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Zn-related center in silicon: negative-$U$ properties

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Abstract. — Photo-EPR and Stark effect photocapacitance investigations of $^{67}$Zn-doped silicon have yielded an orthorhombic Zn-related center whose presence can only be observed under impurity light illumination. The spectral dependences of regeneration and quenching obtained for the EPR signal and photocapacitance at different values of anisotropic electric field reveal the negative-$U$ ordering for the center's acceptor levels, with the (0/-) level lying above the (+/-) level. The negative-$U$ properties of the center and the resonant nature of its $D^0 \leftrightarrow D^-$ and $D^- \leftrightarrow D^{--}$ optical transitions are modelled in terms of the tunneling performed by the reconstructed deep defect between the $D_{2d}$, $C_{2v}$ and $C_{3v}$ symmetry positions corresponding, to $D^0$, paramagnetic $D^-$ and $D^{--}$ states, respectively.

1. Introduction.

Deep centers in semiconductors are defects whose charge and spin correlations are compensated by local low-symmetry lattice distortions [1-10]. Anderson has shown that the result of a compensation of Coulombic repulsion between two electrons at a deep center can be the inversion of the negative-$U$ ordering for the corresponding levels of the defect [1]. The electron that is second to arrive at a two-electron deep center would have a greater binding energy than the first. Deep centers of this variety, represented by double donors, double acceptors and amphoteric defects, can be thought of as an analogue to the Cooper minima and they are usually referred to as negative-$U$ defects [1-9]. The centers formed by such defects are of two distinct kinds: they can be elastic, when the conditions for electron pairing are set by a large lattice relaxation due to the dynamic Jahn-Teller effect [1-4]; or they can be hard — in the case of a rigid lattice where the Coulombic repulsion is offset by the tunneling performed by the center in order to occupy the position of a symmetry corresponding to its charge state [5-8]. The first of the two respective versions proposed has been successfully exploited to clarify many aspects of self-compensation in chalcogenide glasses [1, 3, 4] and crystalline semiconductors [2], while the second has additionally thrown light on a number of issues related to deep defect metastability [5-9].

This paper reports, for the first time, the negative-$U$ properties for double acceptor centers in silicon, of which zinc — the object of the present work — is one of the most studied [11-16].
The data obtained using various techniques suggest that most Zn centers form complexes with shallow acceptors [11-14] and residual deep impurities [15, 16]. No models for these complexes, whose properties are those of double acceptors with usual level ordering, have yet been proposed, even though there are already definitive EPR identifications of CuZn and CrZn centers [17, 18]. Single Zn-centers have mostly been investigated by capacitance spectroscopy; Sah and Herman [13, 14] report a strong field dependence of the thermal emission rate for the \((0/-)\) holes, and they also point out a trend toward crossing in thermal emission rate values exhibited by holes from the two acceptor levels with decreasing strength of the applied electric field. In addition, a level at \(E_v + 0.167\) eV has been detected at field strengths below the value associated with the crossing [13]. These findings led us to hypothesize that the single Zn double-acceptor centers have field-dependent negative-\(U\) properties, which are only displayed at low electric fields. In the present study, the proof of this assumption has been realized through the photo-EPR experiment and photocapacitance spectra for different directions of the applied electric field relative to the crystallographic axes.

Firstly, the spectral distribution of the photoionization cross sections obtained for the orthorhombic Zn-related center (Si-N6L36) [17, 18] from the respective quenching and regeneration dependences yielded by the photo-EPR signals in silicon containing the \(^{67}\)Zn isotope is examined. The paramagnetic \(D^-\)-state of this double acceptor center could only be observed under impurity light pumping conditions as a result of spontaneous negative-\(U\) reaction, \(2D^- \rightarrow D^0 + D^-\), that leads to a nonparamagnetic state as the main state for the defect in the cooled crystal. Secondly, the negative-\(U\) ordering for (0/-)- and (−/−)-optical transitions is observed to be enhanced by the corresponding negative-\(U\) ordering for thermal emission energies to produce also a self-compensation for the Zn-related center (2 \(D^- \rightarrow D^0 + D^-\)), and to give rise to a photocapacitance quenching effect (2 \(D^- + h\nu \rightarrow D^0 + D^-\)). It is shown that the result of the subsequent optical pumping will be, depending on the value of \(h\nu\), either the regeneration or the quenching of the EPR and photocapacitance signals. The disappearance of the quenching effect at higher electric fields are interpreted as a result of a suppression suffered by the negative-\(U\) reaction in the presence of the Stark effect that causes crossing in the energy values for hole emission from the first and the second levels of the Zn-related center. Finally, a comprehensive study of the anisotropic nature of the influence that the electric field exerts on photocapacitance spectra in Si : Zn provides the conclusive confirmation of the orthorhombic \(C_{2v}\) symmetry for the paramagnetic \(D^-\)-state.

