Piezoscopic deep-level transient spectroscopy studies of the silicon divacancy

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It is shown that the divacancy in silicon in the diamagnetic doubly negative charge state has a static trigonal symmetry with inward breathing mode lattice relaxation. There is no measurable Jahn-Teller effect, unlike other charge states of the defect. This conclusion has been drawn from an analysis of the piezoscopic characteristics of the complex derived from high-resolution (Laplace) deep-level transient spectroscopy.

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Divacancy is one of the most commonly observed radiation defects in silicon. The defect exists in four charge states: V_2^+, V_2^0, V_2^-, and V_2^{2-} resulting in the observation of three different energy levels in the band gap using carrier emission experiments such as deep-level transient spectroscopy (DLTS): $V_2(0/+)$, $V_2(-/0)$, and $V_2(2-/-)$. Watkins and Corbett[1] showed that the local symmetry of the divacancy in the V_2^+ and V_2^- charge states is reduced from trigonal D_{3d} to monoclinic C_{2h}, i.e., from the symmetry of two empty sites surrounded by six substitutional atoms to a symmetry with a mirror plane parallel to the axis joining two empty sites.[1] The driving force for this symmetry-lowering Jahn-Teller (JT) distortion comes from partially filled molecular orbitals forming reconstructed bonds between two neighboring silicon atoms. At temperatures above ~40 K this reconstructed bond can switch to another pair of atoms (there are three equivalent pairs as shown in Fig. 1). These equivalent JT configurations are separated by a barrier of around 60 meV.[1] Details of the Jahn-Teller effect, especially for the V_2^- state, are still disputed (see the discussion on *pairing*[1–4] versus *resonant bond*[5–7] models of the JT distortion for the V_2^- state).

It would seem that the nature of the lattice relaxation for the V_2^{2-} state is more certain. In this charge state the e_u orbital is fully occupied resulting in a symmetric charge density with respect to the D_{3d} point-symmetry group. This should give no driving force for a JT distortion and the trigonal symmetry should be maintained (see Refs. 6–9 for details). This general picture has been confirmed by a number of theoretical calculations which also found that the inward breathing mode dominates the relaxation.[4,6] However, an alternative model predicts that two different structures of V_2^{2-} can coexist. In this model[7,8] the fourth electron, instead of filling up the e_u term, prefers to go to the e_g term, which, as is the case for the other charge states, results in the symmetry-lowering $D_{3d} \rightarrow C_{2h}$ and the JT effect.

Although there are a number of electron-paramagnetic-resonance (EPR) measurements for paramagnetic V_2^+ and V_2^- states of the divacancy and a variety of different theoretical analyses, the details of the structures of V_2^+ and V_2^- are still debated.[2–8,10] For the diamagnetic state V_2^{2-} no structural data are available as these would have to come from electrical measurements, which in general are insensitive to the local structure of defects. In the present work we overcome this structural insensitivity by the combination of high-resolution DLTS [Laplace DLTS (Ref. 11)] and uniaxial stress. This shows that the symmetry of divacancy in the V_2^{2-} state is trigonal with an inward relaxation along the trigonal axis.

In order to demonstrate this we have determined the influence of uniaxial stress on the thermal emission of electrons from the double acceptor state $V_2(2-/-)$ to the conduction band which has an activation energy of ~0.23 eV.[12] The stress has been applied along three major crystallographic directions (⟨100⟩, ⟨110⟩, and ⟨111⟩) of suitably cut samples. For some directions the stress lifts the spatial degeneracy of the defect which results in a characteristic splitting pattern of the defect electronic level. As discussed below the number of split lines and their amplitudes reveal the defect symmetry, whereas the stress-induced energy shifts analyzed within the piezoscopic theory[13,14] allow us to obtain more detailed information about the defect-lattice relaxation. If the coordinate system for the piezoscopic tensor is chosen in such a way that it is aligned with the defect characteristic directions then the corresponding component of the tensor

