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Infrared absorption studies of the divacancy in silicon: New properties of the singly negative charge state

J. H. Svensson, B. G. Svensson,* and B. Monemar
Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden

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The infrared optical absorption peak at 0.34 eV in silicon, which is usually associated with the singly negative charge state of the divacancy, has been investigated in electron-irradiated samples with use of different optical excitation conditions. It is proposed that a strong Jahn-Teller distortion makes it possible to populate this charge state, when the defect initially is in the neutral charge state, either by the capture of a photoexcited free electron from the conduction band, or by the direct photoexcitation of an electron from the valence band to a defect orbital. Experimental evidence for the existence of these reactions is presented. A defect level at $E_c-0.54$ eV, frequently associated with the singly negative charge state of the divacancy, is identified as one of the levels from which these photoexcited free electrons originate. The 0.34-eV peak is attributed to an internal transition in the singly negative charge state of the divacancy center, implying the existence of a shallow defect state at approximately $E_c-0.07$ eV for this charge state. Experimental support is given for the existence of this shallow state. A tentative explanation, based on the strong Jahn-Teller distortion of the singly negative charge state, is suggested for the fact that the doubly negative charge state is *not* observed at temperatures below 90 K.

I. INTRODUCTION

The divacancy in silicon is one of the main defects caused by irradiation with γ rays, electrons, or heavier nuclei. It is stable at room temperature, and does not disappear at annealing temperatures lower than 220 °C. Due to its fundamental character and also its importance for technological applications the divacancy has been one of the most extensively studied defects in silicon, both experimentally and theoretically. The model describing the electronic states of the defect as linear combinations of atomic orbitals from the six nearest neighbors has, ever since its introduction by Watkins *et al.* in 1965, been the dominant one.[1] (Fig. 1.)

The divacancy has been studied with different experimental techniques such as electron paramagnetic resonance (EPR),[1] electron-nuclear double resonance (ENDOR),[2,3] photoconductivity,[4,5] infrared absorption,[6,7] and deep-level transient spectroscopy (DLTS).[8,9] From these measurements the divacancy is known to have four charge states in the band gap, ranging from a singly positive, V_2^+, to a doubly negative, V_2^{2-}. The configuration of the defect has D_{3d} point-group symmetry with the high-symmetry axis along the four equivalent $\langle 111\rangle$ directions. In the charge states V_2^+, V_2^0, and V_2^- the defect has orbital degeneracy with unfilled e_g and e_u orbitals. This means that, at low temperatures, the symmetry of the wave functions is lowered to C_{2h} in these charge states, due to a Jahn-Teller (JT) distortion. This is confirmed by EPR results, which show that the charge states V_2^- and V_2^+ both have spin $\frac{1}{2}$ with the symmetry C_{2h}.[1] ENDOR measurements[2,3] for both of these charge states show that the unpaired electron is accomodated in the directed orbitals between pairs of neighboring atoms. The same results also show some deviations from the sp^3-hybridized character of the covalent bonds, indicating strong JT distortion.

Moreover, Sieverts *et al.*[2,3] found that at elevated temperatures, for V_2^+ at 110 K and for V_2^- at 70 K, the jump rate between the members of a triplet of equivalent electronic JT distortion directions is so high that the distortion of each configuration is dynamically "averaged out," and the effective symmetry is increased to D_{3d}.

Photoconductivity,[4,5] infrared absorption,[6,7] and DLTS (Refs. 8 and 9) measurements clearly indicate that the divacancy has three levels in the band gap corresponding to the following transitions:

$$V_2^{+}+e^{-}\rightarrow V_2^{0}:\ E_v+0.31\ \text{eV}\ , \tag{1}$$

$$V_2^{0}+e^{-}\rightarrow V_2^{-}:\ E_c-0.41\ \text{eV}\ , \tag{2}$$

$$V_2^{-}+e^{-}\rightarrow V_2^{2-}:\ E_c-0.23\ \text{eV}\ , \tag{3}$$

It should be mentioned that Young and Corelli[4] argued that the second transition takes place at $E_c-0.54$ eV. Transitions (2) and (3) will be further discussed in a following paragraph.