2. Experiment.

The photo-EPR studies were made on float-zone p-type silicon doped with boron to \(10^{13}\) cm\(^{-3}\). The diffusion of the \(^{67}\)Zn isotope was carried out in sealed quartz tubes at 1 200 °C. In order to ensure a homogeneous distribution of the zinc impurity, the diffusion process was allowed to run for periods of time of up to 40 h. On completion of the diffusion step, the ampoules were quenched to room temperature. Subsequent preparation of the samples included polishing and etching. The total zinc concentration, determined from Hall effect measurements, was on the order of \(10^{16}\) cm\(^{-3}\).

The photo-EPR measurements were performed on X-band EPR spectrometer using samples cooled to 4.2 K. The exploratory tool of orthorhombic Zn-centers (Si-N6L36) was optical pumping. Both the photo-EPR signal and the variations in its amplitude were induced by incandescent light; the monochromatic beam had access to the sample through a quartz window in the cryostat.

The photocapacitance investigations were also employed to identify the model of the Zn-related center. This was made possible by extending the method of capacitance spectroscopy to
Stark-effect measurements. While the standard technique can only provide information on the energy characteristics of a point defect but is unable to locate it in the crystal lattice, the Stark-effect version can perform this function using an investigation of the capacitance signal against the direction in which electric field \([10, 19]\) is applied relative to the crystallographic axes of the Si : Zn single crystal. The present work, therefore, used a photocapacitance analogue of the Stark-effect spectroscopy to study the relationship between negative-\(U\) properties and the charge state's symmetry of the orthorhombic Zn-related center in silicon. The \(n^+ p\) junctions employed for the study were fabricated by conventional planar technology on the face perpendicular to the length of silicon single crystals, which was oriented along \([111], [100]\) or \([110]\) direction. The electric field in the \(n^+ p\) junctions could thus be oriented strictly along the selected crystallographic axis. Diffusion of zinc into these diodes was carried out in sealed quartz ampoules evacuated to \(10^{-6}\) Torr. The boron doping doses and zinc diffusion temperatures were chosen so that the concentration of Zn in the samples amounted to 10% of that of the majority impurity. The photocapacitance spectra were recorded at various values of the electric field on samples cooled to 92 K in a cold finger cryostat were cooling took place under reverse bias conditions. Variations in photocapacitance were photogenerated by allowing the monochromatic light from an incandescent lamp outfitted with a double monochromator.

3. Results.

3.1 PHOTO-EPR DATA. — The Si-NL36 EPR spectrum obtained for Si : \(^{67}\)Zn is presented in figure 1. The sixfold splitting that is evident in this EPR spectrum provides strong evidence for a \(^{67}\)Zn atom as the center's nucleus \((l = 5/2)\). The angular dependence of the Si-NL36 EPR spectrum fits closely the dihedral model \([17, 20]\), suggesting an orthorhombic crystal structure for the paramagnetic state of the Zn-related center, which appears only in the presence of optical pumping with impurity light (see Fig. 1a).