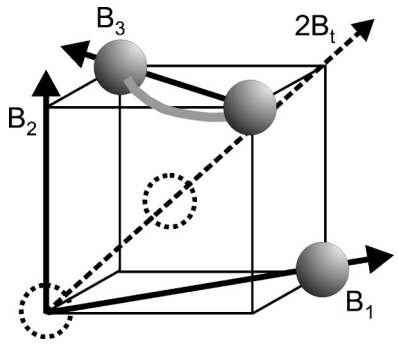

FIG. 1. Components of the piezoscopic tensor for the monoclinic symmetry of divacancy [the mirror plane is $(\bar{1}10)$]. The gray line represents one out of three possible configurations of the reconstructed Si-Si bond. The dashed arrow shows the component for the trigonal symmetry of the defect.

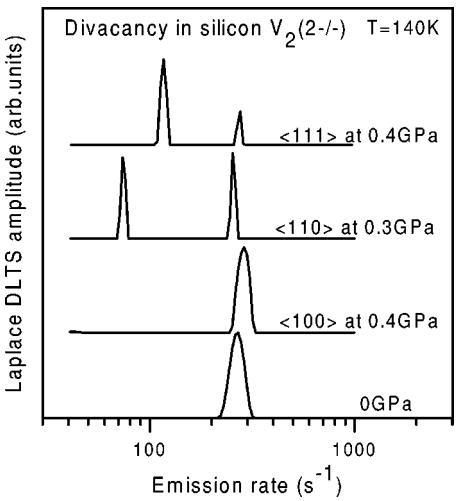

FIG. 2. Laplace DLTS spectra of the $V_2(2-/-)$ level taken with no stress, and the stress applied along three major crystallographic directions of the sample.

describes how the total energy of the defect changes when the defect is stressed along this particular direction. A positive value of the piezoscopic tensor component shows that the compressing stress (conventionally compressive stress has a negative value) applied along the corresponding direction lowers the defect energy. This means that the defect relaxation along this direction is inward.

The samples used for this study were cut in a shape of $1\times2\times7$ mm blocks from either Czochralski or float-zone-grown *n*-type silicon. The samples in each series were prepared from the same wafer with a (110) surface orientation and then cut in different directions so as to have the longest sample edge along one of the major crystallographic directions. The divacancies were produced by either proton implantation with an energy of 525 keV and a dose of $\sim5\times10^9$ cm^{-2} or electron irradiation with an energy of 2 MeV and a dose of $\sim6\times10^{13}$ cm^{-2}. Figure 2 shows the Laplace DLTS spectra for electron emission from the $V_2(2-/-)$ double acceptor level taken with no stress and with stress applied along the three major crystallographic directions. For the stress orientation along the $\langle100\rangle$ direction no line splitting is observed, while for stress in the $\langle110\rangle$ and $\langle111\rangle$ directions the Laplace DLTS peak splits into two components with the amplitude ratios 1:1 and 3:1, respectively. The magnitudes of the split lines sum to the value for the unstressed sample. In the Laplace DLTS experiment the emission rate is measured at a fixed temperature and is proportional to the term $\sigma_e\times\exp(-E_t/kT)$, where σ_e is the carrier capture cross section and E_t is the activation energy for the emission. Direct measurements of the electron-capture process for the defect under stress showed that the influence of the stress on the capture cross section is negligible and the changes in the spectra are due to the effect of the stress on the defect energy level.

