Influence of hydrogen on dislocation donor and acceptor states

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(Submitted 30 December 1981)
Zh. Eksp. Teor. Fiz. **82**, 2068–2075 (June 1982)

The influence of hydrogen on the dislocation electron-hole states produced following low-temperature (700°C) plastic deformation of *n*- and *p*-type silicon single crystals is investigated by the deep level transient spectroscopy (DLTS) technique. It is shown that hydrogenation leads to a sharp decrease of the number of all donor and acceptor dislocation states in the forbidden band deeper than ~0.16 eV. Data on the restoration of the intensities of the various DLTS peaks upon dehydrogenation of the samples by annealing or successive etching-off the hydrogenated layer can be attributed either to the unequal values of the "hydrogen complex" bond for different centers, or to the different efficiencies of the available channels for the diffusion of hydrogen in the deformed crystal.

PACS numbers: 66.30.Jt, 62.20.Fe, 61.70.Jc, 71.55.Dp

INTRODUCTION

It can now be regarded as firmly established that introduction of dislocations into semiconductor crystals, say by plastic deformation, produces in the forbidden band a number of donor and acceptor states, at least some which are due to dislocation broken bonds. An investigation of plastically deformed silicon by the EPR method shows that the paramagnetic centers produced at deformation temperatures $T \leq 700\,^\circ\mathrm{C}$ (*D* centers) can be associated with dislocation broken bonds that form one-dimensional chains. The observed anomalous temperature dependences of the magnetic susceptibility and of the relaxation times for these centers[1] can be explained by assuming the presence of collective effects in such a system.

It would be useful in this connection to find a method that makes it possible to saturate some of the broken bonds, and thus separate the collective effects due to the interaction of neighboring broken bonds from the properties of the individual broken bonds. Such investigations are also of applied interest, since neutralization of dislocation deep levels would make it possible to increase the lifetime of the minority carriers in defected silicon crystal, which is important, for example, for the development of inexpensive solar cells.

One such method can be saturation of the samples with hydrogen. In fact, numerous investigations of amorphous silicon show that saturation of *a*-Si films with hydrogen (e.g., in an RF discharge) leads to a substantial decrease of the density of the broken valence bonds, apparently on account of formation of Si-H bonds (see. e.g., Ref. 2 and the bibliography therein). Benton *et al.*[3] observed vanishing of the electric activity of the point defects produced in crystalline silicon exposed to laser radiation, and Pohoryles observed recently[4] the vanishing of the electric activity of certain deep acceptor levels upon high-temperature (800 °C) plastic deformation of silicon single crystals.

It was shown in Ref. 5 that saturation of plastically deformed *n*-silicon with hydrogen shifts greatly the Fermi level towards the conduction band, an effect that can be attributed to a decrease in the density of the acceptor centers. The saturation with hydrogen was via implantation of protons of energy up to 100 keV in the samples. It is shown in the same reference that saturation with hydrogen decreases greatly the intensity of the luminescence due to the centers produced by plastic deformation. A new luminescence band is then produced and is associated with the hydrogen-containing centers. In the present study we investigate by the method of deep-level transient spectroscopy (DLTS) the influence of hydrogenation on theelectric activity of all the donor and acceptor centers produced upon low-temperature ($T = 700\,^\circ\mathrm{C}$) plastic deformation.