When considering the actual regeneration/quenching processes, it should be remembered that there are two interrelated deep acceptor levels for Zn-related centers in the gap of silicon (Fig. 2). Thus, the reaction leading to regeneration of orthorhombic Zn-related centers, and hence the photo-EPR signal, can proceed \textit{via} both \(D^0 \rightarrow D^-\) and \(D^- \rightarrow D^+\) optical transitions (the respective photo-ionization cross sections being \(\sigma_p\) and \(\sigma_n\)). The corresponding pathways for the quenching reaction are \(D^- \rightarrow D^{--}\) \((\sigma_{p}^\prime)\) and \(D^- \rightarrow D^0(\sigma_{n}^\prime)\) optical transitions. In view of this, the failure of the EPR spectrum to regenerate immediately after cooling in the p-type silicon sample is unambiguous evidence that the neutral, \(D_0\), state of the Zn center under study is nonparamagnetic, as is, in all probability the two electron \(D^{--}\) state. The latter conclusion is supported by the complex form displayed by the corresponding spectral photo-EPR curve, figure 1a, where the alternating regions of quenching and regeneration are reminiscent of the curves commonly associated with the two-level systems having the \(D^-\) state as the paramagnetic one \([7, 8, 18]\).

The time dependences obtained for photo-EPR quenching and regeneration processes were used to derive the photo-ionization cross sections (Fig. 1b). These turned out to agree well with the spectral distribution of the photo-EPR signals recorded, thus establishing the resonance character for the \(D^0 \leftrightarrow D^-\) and \(D^- \leftrightarrow D^{--}\) optical transitions. The observation of a much shorter duration for the above photo-EPR processes in the presence of optical pumping than without it is indicative of the metastable nature of the orthorhombic Zn-related center.

The approach we use in the analysis of the photo-EPR spectral dependences can be best understood in terms of two-electron adiabatic potentials \([7, 8]\); in figure 2 they are presented in the form adapted to the case of the deep double acceptor. Since the full effective charge of a
Fig. 1. — (a) Spectral dependence of quenching and regeneration for the EPR signal (NL36) from Si: ⁶⁷Zn. (b) Spectral dependences \( \sigma_n(\mathcal{O}) \) and \( \sigma_p(\bullet) \) for the orthorhombic Zn-related center in silicon (Si-NL36). Inset: Si-NL36 EPR spectrum in Si: ⁶⁷Zn, \( B_1(100) \).

deep center is related to the occupation number of electrons, it necessarily follows, as figure 2 shows, that in each of its states: the two-electron \( D^- (-n = 2) \), the one-electron \( D^- (-n = 1) \), and the empty \( D^0 \)-state, the center should occupy different positions in the lattice when the electron-vibration interaction (EVI) constant has a nonmonotonic dependence on the center’s charge state, as it does in the absence of any significant lattice relaxation [7, 8]. The equivalent one-electron band diagram, also shown in figure 2, should therefore incorporate two levels — one for the background \( (0/- = E_c - I_1) \) and one for the correlated \( (-/- = E_c - \Delta I) \) electron — so as to allow for the full complement of the center’s charge states; here \( I_2 = I_1 + \Delta I \). Considered from this viewpoint, the maxima seen on the spectral distribution curves of figures 1a and b make up several self-consistent pairs; with each
Fig. 2. — Two-electron adiabatic potentials and equivalent band diagram for the Zn-related center in p-type silicon. (a) $E = 0$; (b) $E_1 [111]$; Configuration coordinates $Q_1$, $Q_2$ and $Q_3$ correspond to directions in silicon lattice (see Fig. 4).

pair corresponding to the quantum energies associated with the $D^0 \rightarrow D^-$, $D^- \rightarrow D^0$ and $D^- \rightarrow D^{--}$, $D^{--} \rightarrow D^-$ transitions.