The energies for transitions (2) and (3) were extracted from DLTS measurements by Evwaraye and Sun.[8] In this context it should be pointed out that the capture cross section extracted for the level at $E_c-0.23$ eV is about one-third of that extracted at $E_c-0.41$ eV. This can possibly be due to the differences in the Coulombic force attracting the electron defining the energy level, and thus we expect the electron defining transition (3) to be attracted by a weaker Coulombic field than the electron defining transition (2). However, the divacancy is highly distorted and the Coulombic force may not be as important here as for a highly localized site. Furthermore, recent results show that the DLTS signals of these two levels are identical as a function of sample depth (from the surface), strongly indicating that they originate from the same defect.[9]

Infrared absorption measurements indicate that the divacancy gives rise to three major peaks at 0.31 eV (3.9 μm), at 0.34 eV (3.6 μm), and at 0.69 eV (1.8 μm). The 0.31-eV peak is commonly attributed[4,5] to the excitation of an electron from the valence band to a defect state of the V_2^+ charge state. The 0.69-eV band has been suggested to be an internal transition within the V_2^0 charge state.[7] Carton-Merlet *et al.*[10,11] have identified the 0.34-eV band as belonging to the V_2^- charge state, using selective optical excitation during absorption measurements.

In this work we present absorption measurements of both boron- and phosphorus-doped, irradiated silicon. Using optical interference filters to select the optical excitation of the sample both before and during the measurements, it is confirmed that the 0.34-eV peak belongs to the V_2^- charge state. Our measurements also show how the optical excitation populates this charge state when the defect initially is in the V_2^0 charge state. The results also confirm the long lifetime and instability of the V_2^- charge state. Strong support for the existence of a defect state close to the conduction band for the V_2^- charge state is also presented. A tentative explanation is given for the experimental fact that, to the best of our knowledge, the V_2^{2-} charge state has not been observed at temperatures below 90 K.

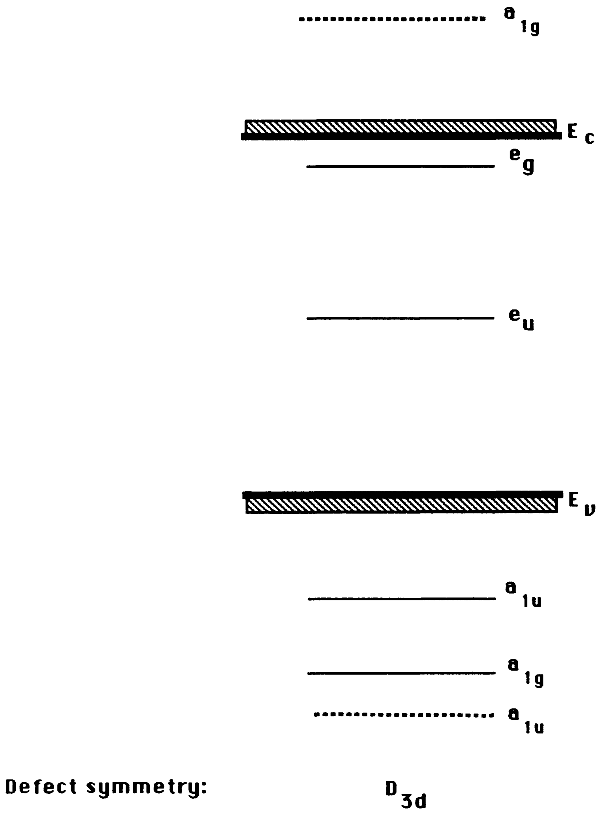

FIG. 1. Electronic states of the divacancy neglecting Jahn-Teller distortion according to the LCAO model introduced by Watkins *et al.* (Ref. 1).

II. SAMPLES AND EXPERIMENTAL PROCEDURE

The samples used in this study were boron- and phosphorus-doped Czochralski-grown (Cz) silicon, irradiated at room temperature with 2-MeV electrons with doses ranging from 1×10^{17} to 2×10^{18} e^-/cm^2.

All measurements were made using a Bruker IFS 113 V Fourier-transform spectrometer fitted with a Hg-Cd-Te detector. Different bandpass filters were used to select the excitation energy. The filters had a typical bandwidth of 0.012 eV at half maximum, except for that used for detecting the 0.34-eV peak, which had a width of 0.08 eV. The filters were mounted in front of the cryostat windows with the 0.34-eV filter facing the radiation source, and the filter used for selection of excitation energy facing the detector. A helium closed-cycle cryostat was used for cooling the samples to a minimum temperature of 9 K. Except where specifically noted, all samples were cooled in darkness, and measured *only* with the optical excitation mentioned in the text.