SAMPLES AND EXPERIMENTAL PROCEDURE

We used single-crystal silicon samples grown by crucibleless zone melting in vacuum, and doped with phosphorus (1.5×10^{16} cm^{-3}) and boron (2×10^{16} cm^{-3}). The samples were deformed by compression along $\langle 110\rangle$ at 700 °C in an argon atmosphere. The degree of deformation was 2%, corresponding to a dislocation density $(1-3)\times10^{9}$ cm^{-2}. Such samples produce a strong EPR signal from the *D* centers associated with the open valence bonds in the dislocation cores. The *D*-center density was $(2-4)\times10^{16}$ cm^{-3}. Annealing the samples at temperatures higher than 700 °C causes the *D* centers to vanish.[6] Plates measuring $3\times4\times0.5$ mm were cut from the center of the sample and were polished first mechanically and then by chemically in a mixture 1HF:7HNO$_3$. The samples were hydrogenated in a quartz tube through which hydrogen was blown at a pressure up to 5 Torr. The hydrogen was atomized in a high-frequency discharge by an inductor placed on the tube and matched to a generator operating at 110 MHz. The volume of the produced plasma was of the order of 10–15 cm^3. The freshly etched samples were placed in the discharge region in a silicon vessel and kept for 1 h at 350 °C, after which the temperature was lowered for 30 min to 100 °C and the samples were taken out of the reactor. The temperature was regulated by varying the high-frequency power absorbed by the discharge, usually 40–70 W. After the samples were hydrogenated, a layer of thickness from 1 to 30 μm was etched off from all sides of the samples in 1HF:7HNO$_3$. The layer

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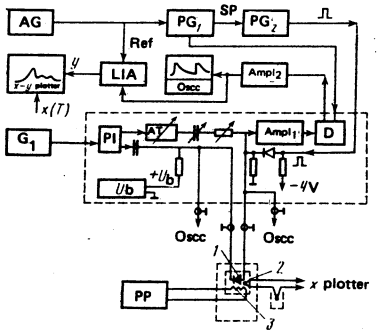

FIG. 1. Block diagram of DLTS spectrometer, 1) Sample, 2) thermocouple, 3) heater (all three are placed in a cryostat 77–350 K). PP) 0–20 V power pack, G_1) high-frequency (1.5 MHz) generator (G-4-102). The dashed box encloses a capacitance bridge. PI) Phase inverter, AT) attenuator, U_b) bias-voltage sourve for sample (0–9 V), Amp_1) amplifier (1.5 MHz), D) detector (1.5 MHz) with switch that closes during the time of the refilling pulse; LIA) lock-in amplifier; PG_1, PG_2) pulse generators (G5-50) to control the switch and the refilling pulses; AG) acoustic generator.

thickness was determined from the etching time determined from the previously measured etching rate. The samples were then washed in HF, distilled water, and alcohol, and Schottky barriers of 1.5 mm diameter were then sputtered on them in vacuum. The Schottky contacts were gold and silver for n- and p-type samples, respectively. An ohmic contact (GaAl or In) was on the opposite side of the sample. The obtained Schottky diodes were used for the DLTS measurements.

The setup used for the DLTS measurements was similar to that described in Ref. 7 (see Fig. 1). The capacitance of the Schottky diode was measured with a bridge at an operating frequency 1.5 MHz. The DLTS spectrum was obtained by measuring the time dependence of the Schottky-diode capacitance at a reverse bias voltage U_b on the diode following application of a carrier pulse of duration t_p and amplitude U_p. During the time of the carrier pulse the reverse bias on the sample decreases from U_b to $U_b - U_p$ and the deep centers that lie lower than the Fermi level capture electrons (in the n-type) or holes (in the p-type). After the termination of the pulse, the electrons trapped by the centers and located in the depleted layer above the Fermi quasilevel are activated into the conduction band and leave the depleted layer, whose thickness is thus decreased. As a result, the diode capacitance increases exponentially (in first-order approximation) with a time constant τ_e. Here $\tau_e^{-1} \propto \sigma T^2 \exp(-\Delta E/kT)$, where σ is the cross section for center capture and ΔE is the activation energy for the thermal ionization of the centers. If a signal proportional to the diode capacitance is applied to a lock-in amplifier, the temperature dependence of the output signal

$$A(T)=\int\limits_{0}^{1/2F} c\,dt-\int\limits_{1/2F}^{1/F} c\,dt$$

has a maximum, since τ_e depends exponentially on the reciprocal temperature. In the presence of several types of centers, several maxima will be observed.[7,8] From the position $T_{\max}$ of the maximum we can determine $\tau_e = 0.425/F$ at $T = T_{\max}$, where F is the repetition frequency of the refilling pulses and of the lock-in-amplifier reference signal. The height Δc of the maximum is proportional to the density of the deep centers in question (more accurately, to the density of the carriers captured by them in equilibrium). The relation between Δc and the density can be found, e.g., in Ref. 9.