In this picture, therefore the enhancement of the photo-EPR signal at $h\nu > 0.475$ eV, seen in figures 1a and b, is attributable to a production of the $D^-$ paramagnetic state as a result of the $(+/- - /-)$ optical transition that accompanies the photocapture of holes induced optically from residual deep centers, in particular CuZn pairs [18]

$$D^{--} + h + h\nu \rightarrow D^-$$  

(1)

The spectral minimum observed here for the photo-EPR signal at $h\nu = 0.575$ eV must, in its turn, be due to the $D^- \rightarrow D^{--}$ optical transition resulting in the transfer of the center from the valence band to the second acceptor level (see Fig. 2):

$$D^- + h\nu \rightarrow D^{--} + h.$$  

(2)

A straightforward identification of the observed center with a common double acceptor with positive-$U$ ordering has two problems. The first problem is that a jump made by the photo-EPR signal at $h\nu > 0.6$ eV is at variance with the $\sigma_{n_2} < \sigma_{p_2}$ relationship established for double acceptors in p-type silicon, and it would also be difficult to account for this jump in terms of the
emission of electrons to the conduction band from the defects in the $D^-\cdot$-state. In the light of the above two-electron adiabatic potentials scheme, we are proposing, instead, that the factor responsible for this effect is the enhancement of the emission of holes as a result of $(0/-)$ optical transitions

$$D^0 + h\nu \rightarrow D^- + h.$$  \hspace{1cm} (3)

As demonstrated by figure 3, the other problem is the difference in magnitude recorded between the initial and the final values of the photo-EPR signal after an excitation/relaxation event, the first part of which was caused by prolonged optical pumping with $0.525 < h\nu < 0.575$ eV light. The most satisfactory explanation for this observation would seem to be the metastability and negative-$U$ ordering as the inherent properties of acceptor levels arising from a competition between the hole photocapture process, $D^-\cdot \rightarrow D^-\cdot$ (1), and the hole photoemission, $D^- \rightarrow D^-\cdot$, that can be accompanied by the hole Auger-capture process:

$$D^- + h\nu \rightarrow D^-\cdot + h$$

$$D^- + h \rightarrow D^0$$ \hspace{1cm} (4)

Fig. 3. — Time dependences for the photo-EPR (Si-NL36) signal (a) $h\nu = 0.525$ eV, (b) $h\nu = 0.525$ eV plus subsequent relaxation after light off.
In other words, the competition between processes (1) and (4) resolves into an optically induced metastable negative-U reaction of the form

\[ 2 \text{D}^- + h\nu \rightarrow \text{D}^{--} + \text{D}^0 \]  

(5)

Supporting evidence that the Auger reaction involving \text{D}^{--}-state does occur — in the form of a spontaneous Auger-dissociation process (negative-U reaction) [2], as it happens — is provided by two times the quenching value observed for the photo-EPR signal on turning off the light \((h\nu > 0.525 \text{ eV})\) at the initial stages of pumping:

\[ \text{D}^0 + h\nu \rightarrow \text{D}^- + h \Rightarrow \text{light off} \Rightarrow \text{D}^- + h \rightarrow \text{D}^0 \Leftrightarrow \text{D}^- \rightarrow \text{D}^{--} + h \]

\[ 2 \text{D}^- \rightarrow \text{D}^{--} + \text{D}^0 \]

(6)

These results suggest that rather than being an ordinary double acceptor, the orthorhombic Zn-related center is a negative-U defect with a paramagnetic state that would readily dissociate into \text{D}^{--} and \text{D}^0 states, provided the sample is cooled. The crucial role of the latter condition is demonstrated by the fact that before application of optical pumping the value of the EPR signal is very low but finite, although it should not be present at all. The reason is again the metastable nature of the defect, which favors its «freezing» in the \text{D}^- -state. This obstacle to dissociation of the \text{D}^- -state is removed however, as figure 3 shows, by the pumped light which gives rise to the above described reaction (5). The dissociation reaction so stimulated proceeds so vigorously that it leaves virtually none of the paramagnetic \text{D}^- -state in the sample, see figure 3. Figure 2 provides a plausible explanation of the causal relationship between the «frozen» condition of the one-electron state and the metastable nature of negative-U defects in the form of the barriers separating the terms that belong to different charge states. It should be noted that the differences between the energies of the two-electron adiabatic potential minima in figure 2 represent the Hall energies for \((0/ -)\) and \((- / - -)\) transitions, which have been determined as \(E_v + 0.2 \text{ eV}\) and \(E_v + 0.17 \text{ eV}\), respectively, using the photo-Hall technique [21]. The notion of a special origin of the «frozen» \text{D}^- -state as reflected in the relatively small number of such centers is further supported by the consideration that, in general, there is no position on the Fermi level where the \text{D}^- -state can be thermodynamically stable. In the case of \(2E_F > E_A + E_D\), thermodynamic equilibrium considerations suggest that all the defects should be in the \text{D}^{--}-state. Conversely, under the \(2E_F < E_A + E_D\) conditions, all the defects will be in the \text{D}^0-state. The \(2E_F = E_A + E_D\) condition must, in its turn, produce a mixture comprising solely neutral and two-electron states. It is noteworthy that all of the above features, which we regard as a manifestation of the negative-U properties of orthorhombic Zn-related centers, have been consistently revealed by the same centers in n-type silicon [21]. In the context of the present discussion of the p-type silicon, the most important argument for the negative-U properties of double acceptors is that these properties can be observed only in the presence of reactions (5) and (6).

