Anisotropic Stark effect at a deep center in silicon

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An anisotropic Stark effect at a deep center with a negative correlation energy in a silicon lattice has been studied. The effect is seen as a sharp change in the photocapacitance as the direction of the external electric field with respect to the crystallographic axes is varied.

Deep centers in semiconductors have interrelated charge and spin correlations with local low-symmetry lattice distortions.[1–5] Anderson[1] has shown that this cancellation of the Coulomb repulsion may lead to an inversion in the order of levels (negative-U properties) for the first and second electrons which are trapped at a doubly charged deep center. In this case, the deep center is an analog of a Cooper pair with a small correlation length. Negative-U properties are exhibited by deep defects of two types: "elastic" defects, in which the electron pairing stems from a pronounced relaxation of the lattice due to a dynamic Jahn-Teller effect,[1–3] and "rigid" (metastable) defects, for which the Coulomb repulsion is offset by a tunneling of the center between sites of different symmetry in the lattice.[4,5] In addition, the dependence of the electron-vibration interaction on the number of electrons at a center stimulates linear and quadratic Stark effects.[5] In an external electric field, these Stark effects control the metastability of the deep defect and may therefore induce or suppress negative-U properties.

In the present letter we illustrate the important role played by the Stark effects in studies of the interrelation between metastability and negative-U properties of deep defects, using as examples the results of photocapacitance studies of a double zinc acceptor in silicon. We demonstrate the advantages of using an electric field which is oriented along certain crystallographic axes in the capacitance spectroscopy. With the appropriate orientation, the capabilities of this type of spectroscopy for identifying models of deep defects in semiconductors are substantially improved.

The photocapacitance study of zinc-doped planar n^+p diodes was carried out at $T = 92$ K. The conditions for the zinc diffusion were selected to bring the zinc concentration to a level on the order of 10% of the initial concentration of the boron dopant. The spectrum of the photocapacitance signal was recorded for various values of the electric field as the samples were illuminated with monochromatic light. The light source was an incandescent lamp with a double monochromator. In its usual form, the method of capacitance spectroscopy provides information on only the energy characteristics of the point center of interest. It is essentially useless for identifying the position of this center in the crystal lattice. However, that information can be provided by piezoelectric and Stark-effect versions of the method, which make it possible to study the behavior of the capacitance signal as a function of the direction of a uniaxial compression[6] and of an electric field[7] with respect to the Si:Zn crystallographic axes.