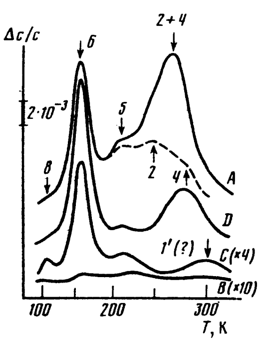

FIG. 2. DLTS spectra of n-type sample ($U_b = U_p = 3$ V, $t_p = 40$ μsec, $\tau_e = 4$ msec): A) sample No. 1 (1.5×10^{16} P atoms/cm^3, $\varepsilon = 2\%$); B) No. 1, H, 1 μm (hydrogenated sample No. 1, a 1-μm layer was removed after hydrogenation); C) No. 1, H, 7 μm: D) No. 1, H, 7 μm, annealed 30 min at 500° C. The dashed curve shows the spectrum obtained in Ref. 10.

When F changes, the positions of the maxima change with temperature and it is possible to obtain $\tau_e(T)$ for all center plots from which it is easier to calculate ΔE. We have assumed that the center ionization energy ΔE determined in this manner is equal, accurate to about 0.05 eV, to the depth of the energy level relative to the bottom of the conduction band (in n-type samples) or the top of the valence band (in p-type samples). Numerous experimental studies of the application of the DLTS method to investigations of point defects show that this assumption is sufficiently well founded.

RESULTS OF EXPERIMENTS

Figures 2 and 3 show typical DLTS spectra A of deformed samples of n and p type, respectively. All the characteristic peaks of spectra A in Figs. 2 and 3 coincide with those observed[10,11] in samples with dislocations. The numbering of the peaks corresponds to the energy scheme proposed for the dislocation states in Ref. 10. As follows from Refs. 10 and 11, in the A

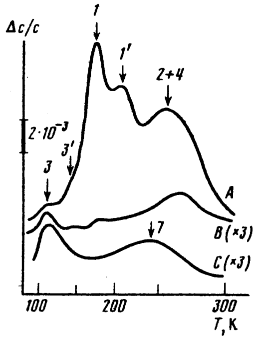

FIG. 3. Spectra of p-type sample: A) Sample No. 12 (2×10^{16} B atoms/cm^3, ε=2%); B) No. 12, H, 4 μm; C) No. 12, annealed 30 min at 780 °C.

spectra, the peak near 270 K (Fig. 2) or 250 K (Fig. 3) consists of two strongly overlapping peaks corresponding to states 2 and 4. The position of the maximum of this peak differs in different samples, since it depends on the ratio of the intensities of peaks 2 and 4.

We note that the DLTS spectra carry information on the density of the centers in a surface layer whose thickness is of the order of the depleted layer of the Schottky barrier, 0.3 μm in our case. The surface states can in this case be readily distinguished from the volume states by plotting the amplitudes of the spectra against the amplitude of the refilling-pulse amplitude U_p. Actually, at $U_p < U_b$ the depth of the depleted layer decreases during the charging-pulse time, and some of the volume states, which turn out to be lower than the equilibrium Fermi level (in n-type samples), capture electrons. Near the surface, however, the bending of the bands, as before, is large enough, so that all the deep states lie higher than the equilibrium Fermi level, and are not subject to charge exchange. If the centers are uniformly distributed over the volume, the amplitude of the corresponding DLTS peak, which is proportional to the number of charge-exchanging centers, increases monotonically (almost linearly) with increasing U_p. The surface states, however, begin to exchange charge and produce a DLTS signal only if $U_p \gtrsim U_b$. Figure 4 shows by way of example plots of this type for the volume states 2 + 4 in the absence and presence of surface states. The peak of the surface states is superimposed on the 2 + 4 peak. At a certain surface finish and surface preparation of the samples prior to the deposition of the Schottky barriers, the density of the surface states did not exceed $(1-2)\times 10^9$ cm^{-2} and they did not affect our measurements.