Increasing the pumping light energy to over 0.8 eV produces rapid quenching of the EPR signal, figure 1, by causing the electrons to be stripped off the centers in the \text{D}^- -state and exciting them to the conduction band:

\[ \text{D}^- + h\nu \rightarrow \text{D}^0 + e^- \]  

(7)

In terms of efficiency, this process exceeds the emission of electrons and holes that is driven by the EVI-charge correlations mechanism. The drop in the photo-EPR signal observed on application of short wavelength light could, in principle, be due to capturing photoexcited holes at the \text{D}^- -state, especially in view of the bandgap absorption as the background for the reaction. However, each of the various values of the spectral minimum (or alternatively, the
maximum in the case of \( \sigma_n \) recorded experimentally under high energy illumination conditions was found to be associated with a specific type of the Zn-related center [21]. This observation provides compelling evidence for the dominant role played by the electron emission reaction (7) in the quenching of the photo-EPR signal at \( h\nu > 0.8 \text{ eV} \). Similar origin of the \( \sigma_n \) maximum, in the case of \( h\nu = 1.25 \text{ eV} \), was established from the self-consistency in the energies required for the \( D^0 \rightarrow D^- + h \) optical transition as opposed to the \( D^- \rightarrow D^0 + e \) optical transition. These experiments have additionally confirmed the correctness of the adiabatic potential scheme.

The results described above, which are obtained for the spectral dependences of the photo-EPR signal and the \( \sigma_m \) photo-ionization cross sections, imply that the \( D^0 \leftrightarrow D^- \) and \( D^- \leftrightarrow D^{--} \) optical transitions must occur in resonance, which, in turn, means that the separations between the positions occupied by the orthorhombic Zn-related center in its different charge states, i.e. the configurational shifts \( Q'_1, Q'_2 \) and \( Q'_3 \) can be estimated. We propose to accomplish this task by means of a model that is described below.

3.2 Model. — A strong interrelationship between charge correlations and low-symmetry lattice distortions, now established for most deep centers [1-10], forms the basis of the present model for Zn-related centers. Given a nonmonotonic dependence of the EVI constant on the number of electrons present at the center, it is to be expected that in each of its charge states the center will occupy a unique equilibrium position in the lattice, possessing a local effective correlation energy \( U \) of a given magnitude and sign [7, 8].