A survey of the characteristics of the samples used in this study is given in Table I.

TABLE I. Survey of the samples used in the study. The Fermi-level position was determined at 10 K for samples P1, P2, P3, and P4 and at room temperature for the other samples (B denotes boron and P denotes phosphorus). The labels 1–3 have the following meaning: 1, Measured without bandpass filter. 2, Measured with bandpass filter (0.29–0.37 eV) after cooling in darkness. 3, Same as in case 2, but with measurement made after excitation with white light for 10 min at 9.0 K.

Sample	Dopant concentration (atoms/cm^3)	Irradiation dose (e^-/cm^2)	Absorption of the 0.34-eV peak (cm^{-1}) 1	2	3	Fermi level (eV)
P1	P: 1.0×10^{17}	4.0×10^{17}	0.020			$>E_c-0.17$
P2	P: 1.0×10^{17}	7.0×10^{17}	0.058	0.062	0.049	$>E_c-0.17$
P3	P: 1.0×10^{17}	1.0×10^{18}	0.65	0.074	0.078	$>E_c-0.17$
P4	P: 1.0×10^{17}	1.5×10^{18}	0.079	0.102	0.096	$>E_c-0.41$
P5	P: 5.0×10^{14}	1.0×10^{18}	0.050	0.037	0.070	$<E_c-0.41$
B1	B: 5.0×10^{14}	1.0×10^{18}	0.046	0.009	0.040	$<E_c-0.60$

III. EXPERIMENTAL RESULTS

Figure 2 shows the 0.34-eV (≈ 3.6 μm) peak at different temperatures for sample P4 (see table for explanation of sample designations), where the Fermi level is above $E_c - 0.41$ eV. The peak at 0.34 eV is the no-phonon line and the peaks at 0.36 and 0.37 eV are replicas due to phonons created in the excitation process.[11] The 0.34-eV peak broadens slightly with increased temperature until it disappears at temperatures above 90 K.

Figure 3 shows the optical excitation spectrum of sample B1. Figure 3(a) illustrates the absorption during a normal measurement without bandpass filtering and, consequently, with excitation from surrounding sources as well as the ir source of the instrument ($0 < h\nu < 1.3$ eV). Figure 3(b) shows a spectrum from the same sample cooled in darkness and with a bandpass filter restricting the excitation to the range of 0.29–0.37 eV. Figure 3(c) shows the results from a similar measurement, but after excitation with visible light for 10 min at 9 K. Table I gives the absorption values of the 0.34-eV peak for all the samples used, following the same procedure as for the sample in Fig. 3.

Figure 4 shows the absorption of the 0.34-eV peak of sample B1 at 9 K when exposed to optical excitation of different photon energies, selected with different bandpass filters.

The position of the Fermi level is estimated from room-temperature resistivity measurements and, for some phosphorus-doped samples, from the absorption peak at 0.11 eV due to the negative charge state of the vacancy-oxygen center with a level at about $E_c - 0.17$ eV.[12] The

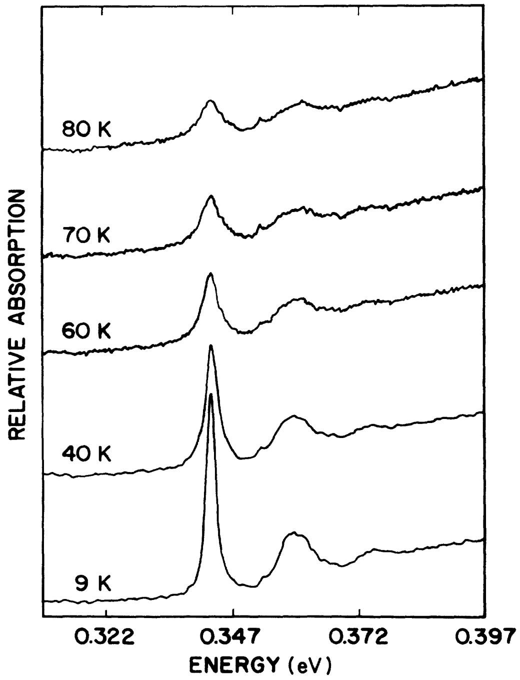

FIG. 2. Temperature dependence of the 0.34-eV peak.