An investigation of the kinetics of the charging of states 1–7 during the time of the refilling pulse, i.e., of the dependences of the DLTS-peak amplitude on t_p, shows (see also Ref. 10) that in nonhydrogenated samples the number of carriers captured by these centers is limited not by the number of the centers, but by the Coulomb interaction of the captured carriers, as follows from the logarithmic dependence of the number of captured carriers on t_p. It follows therefore that centers 1–7 are unevenly distributed in the crystal volume. This is discussed in greater detail in Ref. 10.

After hydrogenation of the samples, the amplitudes of all the peaks in the DLTS spectra decrease steeply (see spectra B in Figs. 2 and 3). Figure 5 shows the scheme of the energy levels produced in the samples after plastic deformation, while Table I shows the densities of the electrons and holes captured by these levels, as calculated from the amplitudes of the DLTS peaks using the equations of Ref. 9. As seen from the table, hydrogenation of the samples lowers very greatly (by dozens of times) the number of all the dislocation states observed by the DLTS method in a subsurface layer up to 7–10 μm deep. An investigation of the charging kinetics of the centers shows that the amplitude of the peaks is limited now not by the Coulomb interaction of the trapped carriers, but by the number of centers. With this fact taken into account, it follows from the table that the density of all the dislocation states in hydrogenated samples, at a depth 1.5–2 μm does not exceed 5×10^{13} cm^{-3}, whereas the initial D-center density, obtained from EPR data, was not lower than 10^{16} cm^{-3}. We note that treatment of the samples in hydrogen-free (air) discharge under conditions does not alter the spectra noticeably.

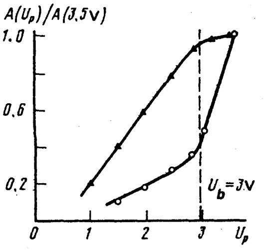

FIG. 4. Amplitudes of peaks of the states (2+4) vs. U_p in the presence (○) and absence (▲) of surface states. $U_b = 3$ V, $t_p = 40$ μsec, $\tau_e = 4$ μsec. ▲) No. 1; ○) No. 3, H, 7 μm.

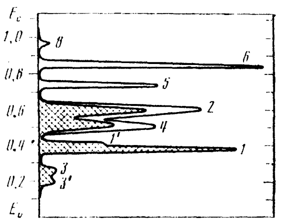

FIG. 5. Schematic representation of the energy spectrum of the dislocation states in samples No. 1 (n-type) and No. 12 (p-type). The states in the p-type sample are shaded (E_v and E_c are the energy levels corresponding to the top of the valence band and to the bottom of the conduction band, respectively).

In hydrogenated samples, the energy positions of the DLTS peaks correspond in first-order approximation to the energy scheme for nonhydrogenated samples (Fig. 5). A tendency can be noted, however, towards a de-

TABLE I. Number of captured electrons (n-type) or holes (p-type), 10^{14} cm^{-3}.