Figure 4 shows that the two-electron adiabatic potentials scheme embodying the above concept as its principle for localizing the center’s charge states is a true representation of the real lattice space inasmuch as it is capable of taking the different directions of the actual configurational coordinates into account [7, 8, 10]. Based on figures 2 and 4, we find excellent agreement between the ratio of \( Q'_1 : Q'_2 : Q'_3 \) values as determined from the present photo-EPR data and the ratio of distances separating the interstitial positions — \( D_{2d} \), \( C_{2v} \) and \( C_{3v} \) — occupied by the deep center in the real lattice. This knowledge allows us to construct a model for the single Zn center in silicon, which is presented in figure 4. The model suggests that the location for the reconstructed double acceptor, \( D^{--} = (\text{Zn}, V_{\text{Si}})^- \) (\( n = 2 \)), is the \( C_{3v} \) tetrahedral interstitial position (see, for example, Ref. [22]), while the possible positions for the center in its one-electron \( D^- = (\text{Zn}, V_{\text{Si}})^- \) state (\( n = 1 \)) and empty \( D^0 = (\text{Zn}, V_{\text{Si}})^0 \) state (\( n = 0 \)) must be such as to satisfy the symmetry conditions imposed, respectively, by \( C_{2v} \) and \( D_{2d} \). Figure 4 demonstrates that the orthorhombic Zn-related center fully meets the \( C_{2v} \)-symmetry requirement. Our model further postulates [7, 8] that any change in the center’s charge state will cause the reconstructed defect to tunnel from one of its equilibrium positions to the other. This tunneling movement by the center between the \( C_{3v} \), \( C_{2v} \) and \( D_{2d} \)-symmetry positions is to compensate for the Coulombic repulsion of electrons in the presence of a sufficiently rigid lattice. Because of its negative-\( U \) properties, the orthorhombic Zn-related center in the \( D^- \)-state is unstable under the \( C_{2v} \)-symmetry conditions, and should therefore transit — through a spontaneous dissociation reaction — to either \( D^{--} \)- or \( D^- \)-state, thus changing its symmetry position to \( C_{3v} \) or \( D_{2d} \) respectively. The center may subsequently revert to its initial state, however, having absorbed or emitted a charge particle owing to impurity light illumination (Fig. 4).

The corresponding reactions were treated using the two-electron adiabatic potentials diagram (Figs. 2 and 4), yielding the following thermal and optical ionization energies for the negative-\( U \) Zn-related center:

\[
D^0 \rightarrow D^- \Rightarrow E_v + 0.25 \text{ eV} ; \quad E_v + 0.62 \text{ eV} \\
D^- \rightarrow D^{--} \Rightarrow E_v + 0.19 \text{ eV} ; \quad E_v + 0.5 \text{ eV} .
\]
As can be seen in figures 2 and 4, our Hall effect data for the defect ionization energies correspond to the gaps between the minima representing the D$^{-}$ and D$^{++}$ transitions in the diagram, while the values obtained for the thermal ionization energies take into account the barrier to be overcome by the center as it tunnels between different charge states.

We shall conclude this discussion with two brief remarks. The defect behavior virtually similar to the $T_d \leftrightarrow D_{2d} \leftrightarrow C_{2v}$ transitions performed by the center as it changes its charge state.
has been reported for oxygen therm donors [23], interstitial boron [2] and the gold-related center [24] in silicon. The adiabatic potentials of charged (D~ and D\textsuperscript{−}) states experience a shift from the fixed C\textsubscript{2V}- and C\textsubscript{3V}-symmetry positions under the action of the Stark-effect induced by applied or internal electric fields [8], which is the basis of the photocapacitance spectroscopy in anisotropic electric fields.

3.3 Stark-effect spectroscopic data. — Since the Zn-related centers in silicon give rise to two interrelated deep acceptor levels, illuminating the p-type samples with impurity light, it should be possible to induce emission of holes, thus providing the basis for photocapacitance studies. The results of an experiment carried out along these lines for different values of anisotropic electric field in Si:Zn are shown in figure 5.

Following a zero bias pulse that set the initial hole occupancy, reverse bias was applied that caused most levels in the depletion region to be filled with holes. If the temperature conditions of the experiment are appropriate for thermal emission of holes from either or both impurity levels, then one should expect a gradual rise in the capacitance signal. This is just what was observed at \( V_R = 20 \) V (\( E_1 \{111\} \)), figure 5a. No such rise, however, was observed when \( V_R = 1 \) V was applied, figure 5 (a, b and c). Instead, after the « short-circuiting » step, the photocapacitance continued to decline dramatically at a rate that could be made still faster by the application of optical pumping (0.3 eV < \( h\nu < 0.5 \) eV). Since all defects with normal level ordering that populate the lower half of the energy gap would normally be expected to induce photo- and thermoemission of holes (with a corresponding enhancement in the photocapacitance signal), the anomalous behavior exhibited by zinc for weak electric fields in that it tends to stabilize the emitted holes within the bounds of the depletion region should be interpreted as the result of a negative-\( U \) reaction (either thermal or optical origin): \( 2 \) D\textsuperscript{−} = D\textsuperscript{0} + D\textsuperscript{−} (92 K, 0.3 eV < \( h\nu < 0.5 \) eV), and in any case, could serve as a signature of a defect with negative-\( U \) level ordering.

