in the intensities of the individual lines with increasing temperatures is not described by an exponential law, but even a rough estimate of the activation energy indicates that not one line of the spectrum can be associated with an electronic transition between a band and a dislocation state, since a simple subtraction of the transition energy from the band widths yields a considerably higher energy. We propose therefore that the individual lines of the dislocation spectrum are governed by two types of electronic transitions, namely a transition with decay of the excitation bound on the center, which has a strong temperature dependence, and a transition of the donor-acceptor type, which yields a weak temperature dependence.

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