Level No.	3,3'	1,1'	2+4	5	6	8	7
Energy, rel. to E_v, eV	0.27–0.2	0.4	0.5–0.62	0.75	0.86	0.98	0.3÷0.4
№ 1	–	–	15	6	14	?	–
№ 12	0.8	10	10	–	–	–	–
№ 1, H, 1.5 μm	–	~0.3(?)	⩽0.2	~0.4	~0.3	0.1	–
№ 12, H, 1.5 μm	0.1	~0.2	~0.1	–	–	–	–
№ 1, H, 7 μm	–	0.6(?)	0.3	1	3	0.4	–
№ 12, H, 4 μm	0.3	0.4	0.6	–	–	–	–
№ 1, H, 7 μm, annealed 30 min at 500° C	–	–	6	2	16	0.5	–
№ 12, H, 7 μm, annealed 30 min at 500° C	1	5	7	–	–	–	–
№ 3	–	–	–	6	–	–	–
№ 3, H, 7 μm	–	–	–	0.2	–	–	–
№ 3, H, 11 μm	–	–	–	1	–	–	–
№ 3, H, 21 μm	–	–	–	4	–	–	–
№ 12, annealed 30 min at 780° C	0.8	–	–	–	–	–	0.7
№ 12, annealed 30 min at 780° C H, 4 μm	<0.1	–	–	–	–	–	<0.1
№ 12, annealed 30 min at 780° C H, 11 μm	0.8	–	–	–	–	–	0.6

Note. Sample No. 1) n-type, 1.5×10^{16} cm^{-3} P at., $\varepsilon = 2\%$; No. 12) p-type, 2×10^{16} cm^{-3} B at., $\varepsilon = 2\%$; No. 3) n-type, 4×10^{16} cm^{-3} P at., $\varepsilon = 2\%$, annealed 30 min. at 780 °C. The letter H means that the sample was hydrogenated, and the number indicates the thickness of the removed hydrogenated layer.

crease of the effective cross sections σ for center capture with increasing degree of hydrogenation (see Figs. 2 and 3). As follows from the same figures, one can clearly observe in hydrogenated samples the new peaks 3′ and 8, which are difficult to distinguish in nonhydrogenated samples. Their amplitudes, just as those of the other peaks, increase with increasing depth or with decreasing degree of hydrogenation. An analysis of the available data does not allow us to state that these centers are produced by the hydrogenation process.

Since the relation between the intensities of different spectrum peaks varies with depth in the hydrogenated samples, it can be though that the states 3, 3′ and 8 are hydrogenated at a smaller depth, and 2 + 4 and 1 at the largest depth. It is probably this which made it possible to observe distinctly the states 8 and 3′, whose density is low and which are maked by other peaks in nonhydrogenated samples. At present it is not finally clear whether this is due to the specifics of the diffusion of the hydrogen along the dislocations or to the difference between the binding energies of hydrogen atoms with various types of centers.

Thus, hydrogenation does not produce, in any significant concentrations, any new centers, at least in the range from $E_c-0.16$ eV to $E_v+0.16$ eV, which is "surveyed" by the DLTS spectrometer.

As follows from Fig. 2 and Table I, annealing of hydrogenated samples for 30 min at 500 °C does not restore significantly the intensities of practically any of the peaks. We have here again a manifestation of the logarithmic dependence of the peak amplitudes on the duration of the refilling pulses, thus pointing to a Coulomb limit on the occupation numbers of centers 1–7. Annealing for 1 hr at 500 °C does not change significantly the initial spectrum of the deformed sample.

We note that since the observed DLTS peaks are substantially broadened compared with the instrumental function, the density data listed in Table I may be somewhat underestimated. However, the absolute error does not exceed 100–150%, with the possible exception of states 7, where the "peak" is very broad.

DISCUSSION OF RESULTS

In our preceding[10] DLTS investigation of plastically deformed silicon we discussed the specifics of DLTS measurements in the case of dislocation states, and also discussed on the basis of a comparison of the results with Hall-effect, EPR, and photo-EPR data, the possible nature of the states 1–7 (see Table I and Fig. 5). This comparative analysis led us to the assumption that the states 1 are broken dislocation bonds (unpaired valence electrons), which produce the observed EPR signal, and the states 2 correspond to additional electrons captured by these broken bonds. States 3 are certain acceptor states that arise near the dislocation cores or in the dislocation cores during the course of the plastic deformation. Upon annealing of the plastically deformed samples at $T > 700$ °C the dislocation EPR signal vanishes, a fact that correlates with the vanishing of the states 1, 1′, and 2.[10,6] It can be assumed that this is the result of reconstruction of the dislocation cores, which leads to pairwise closing of the broken bonds.[6,12] One can therefore not exclude the possibility that the states 5 correspond to one of the types of the reconstructed dislocations, since the states 5 are not annihilated by this annealing.[10]