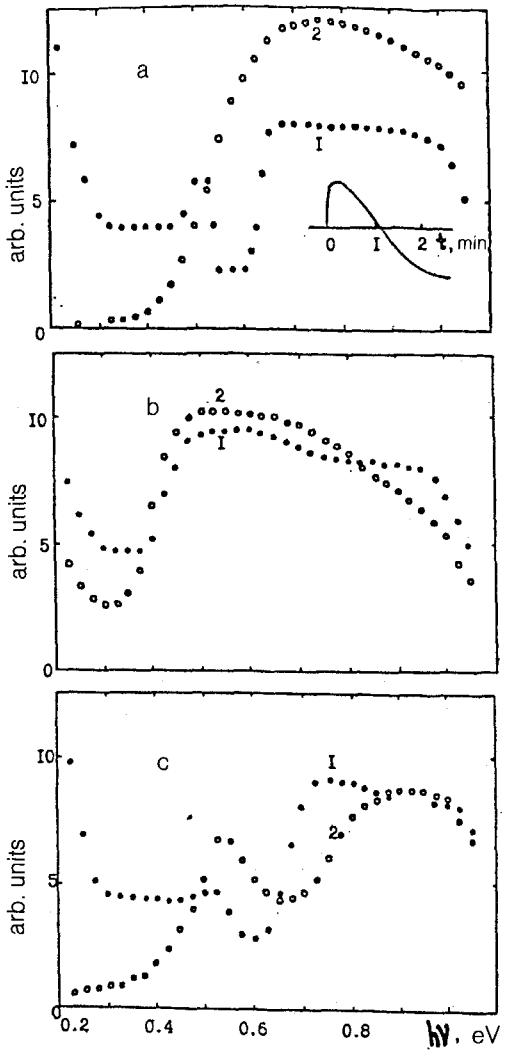

FIG. 1. Spectra of the photocapacitance in Si:Zn for various orientations of the electric field. a: E‖[111]), b: E‖[100]), c: E‖[110]). 1—$V_R = 1$ V; 2—$V_R = 20$ V. The inset shows the kinetics of the photocapacitance in the case $h\nu = 0.55$ eV, $V_R = 1$ V, (E‖[111]).

Accordingly, the n^+p junctions studied in the present experiments were placed strictly perpendicular to an edge of the single crystal oriented along one of the crystallographic axes ([111], [100], or [110]). This measure made it possible to orient the electric field along a specific crystallographic direction.

Figure 1 shows spectral curves of the photocapacitance of Si:Zn for various values of the anisotropic electric field. We see that the orientation and the strength of the electric field can have either a stimulating effect or a retarding effect on the $Zn^0 \rightarrow Zn^-$

and $Zn^- \rightarrow Zn^{--}$ optical transitions, which are responsible for the increase in the photocapacitance in p-type silicon. This result is a bit surprising, since, for the standard order of levels of the double zinc acceptor in the band gap of silicon, thermal and optical transitions of the (valence band)-(extrinsic level) type should always lead to an increase in the capacitance signal.[8] However, this increase in the photocapacitance is observed only in strong electric fields, in the orientations $\mathbf{E}\|[111]$ and $\mathbf{E}\|[110]$ (Fig. 1). In a weak electric field, in any of the three orientations, we detected a dramatic quenching of the photocapacitance after the samples were cooled and "short-circuited" ($V_R = 1\ \text{V} \rightarrow V_R = 0 \rightarrow V_R = 1\ \text{V}$). This quenching was accelerated at $h\nu < 0.4$ eV (Fig. 1). If the acceptor levels of the point center are in the standard order, then in the initial stage of the short-circuiting, as the electric field across the n^+p junction is reduced to zero ($V_R = 0$), the electrons leave these levels because of recombination with the injected holes. This effect is seen as a decrease in the capacitance signal. The subsequent increase in the electric field ($V_R > 0$) induces a thermionic emission of photoemission of holes ($Zn^- \rightarrow Zn^{--} + h$). These effects should be accompanied by a progressive increase in the capacitance of the test sample. The anomalous quenching of the capacitance signal in weak electric fields ($V_R = 1$ V) is thus unambiguous evidence of a stabilization of holes near the n^+p junction (a contraction of the depletion region). This conclusion is in turn an attribute of a negative-U reaction triggered by the short-circuiting

$$2Zn^- \rightarrow Zn^{--} + Zn^0 \Leftrightarrow Zn^- \rightarrow Zn^{--} + h,\ \ Zn^- + h \rightarrow Zn^0. \qquad (1)$$

Since the Zn^- centers are in progressively stronger fields with distance from the boundaries of the depletion region into the n^+p junction, light with an energy greater than $h\nu = 0.4$ eV is required for photodissociation of the residual concentration of these centers. This photodissociation of Zn^- centers, accompanied by a further contraction of the depletion region, was observed at $0.55\ \text{eV} \leqslant h\nu \leqslant 0.62$ eV in the electric field orientations $\mathbf{E}\|[111]$ and $\mathbf{E}\|[110]$ (Fig. 1, a and c):

$$2Zn^- + h\nu \rightarrow Zn^{--} + Zn^0 \Leftrightarrow Zn^- + h\nu \rightarrow Zn^{--} + h,\ \ Zn^- + h \rightarrow Zn^0. \qquad (2)$$