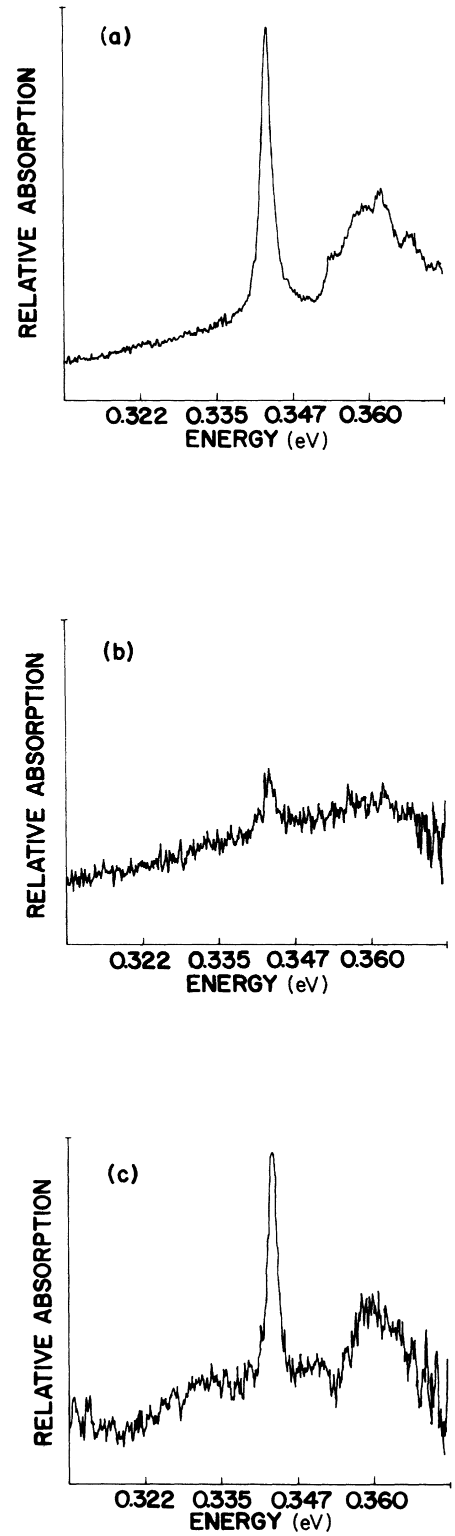

FIG. 3. (a) Absorption spectrum of sample B1 when measured with simultaneous optical excitation from the ir source. (b) Same as (a), but with the sample cooled in darkness and with a bandpass filter selecting the excitation energy in the range 0.29–0.37 eV. (c) Absorption curve obtained from a measurement under conditions similar to those in (b), but after excitation of the sample with white light for 10 min at 9.0 K.

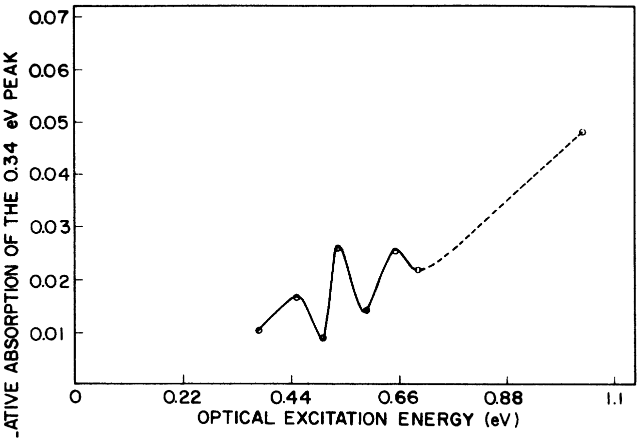

FIG. 4. Relative absorption strength of the 0.34-eV peak vs optical excitation photon energy.

peak at 0.69 eV (1.8 μm) was not observed in any sample or under any conditions used in this work. We believe that this peak does not originate from the divacancy, but from a higher-order vacancy-related complex. This will be discussed in more detail in a subsequent paper.[13]

IV. INTERPRETATION OF THE DATA

A. Identification of electronic charge states

First, let us consider the energy-level scheme in Fig. 1. The levels originate from one-electron molecular orbitals consisting of linear combinations of the six broken-bond orbitals surrounding the defect. Shown in Fig. 1 are the energy levels corresponding to the molecular orbitals transforming according to the irreducible representations of the D_{3d} point-group symmetry. Under the assumption that a single vacancy essentially has an electron-repulsive perturbation potential, one would expect a state with a wave function with a node symmetrically located between two adjacent vacancies to be energetically below a state with a wave function without a node. On this basis, a state corresponding to an odd-parity wave function is expected to have a lower energy than one corresponding to an even-parity wave function. The e-symmetry components are in a plane perpendicular to the defect main axis and the a_1-symmetry components are directed along the main axis. The e states are in this case less affected by the defect potential than the a_1 states. One thus expects the splitting between the e_u and e_g [π-like molecular orbitals (MO's)] states to be smaller than the splitting between the a_1 (α-like MO) states.