As mentioned above, according to the EPR data the number of broken bonds in samples deformed in analogy with samples 1 and 12, is of the order $(2-4)\times10^{16}$ cm^{-3}, i.e., larger by an order of magnitude than the number carriers captured by them (see Table I). This agrees with the fact that carrier capture is limited by the Coulomb interaction of the carriers with one another, and corresponds to the dislocation model. Indeed, estimates of the mutual Coulomb interaction of additional electron or holes captured by dislocation cores show that the ratio of their number to the number of atoms of the dislocation cores that can have broken bonds cannot exceed 10–20%. Therefore a decrease by even a factor of two in the DLTS peaks 1 and 2 that correspond to dislocation broken bonds, accompanied by the vanishing of the logarithmic dependence of the peak amplitudes on t_p, means in fact that the number of dislocation broken bonds having electric activity was decreased by at least 90%, i.e., by a factor of 10.

As already indicated above, the states 5 can be connected with reconstructed dislocations, i.e., dislocations whose cores are restructed in such a way that the broken bonds are pairwise joined. It can then be stated (see Fig. 2) that hydrogenation is effective both with respect to states connected with free dislocation broken bonds, and with respect to states connected with reconstructed dislocations. This follows also from experiments on annealed samples (see Table I) in which there is no EPR signal (see also Ref. 4).

Thus, if the reconstructed dislocation bonds correspond to definite (deep) states in the forbidden band, the following question arises: Which mechanism of hydrogen interaction with such dislocation leads to loss of their electric activity? It can be assumed that during the first hydrogenation state a "weak" Si–Si dislocation bond is broken in accord with reaction

$$\mathrm{Si{-}Si+H\rightarrow Si{-}H+Si{-}},$$

i.e., besides the Si–H bonds, broken bonds appear on the dislocations. At a certain (low) hydrogen concentration, the DLTS spectra of the annealed samples in which there is no dislocation EPR signal should then acquire peaks of states 1 and 2, corresponding to the dislocation broken bonds. Our attempts to observe in the experiments on dehydrogenation certain peaks corresponding to hydrogenation in DLTS spectra of samples annealed at 800 °C were, however, unsuccessful. It appears that no broken bonds appear upon hydrogenation.

On the other hand, the assumption that the reaction

$$\mathrm{Si{-}Si+2H\rightarrow Si{-}H+Si{-}H}$$

takes place immediately is hardly justified. Indeed, since this is reaction of second order in H, hydrogenation of the reconstructed bonds (of state 5) should proceed at a much slower rate compared with the broken bonds (states 1 and 2), but this is not observed.

A possible mechanism of interaction between hydrogen and the reconstructed dislocations is the formation of Si–H–Si bonds on the dislocations. A theoretical analysis of such a complex is contained in Ref. 13, where it is proposed that it plays an important role in the formation of the electronic properties of hydrogenated amorphous silicon. Favoring the existence of hydrogen bound in this manner in *a*-Si:H are also the results of Ref. 14.

In the case of amorphous silicon, however, as follows from Ref. 13, there can exist in the forbidden bond both shallow and deep levels connected with Si–H–Si. From our DLTS experiments it follows that if the indicated mechanism does take place, the states connected with the Si–H–Si dislocation chains are at any rate not deeper than ~0.16 eV.

It cannot be excluded that the reaction

$$\mathrm{Si{-}H{-}Si+H\rightarrow 2Si{-}H},$$

takes place subsequently and that the hydrogenation reduces to formation of Si–H bonds on the dislocations, just as in the case of the non-reconstructed dislocations. In this case the intermediate Si–H–Si complexes will likewise not lead apparently to deep levels, since they are not revealed by dehydrogenation experiments.

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Translated by J. G. Adashko