The enhancement of the photocapacitance signal at \( h\nu = 0.5 \) eV, figure 5 (a and c), might well be taken as evidence of the hole photoemission induced by (−/−) optical transitions from residual Zn\textsuperscript{−} states closed to the bound of the depletion region.

The stabilization of photoholes within the depletion region has been again recorded at 0.55 eV < \( h\nu < 0.62 \) eV, figure 5. At this energy the photocapacitance signal first showed an increase with time of optical pumping, and then a decrease with the final amplitude being less than its initial value. This observation constitutes convincing evidence for the photodissociation of residual Zn\textsuperscript{−} states as a result of the Auger process of the type (4)-(6) depending on the distance between the Zn-related center and the bound of the depletion region: at 0.5 eV < \( h\nu < 0.55 \) eV \( \rightarrow \) D\textsuperscript{−} + \( h\nu \rightarrow \) D\textsuperscript{−} + D\textsuperscript{0}; at 0.55 eV < \( h\nu < 0.62 \) eV \( \rightarrow \) 2 D\textsuperscript{−} + \( h\nu \rightarrow \) D\textsuperscript{−} + D\textsuperscript{0}. Thus, the competition between (−/−) and (−/0)-transitions would account for the observation of a double quenching experienced by both photocapacitance signal at 0.55 eV < \( h\nu < 0.62 \) eV, figure 5 (a and c), and its kinetic dependence at \( h\nu = 0.55 \) eV, figure 5a.

Further increase of the pumping light energy at \( V_R = 1 \) V, figure 5, led to an enhancement in the photocapacitance, due to an increased rate for the (0/−) transitions, and it was only at much higher illumination energies, which made it possible for electrons emitting from charged zinc centers to cross over to the conduction band, that a somewhat slower rise of the photocapacitance was observed.

It follows that the likeliest candidate for a mechanism that would account for the precipitous photocapacitance drop is the negative-\( U \) reaction that has already been mentioned, viz. 2 D\textsuperscript{−} = D\textsuperscript{−} + D\textsuperscript{0}. This reaction takes place when lowering the temperature in the sample from 293 K to 92 K, and it gives rise to the Zn-related center in the D\textsuperscript{−}-state when operating beyond the depletion region, but the centers that arise from its operation within the depletion
Fig. 5. — Spectral dependence of photocapacitance for p-Si:Zn. (a) $E_I [111]$, (b) $E_I [100]$, (c) $E_I [110]$. 1) $V_R = 1$ V, 2) $V_R = 20$ V. Inset: kinetic dependence of the photocapacitance signal in Si:Zn at $h \nu = 0.55$ eV.

region are all in the $D^-^-$ state. As a result of equalization in total charge between the inside and outside of the depletion region that sets in on application of a zero bias pulse, the $D^-^-$-states within the depletion region convert to $D^-^-$-states through capture of a hole $D^-^+ + h \rightarrow D^-$. When reverse bias is then applied, the negative-$U$ reaction gains substantial impetus, making the depletion region narrower and causing the concomitant drop in the
photocapacitance signal we recorded in the experiment, figure 5. After « short-circuiting » step the residual $D^-$-states remain only near the bound of the depletion region and dissociate at 0.55 eV < $h\nu$ < 0.62 eV ($2D^- + h\nu \rightarrow D^0 + D^-^\cdot$).