In this model the charge states $V_2{}^+$, $V_2{}^0$, and $V_2{}^-$ have one, two, and three electrons, respectively, in the e_u molecular orbitals. These partially filled orbitals are degenerate and thus unstable with respect to a JT distortion,[1] which lowers the symmetry to C_{2h} at low temperatures. Accordingly, the e_u and e_g states split:

$$e_u \rightarrow a_{1u} + b_{1u} \ , \quad e_g \rightarrow a_{1g} + b_{1g} \ .$$

The EPR signal associated with the divacancy[1-3] arises from the $V_2{}^+$ and $V_2{}^-$ charge states. From the EPR results the following is known.

(i) The $V_2{}^-$ charge-state wave function observed in EPR has approximately 10% s character and the $V_2{}^+$ charge state has approximately 13% s character, as given by ENDOR data.[2,3]

(ii) Both the $V_2{}^-$ and $V_2{}^+$ charge states have spin $\frac{1}{2}$.

Since the states observed have some s character, only b_{1u} and a_{1g} states are possible for these charge states. The molecular orbitals for the $V_2{}^-$ charge state are shown in Fig. 5. The $V_2{}^+$ charge state has one electron in the b_{1u} orbital, the $V_2{}^0$ charge state two.

B. The origin of the 0.34-eV peak

In order to explain the results in Fig. 3, we attribute the 0.34-eV peak to the $V_2{}^-$ charge state. This is consistent with the fact that the 0.34-eV peak is only observed after cooling and after photoexcitation with energies higher than 0.37 eV, i.e., when the Fermi level is below $E_c - 0.41$ eV and the defect is initially in the $V_2{}^0$ charge state. If no optical excitation of high enough photon energy is present, the defect will remain neutral. The appearance of the peaks with thresholds of about 0.44, 0.54, and 0.65 eV, respectively (Fig. 4), is attributed to the filling of the a_{1g} defect orbital (Fig. 5) with a corresponding change of charge state to $V_2{}^-$.

The filling may take place by (i) capturing an electron from the conduction band, or (ii) an internal transition followed by a filling of the initial state with an electron,

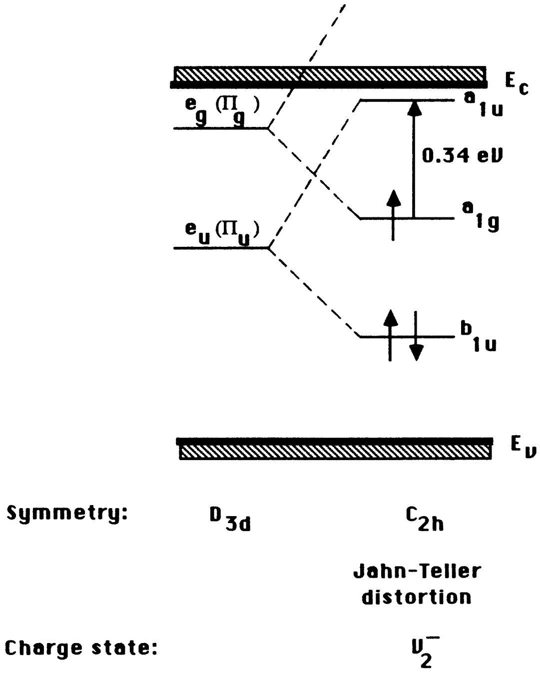

FIG. 5. The e-symmetric electronic levels in $V_2{}^-$ before and after the onset of JT distortion. The suggested transition associated with the 0.34-eV peak is shown.

or (iii) direct optical excitation of an electron from the valence band to the defect orbital.