A negative-U mechanism for the photodissociation of the zinc centers is also supported by two experimental results: The positive step ($h\nu < 0.55$ eV) and the negative one ($h\nu < 0.62$ eV) in the photocapacitance are equal (these steps correspond to the generation and capture of a photoexcited hole). The kinetics of the photocapacitance at $h\nu = 0.55$ eV accurately reflects the kinetics of a negative-U reaction (Fig. 1). With a further increase in the energy of the pump photon, the negative-U reaction is suppressed by the progressively increasing contribution from $(0/-)$ transitions ($h\nu > 0.6$ eV). These transitions remain predominant up to $h\nu > 1$ eV, at which point the quenching of the photocapacitance due to optical transitions of electrons into the conduction band, $Zn^{--} + h\nu \rightarrow Zn^- + e$, $Zn^- + h\nu \rightarrow Zn^0 + e$, is stimulated. The spectra of the photocapacitance thus indicate that the double zinc acceptor in silicon is a negative-U defect with optical ionization potentials $E_v + 0.62$ eV and $E_v + 0.5$ eV for the first $(0/-)$ and second $(-/--)$ levels, respectively.

As was mentioned above, the orientation of the electric field affects the quenching of the photocapacitance. This effect is seen most vividly in the orientations $\mathbf{E}\|[111]$

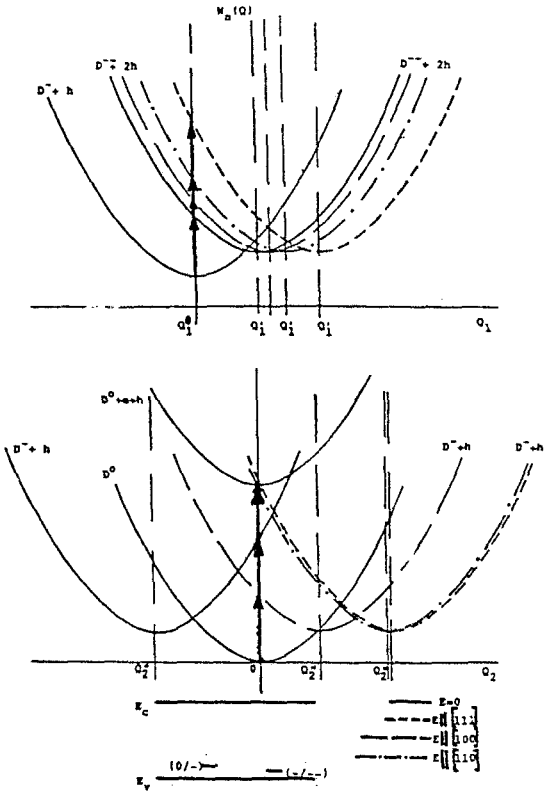

FIG. 2. Two-electron adiabatic potentials and equivalent one-electron band scheme of a zinc center in silicon. The arrows show optical transitions.

and $\mathbf{E}\|[100]$ (Fig. 1). In the first case, there is a complete suppression of the negative-U reaction, (1), with increasing electric field. In the second case, we see instead an activation of this reaction. The anisotropic effect of the electric field on the photocapacitance spectra is thus evidence of an interrelation between the negative-U properties and the symmetry of the various charge states of the zinc center in silicon. The dynamics of the change in the energies of the resonant $Zn^{-}\leftrightarrow Zn^{--}$ and $Zn^{0}\leftrightarrow Zn^{-}$ optical transitions in an electric field is described on the basis of the model of a deep reconstructed defect which undergoes a tunneling between interstitial positions of different symmetries in the course of a charge exchange: $D_{2d}(D^0=(Zn_iV_{Si})^0)$, $C_{2V}(D^-=(Zn_iV_{Si})^-)$, $C_{3V}(D^{--}=(Zn_iV_{Si})^{--})$ (Figs. 2 and 3). They may change under conditions corresponding to the linear and quadratic Stark effects.[5] In this case, the charge exchange of the zinc center should be examined in a 3D system of adiabatic potentials (Figs. 2 and 3). This system differs from a 1D system in that it clearly demonstrates the Stark shifts of the charge states along the various crystallographic axes. The configurational coordinates Q_1, Q_2, and Q_3 connect pairs of different charge states of the zinc center (Fig. 3). The positions of the minima of the adiabatic