The observed pattern of splittings is characteristic for a defect of trigonal symmetry. The DLTS technique measures the rate of the $V_2^{2-}\rightarrow V_2^{-}+e_c^{-}$ process. The stress can affect both the initial and final states of the defect. A simple analysis of the rate equation shows that a splitting of the initial state into two components results in the appearance of two different ionization rates (the Laplace DLTS line splits), while a similar splitting of the final state only changes the ionization rate to the sum of the ionization rates to both components of the final state[15] (there is an additional shift of the Laplace DLTS line). In the present case, the observed pattern of splittings, as shown in Fig. 2, reflects the true (or apparent) trigonal symmetry of the initial state (V_2^{2-}) of the process. The symmetry of the final state and, consequently, its response to the stress will contribute to the overall effect of stress on the rates of the $V_2^{2-}\rightarrow V_2^{-}+e_c^{-}$ process. If the energy of the JT configurations of the final state (V_2^{-}) splits by ΔE_{JT} then the higher final state contributes to the total changes of the emission rate by a factor of $\exp(-\Delta E_{JT}/kT)$ less then the lower one. The piezoscopic tensor for the final state (V_2^{-}) has been evaluated in Ref. 1 and this allows us to determine values of ΔE_{JT} at the lowest stress where a splitting of the Laplace DLTS line is observed (around 0.2 GPa). For the $\langle111\rangle$ and $\langle110\rangle$ stress directions the contribution of the higher final level to the total stress coefficient is 4% and 2%, respectively, and so is negligible for higher stresses.

In order to connect the results with a specific model of the defect we note that there are two possible cases that would lead to the observation of trigonal symmetry of the V_2^{2-} initial state in uniaxial stress DLTS: (i) The symmetry of the divacancy in the V_2^{2-} charge state is a true static trigonal symmetry. (ii) The observed trigonal symmetry is apparent and results from an efficient thermal averaging of the monoclinic C_{2h} symmetry; a similar situation applies to EPR of V_2^{-} at high temperatures.[1] Hence, the observation of a trigonal pattern does not determine the structure of the defect unambiguously. In order to do this we must examine the magnitude of stress-induced level shifts (see Fig. 3) for the various stress directions. We find that these shifts deviate from those predicted by the piezoscopic theory for a simple trigonal defect.[14] This observation can be used to distinguish between the cases where (i) the deviation is caused by the change in the symmetry of the defect from trigonal to monoclinic during the ionization process, and (ii) the deviation is caused by the thermal averaging of the initial state.

The effect of stress on the defect total energies in both charge states can be found from the following relation: $\Delta E=\Sigma_{ij}B_{ij}\varepsilon_{ij}$, where ε_{ij} are components of the strain tensor and B_{ij} are components of the corresponding piezoscopic tensor in a given charge state. If, for example, the stress is applied to the sample along the $\langle111\rangle$ direction then there are two different configurations of the defect in respect to the stress. If the total energies of both configurations of the divacancy in the V_2^{-} charge state separate by $D^{-}_{\langle111\rangle}\times P$ (where P is the stress) then the splitting of the $V_2(2-/-)$ energy level is $D_{\langle111\rangle}=D^{-}_{\langle111\rangle}-D^{2-}_{\langle111\rangle}$, where $D^{2-}_{\langle111\rangle}$ is the splitting of the defect total energy in the other charge state. In this approach the effect of the stress on the band gap cancels out because no selection rules apply for the thermal emission process leaving the emitted electron at the bottom of the conduction band for both configurations.

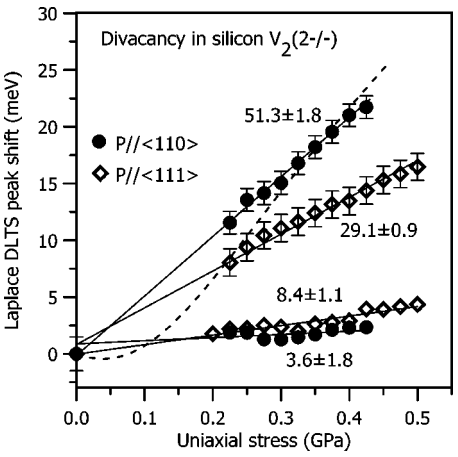

FIG. 3. Laplace DLTS peak shifts {equal to $-kT\ln[e_n(P)/e_n(P=0)]$, where e_n is the peak emission rate} for two directions of the stress (slopes of the lines are given in units of meV/GPa). The fitted lines converge within experimental error to the plot origin (the origin point is not used in the linear regression analysis). The dashed line shows a hypothetical stress shift of the high-frequency (51.3 meV/GPa) line for the ⟨110⟩ stress direction (calculated for $B_3^-=32$ eV,[1] $B_3^{2-}=22$ eV, and a zero shift of the conduction band), if the JT reconfiguration process is present for the V_2^{2-} state.