The first suggestion appears to be the most likely, since (ii) can be ruled out, according to Fig. 3. For (ii) we would observe the 0.34-eV peak only when exposed to light with energy close to the energy of the internal transition, which is not the case. Figure 4 gives strong support for reactions (i) and (iii). As there is an energy threshold for the observation of (iii) at approximately 0.60–0.70 eV, we attribute the variation of the concentration of the $V_2{}^-$ charge state for excitation energies between 0.35 and 0.60 eV to originate from reaction (i). In this energy region the ionization of $V_2{}^-$ into the conduction is an important process. This process seems to be most efficient at 0.50 eV, where we observe a minimum absorption of the 0.34-eV peak in Fig. 4. We attribute the increase in absorption observed for excitation energies at 0.54 eV to the excitation into the conduction band of an electron from the defect with a level at $E_c-0.54$ eV found in photoconductivity measurements.[4] This increase in concentration of free electrons will—by a capture process—contribute to the increase of the concentration of $V_2{}^-$. We leave the weaker increase in absorption observed at 0.44 eV unexplained.

We attribute the increase at 0.65 eV to reaction (iii). The small decrease in absorption at slightly higher photon energies indicates a broader energy spectrum extended on its high-energy side, as expected for an excitation from the valence band to a bound state of a defect. The increase can be caused by more than one process as the number of possible different excitations increases with optical excitation energy. A general increase has been reported for excitation energies higher than 0.70 eV by Carton-Merlet *et al.*[10]

It is important in this context to point out other processes that affect the concentration of $V_2{}^-$ during optical excitation of the sample. Reaction (iii) and possibly other unknown reactions will create free holes that can recombine with electrons bound to $V_2{}^-$ and thus alter the charge state. Experimentally, we know that band-gap illumination strongly enhances the concentration of $V_2{}^-$, indicating that the hole-capture cross section is small for this charge state. Furthermore, considering the position of the Fermi level in this sample, we know that the steady-state concentration of free holes at excitation energies lower than 0.65 eV must be low due to a low concentration of defects with levels in the band gap that can accommodate an electron optically excited from the valence band.

When the temperature is raised, the jump rate between different distorted configurations increases, as mentioned before, and at 80 K for the $V_2{}^-$ charge state the jump rate is so high that the defect does not relax in the low-symmetry configuration between the "jumps." The "average" symmetry observed is, in this case, D_{3d} for the $V_2{}^-$ charge state. Accordingly, the energy-level scheme in the low-symmetry case (Fig. 5) may no longer be true at temperatures higher than 80 K, which explains the temperature dependence of the 0.34-eV peak (Fig. 2). In this context it is also important to point out that the estimated energy position of the lowest energy level of each charge state is not exact. The level at $E_c-0.41$ eV has been determined using DLTS and photoconductivity techniques, and the energy position is evaluated at temperatures around 220 and 80 K, respectively. At these temperatures motional-averaging effects are quite strong. The estimated activation energy for changing the distorted configuration of the $V_2{}^-$ charge state is approximately 0.06 eV.[1] One can thus expect the ground state of the $V_2{}^-$ charge state to be lower than $E_c-0.41$ eV.

The disappearance of the 0.34-eV peak for sample P1 when measured with a bandpass filter gives strong support to the existence of a defect state close to the conduction band in the relaxed (C_{2h}) symmetry configuration of the $V_2{}^-$ charge state. In this sample the Fermi level is high enough for this state to be occupied. The exact position of this state is difficult to estimate since the relaxed energy of the ground state of the transition is not known. A rough estimate gives a value between $E_c-0.07$ and $E_c-0.13$ eV. We thus identify the peak with the transition shown in Fig. 5, although this is in contradiction with parts of results from earlier work.[6] The shape of the peak indicates that the lattice distortion taking place in the transition is small.

C. The doubly negative charge state

If the defect is in the $V_2{}^{2-}$ charge state, there will be no splitting of the e_u level due to JT distortion, as mentioned earlier. The symmetry of this charge state should be D_{3d} with the e_u level (Fig. 1) unsplit, although it is likely that additional non-symmetry-breaking relaxation occurs (breathing-mode relaxation). The symmetry of this charge state has not been verified experimentally since no EPR signal has been found, implying that the uppermost level of this charge state has two paired electrons. We consider a level containing four energetically degenerate electrons very unlikely. The uppermost level of the $V_2{}^{2-}$ charge state is at $E_c-0.23$ eV. The $E_c-0.23$ eV level is well documented at temperatures exceeding 100 K.[8] We can conclude that the differences in lattice distortion between the $V_2{}^{2-}$ and the $V_2{}^-$ charge states in this case are large.