It can be seen that the direction of the electric field can either oppose or promote the negative-$U$ reaction, cf. $E_1$[111] and $E_1$[100] in figure 5. In the first case, the effect of the increasing field is to quickly suppress the thermally and optically induced self-compensation, figure 5a. In the second case, it is to accelerate the photocapacitance quenching process, figure 5c. Anisotropic influence of the electric field on the photocapacitance spectra bears evidence of a link that exists between the negative-$U$ properties and the field-dependent metastability mechanism of the Zn-related center in silicon. Figure 2 suggests that there is a definite relationship between the rigidity of deep centers and therefore the probability for the above described processes of photocapacitance quenching and regeneration, on the one hand, and the magnitudes of the ratio of the $Q_1$, $Q_2$ and $Q_3$ values on the other. The presence of the Stark effect contributes significantly to making these values highly sensitive to the applied electric field. Indeed, as can be seen in figure 2, the negative-$U$ properties of the Zn-related center are suppressed under the action of the linear and quadratic Stark-effects [7, 8, 10] which arise from the applied electric field and induce the shifts of the adiabatic potentials of charged states ($D^-$ and $D^-^\cdot$) from the fixed C$_{2V}$- and C$_{3V}$-interstitial positions, see figures 2 and 6. The magnitudes of these shifts responsible for the metastable behavior of the Zn-related center depend on its charge state and the angle at which the electric field $E$ is inclined to the [110] and [111] crystallographic directions: $\delta Q'_1 = (2eE/\kappa) \cos \Theta_1$; $\Theta_1 = [E_1[111]]$; $\delta Q'_2 = (eE/\kappa) \cos \Theta_2$; $\Theta_2 = [E_1[110]]$, where $\kappa$ is the force constant for the defect’s local vibration mode. Thus, despite the negative-$U$ ordering of the lower and the upper levels, the metastability induced by the Stark effect prevents the spontaneous dissociation of the $D^-$-state, figures 2, 4 and 6. Subsequent optical pumping promotes the enhancement in the photocapacitance signal because of the effective photoemission of holes: $D^0 + h\nu \rightarrow D^-^\cdot + h$; $D^- + h\nu \rightarrow D^-^\cdot + h$.

By fitting the experimental values obtained in figure 5 to the fixed separations between « ideal » C$_{3V}$, C$_{2V}$ and D$_{2d}$ lattice positions, see figures 2, 4 and 6, it is possible to determine the direction for the short-range anisotropic Stark interaction and hence confirm the C$_{2V}$-symmetry of the Zn-unstable state.

Thus, Stark-effect measurements performed on Si:Zn samples placed is an anisotropic electric field have confirmed the tunneling nature of the Zn-related center and supported the assignment of the $D^-^\cdot$, unstable $D^-$ and $D^0$ states to interstitial positions with C$_{3V}$-, C$_{2V}$- and D$_{2d}$-symmetry, respectively, in silicon lattice. The measurements also showed that the anisotropic electric field is a controlling factor in interrelation of negative-$U$ properties and metastability of deep defects in semiconductors.

4. Summary.

An photo-EPR and Stark-effect spectroscopic study have yielded Si-NL36 orthorhombic Zn-related center in silicon, which is observable only under the impurity light illumination conditions and is a likely candidate for the $D^-$-state of a single acceptor. The spectral dependences of regeneration and quenching for the EPR signal and the photocapacitance in electric fields oriented along crystallographic axes in Si:Zn provide convincing evidence for inversion of the first and the second acceptor levels to produce negative-$U$ ordering. The driving force for the negative-$U$ reaction involving double acceptors in p-type silicon has been identified as Auger recombination of photoexcited carriers. To account for the center’s negative-$U$ properties and the resonant mode of its $D^0 \leftrightarrow D^-$ and $D^- \leftrightarrow D^-^\cdot$ optical transitions, a model for the reconstructed double acceptor has been proposed, based on the
tunneling by the center between C\textsubscript{3v}, C\textsubscript{2v} and D\textsubscript{2d} interstitial positions in accordance with its charge state. In the model, the orthorhombic D\textsuperscript{−}-state of a single Zn-related center, which is unstable, dissociates spontaneously into those of D\textsuperscript{−−} or D\textsuperscript{0}, from which states the center tunnels back to its nonequilibrium position characterized by C\textsubscript{2v} symmetry through D\textsuperscript{0} → D\textsuperscript{−} or D\textsuperscript{−−} → D\textsuperscript{−} transitions induced by the pumped light.

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References


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