For a trigonal defect the energy-level splittings are $D_{\langle 111\rangle}=\frac{4}{3}B_t s_{44}$ and $D_{\langle 110\rangle}=B_t s_{44}$, where the B_t component is directed along the defect trigonal axis ⟨111⟩ (a similar notation to Ref. 14 is used, see dashed arrow in Fig. 1) and s_{44} is a component for the silicon elastic compliance tensor $s_{44}=12.56\times10^{-3}$ GPa^{-1}. In order to analyze the two models (i) and (ii) presented above the following parameter is introduced: $\alpha=\frac{4}{3}D_{\langle 110\rangle}-D_{\langle 111\rangle}$. It demonstrates for a given model a departure of the energy-level shifts from the case when the initial and final states of the ionization process have a trigonal symmetry ($\alpha=0$). From the data presented in Fig. 3 the experimental value of $\alpha=43\pm7$ meV/GPa is obtained. Another important feature of the data presented in Fig. 3 is that all lines converge in the $\Delta E_t=0$, $P=0$ point (in all cases this point has not been used for the linear regression analysis).

For both models (i) and (ii) the piezoscopic analysis of the ionization final state is the same. It is assumed (following the Watkins and Corbett model) that the symmetry of the V_2^- state is monoclinic and due to the fact that the ionization process always favors the lowest level from the levels split by the JT effect this lowest level is taken as the final state of the ionization process. Our experiments do not allow us to obtain more than one value of the piezoscopic tensor component so it is assumed that for the V_2^- state $B_1^-=B_2^-=0$, which means that the compression along the Si-Si reconstructed bond defines predominantly the response of the defect to the stress. When the stress is applied along either ⟨111⟩ or ⟨110⟩ direction the total energy of V_2^- splits into two components. The stress-induced splittings between these components are $D^-_{\langle 111\rangle}=s_{44}B_3^-/3$ and $D^-_{\langle 110\rangle}=(s_{11}-s_{12}+s_{44})B_3^-/4$, where other components for the silicon elastic compliance tensor are $s_{11}=7.68\times10^{-3}$ and $s_{12}=-2.14\times10^{-3}$ GPa^{-1}. Watkins and Corbett also assumed that $B_1^-=B_2^-=0$ and concluded that $B_3^-=32$ eV.

In case (i), the static trigonal symmetry of V_2^{2-}, the initial state of the ionization process does not contribute to α, thus according to the above formula, $\alpha=(s_{11}-s_{12})B_3^-/3$ and it represents only the splitting of the divacancy energy level in the V_2^- state. Comparing the theoretical and experimental values of α we conclude that $B_3^-=13\pm2$ eV, which is about a factor of 2 less than the value obtained by Watkins and Corbett. The agreement may be considered satisfactory taking into account the approximations of both analysis.