An experimental fact yet to be explained is the appearance of the 0.34-eV peak when the Fermi level is well *above* $E_c-0.23$ eV, and the defect therefore should be in the $V_2{}^{2-}$ charge state. One possible explanation is an instability of the $V_2{}^{2-}$ charge state at lower temperatures (<80 K). If an electron in the level at $E_c-0.23$ eV in the $V_2{}^{2-}$ charge state of the defect is photoexcited to the conduction band, the defect can relax the $V_2{}^-$ charge state with symmetry C_{2h}. If sufficient thermal energy is not available, the capture rate for electrons of the $V_2{}^-$ charge state with a corresponding reorientation to D_{3d} symmetry can be low. At higher temperatures (>80 K), where motional effects are strong and the effective symmetry in the $V_2{}^-$ charge state is increased to D_{3d}, the $V_2{}^{2-}$ charge state should be more populated.

Another possibility, which has been proposed by Lindefelt and Wang,[14] is the existence of two different configurations of the $V_2{}^{2-}$ charge state. The configuration of the $V_2{}^{2-}$ charge state of Fig. 5 has a fully occupied gap level and thus a totally symmetric charge state (with respect to the point group D_{3d}). According to the Hellmann-Feynman theorem, it is possible to deduce

$$\bar{F}(R\bar{Q}_p)=R\bar{F}(\bar{Q}_p) \quad (4)$$

if $\rho(R\bar{r})=\rho(\bar{r})$, where R is an orthogonal 3×3 matrix corresponding to a group operation and $\bar{F}(\bar{Q}_p)$ is the force acting on the nucleus at $\bar{Q}_p$ due to the electronic charge density $\rho(r)$. This statement shows that if the charge density is totally symmetric, the electronic force also has the symmetry of the lattice.

If one electron is added to the a_{1g}-symmetric charge state, the result will be a totally symmetric charge density, and therefore a non-symmetry-breaking force with respect to the group C_{2h}. In principle, it is thus possible to have *two* different symmetry configurations for the V_2^{2-} charge state, with the $V_2^{2-}(C_{2h})$ charge state expected to be lowest in energy.

The former model is capable of explaining our experimental results, while it is not obvious how to extract the results from the latter. It should be emphasized that the two models are tentative suggestions, and that further experimental and theoretical studies are necessary to establish either of the models.

D. Jahn-Teller distortion of V_2^-

Most of our results are based on the assumption of a strong JT distortion in the V_2^- charge state. We have several proofs that this is indeed the case. We know that the orbital containing the a_{1g} level in Fig. 5 has an s content of about 10%. Since the e_u and e_g orbitals have no s components, the s content of the a_{1g} orbital is solely due to JT distortion. We also know that the lifetime of the V_2^- charge state for the sample in Fig. 3 is very long. Even at temperatures as high as 40–50 K the lifetime is more than 6 h.

V. SUMMARY AND CONCLUSIONS

We have given strong evidence confirming that the peak at 0.34 eV belongs to the V_2^- charge state of the divacancy. We also present substantial evidence that the divacancy in the V_2^0 charge state can capture an electron from the conduction band and relax into the V_2^- charge state, when the Fermi level is below $E_c-0.41$ eV. It appears likely that the electrons are excited optically from other defects and/or from the valence band to the conduction band. Further, we have shown that the $E_c-0.54$ eV level most surely does *not* belong to the divacancy. The change in charge state can also be caused by direct excitation of an electron from the valence band to the defect.

We have also found evidence for the existence of a defect state in the V_2^- charge state at $\approx E_c-0.07$ eV in the linear-combination-of-atomic-orbitals (LCAO) model of the divacancy, observed as the excited state of the transition corresponding to the absorption peak at 0.34 eV.

We also propose the following.

(i) The V_2^{2-} charge state is unstable when optically excited at low temperatures (<70 K). After an electron has been excited to the conduction band, the defect will relax the V_2^- charge state with symmetry C_{2h}.

(ii) The disappearance of the 0.34-eV peak at approximately 90 K is caused by the high frequency of thermally induced shifting of Jahn-Teller–distortion direction in this temperature region.

The latter suggestion need further experimental verification.

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*Permanent address: Department of Solid State Electronics, The Royal Institute of Technology, P.O. Box 1298, S-164 28 Kista, Sweden.

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