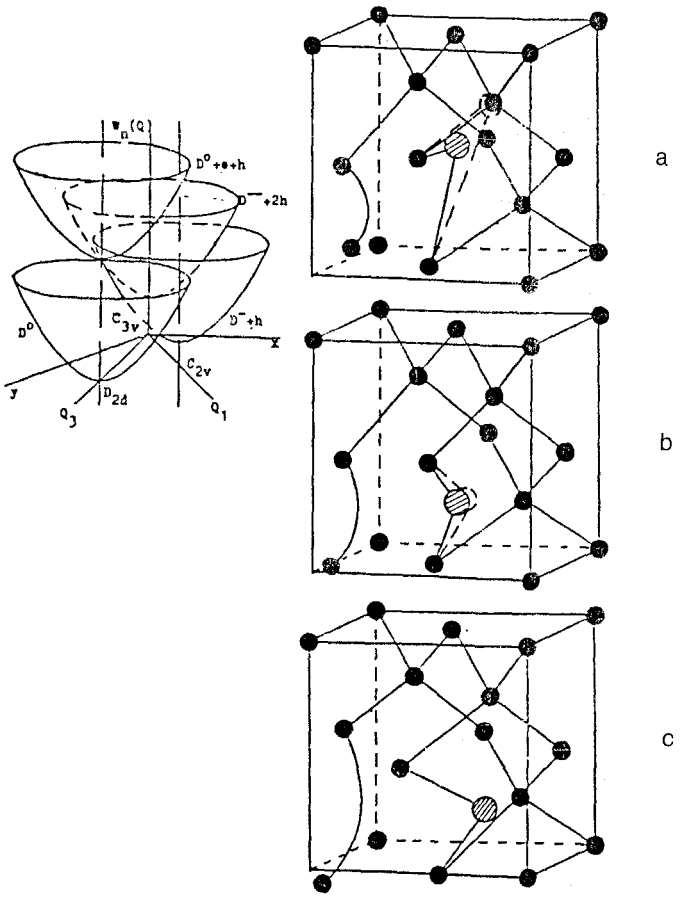

FIG. 3. Model of a reconstructed double acceptor in silicon. a—D^{--} state; b—D^-; c—D^0. Also shown here is a three-dimensional diagram of the two-electron adiabatic potentials for a zinc center in silicon. The dashed lines show the displacement of a zinc center in an electric field ($\mathbf{E}\|[111]$).

potentials differ by an amount equal to the Hall energies of the first level ($E_v + 0.2$ eV; Fig. 1b) and the second one ($E_v + 0.17$ eV; Fig. 1a), respectively, which have been observed in these samples in a photo-Hall study. The Stark shifts of the D^- and D^{--} states also depend on the orientation of the external electric field: $\delta Q_1' = 2\delta F'/\kappa$ for the D^{--} state and $\delta Q_2'' = \delta F''/\kappa$, where κ is a force constant, δF is the corresponding change in the electron-vibrational coupling constant in an electric field,[5]

$$\delta F' = eE\cos(\mathbf{E},[111]), \quad \delta F'' = eE\cos(\mathbf{E},[110]). \tag{3}$$

We see that the behavior of the adiabatic potentials when the Stark shifts are taken into account gives a good description of the suppression of the negative-U reaction with increasing strength of an electric field along the [111] axis. It also gives a good

description of the weakening of the metastable properties of the zinc center in the orientation $\mathbf{E}\|[100]$.

In summary, the Stark effect seen here has made it possible to identify the model of a double zinc acceptor in silicon in which a deep center undergoes a tunneling between positions of different symmetry ($D_{2d} - C_{2V} - C_{3V}$) in the course of a charge exchange ($Zn^0 - Zn^- - Zn^{--}$). We have shown that the use of an "anisotropic" electric field in capacitance spectroscopy makes it possible to determine the symmetries of the various charge states and to identify the metastable properties of deep defects in semiconductors.

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