In the case (ii) the apparent trigonal symmetry of V_2^{2-} results from the dynamic or static Jahn-Teller effect. Watkins and Corbett showed that divacancy in the V_2^- state at temperatures above 40 K reconfigures quickly between equivalent JT configurations, which leads to observation of the apparent trigonal instead of monoclinic symmetry. The Laplace DLTS measurements for $V_2(2-/-)$ are carried out typically at around 140 K, where the reconfiguration rate of the JT distortion is around 10^{10} s^{-1} (the thermal emission rate at this temperature is around 100 s^{-1}, see Fig. 2). This possible averaging process for the V_2^{2-} state could have an important consequence for the observed stress-induced level shifts. For low stresses, where the level separation is not large, the level averaging process should be very effective. For larger stresses the lowest level should be predominantly populated and its stress-induced shift will represent the effective level change. In a general case, these two regimes, if present, may result in the level response to the stress appearing to be *nonlinear*. The strongest nonlinear effect for the V_2^{2-} state could be observed in the ⟨110⟩ stress direction for the line having the highest-stress dependence (51.3 meV/GPa in Fig. 3). This line corresponds to the stress directed perpendicularly to the *V*-*V* axis (e.g., along the B_3 component in Fig. 1). For a given stress direction there are always three configurations of the reconstructed bond. In the above case for one of the configurations the reconstructed bond is parallel to the stress and has a stress coefficient proportional to (assuming $B_1^{2-}=B_2^{2-}=0$) $2s_{11}+2s_{12}+s_{44}$.[16] In the high-stress (or low-temperature) regime, when the JT reorientation stops, this stress coefficient should define the stress-induced shift of this peak. The other two configurations of the reconstructed bond have stress coefficients proportional to $s_{11}+3s_{12}$. In the low-stress regime, when the JT averaging between these three configurations is effective, the stress coefficient of the averaged energy level should be $(4s_{11}+8s_{12}+s_{44})/3$. As a result, a transition from the low- to high-stress regime should increase the stress coefficient of this peak by a factor of 3.[17] In Fig. 3 the dashed line shows a hypothetical stress shift of the high-frequency (51.3 meV/GPa) Laplace DLTS line for the ⟨110⟩ stress direction (calculated for $B_3^-=32$ eV,[1] $B_3^{2-}=22$ eV, and a zero shift of the conduction band), if the JT reconfiguration process is present for the V_2^{2-} state. The observed shifts of the stress-split energy levels (Fig. 3), when extrapolated to zero stress within an experimental error, converge to the zero energy point. This lack of the expected nonlinearity means that only one of the two regimes mentioned above can be observed. For the dynamic JT effect to

be present (the low-stress regime) the condition $\Delta E_{JT} \ll kT$ even at 0.5 GPa (in the $\langle 110 \rangle$ stress direction) has to be fulfilled. This leads to an unrealistic constrain: $|B_3^{2-}| < 0.3$ eV, which would mean that the divacancy in the V_2^{2-} state is, unlike the V_2^- state, practically insensitive to the stress applied along the reconstructed Si-Si bond. The other regime needs $\Delta E_{JT} > kT$ even at 0.05 GPa, which for the $\langle 111 \rangle$ stress direction leads to another unrealistic constrain: $B_3^{2-} > 130$ eV. As a result, the above analysis allowed us to conclude that the observed shifts of the stress-split energy levels cannot be explained if either static or dynamic *monoclinic* symmetry for the V_2^{2-} state is assumed.

The model of the static trigonal symmetry of the V_2^{2-} state allows us to obtain directly the value of the B_t component, which describes the lattice relaxation along the defect trigonal axis $B_t = 2.0 \pm 0.6$ eV. The positive value of B_t could be expected as one could easily imagine that in the crystal an open volume emptied by two missing atoms must result in an inward collapse of the surrounding lattice. The sign of B_t also confirms conclusions of all theoretical analyses of divacancy where a substantial shortening of the silicon-silicon bonds around divacancy is reported.[4,6]

In summary, we have shown experimental evidence for the static trigonal symmetry of the divacancy in silicon when it is in the doubly negative V_2^{2-} charge state. Our results also show that during the ionization of V_2^{2-} a change of the complex symmetry occurs. This effect can be additionally supported by the fact that for the $V_2(2-/-)$ level a much larger entropy factor and temperature dependence of the electron-capture cross section has been observed than for the $V_2(-/0)$ level.[18]

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