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Site symmetry of the $EL2$ center in GaAs

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A study has been made of the effects of uniaxial stress on the photocapacitance quenching phenomenon associated with the $EL2$ center in GaAs. The results show directly that the defect is a complex with C_{3v} (trigonal) site symmetry. The internal optical excitation assigned to the $EL2$ center is shown not to be directly related to the photoquenching transition. The implications of these results with respect to models of $EL2$ and its photoquenching mechanism are discussed.

The $EL2$ center in GaAs has been the subject of a great deal of attention in recent years, both because of its unusual properties and its technological importance. Despite numerous experiments in many laboratories, its identity and structure have not been completely elucidated.[1]

There is a large body of evidence associating the $EL2$ center with the As_{Ga} antisite defect.[1] In addition to stoichiometric correlations,[2,3] the As_{Ga} antisite defect has been associated with $EL2$ because of electron paramagnetic resonance (EPR) observations, especially based on the similar photoquenching behavior of both $EL2$ and the As_{Ga} EPR signal.[4,5] Although optical absorption measurements under uniaxial stress[6] have led to the conclusion that the antisite defect is in an undistorted nearest-neighbor environment with the full T_d site symmetry of the lattice, EPR-related studies indicate that different As_{Ga} complexes can exist,[7-10] and that the isolated As_{Ga} is not associated with $EL2$ (Refs. 10 and 11). In addition, a great deal of evidence indicates that there are different kinds of $EL2$ centers.[12-14] Therefore, it would appear that $EL2$ consists of one or more kinds of defect complexes which involve the As_{Ga} antisite, and several models have been proposed.[12,15-19] Recently, an arsenic-antisite–arsenic-interstitial complex was observed in optically detected EPR and electron-nuclear double-resonance experiments.[20] It was inferred from its optical and photoquenching properties that this complex corresponds to $EL2$. However, no direct structural information has been obtained for the $EL2$ center.

Piezospectroscopic methods provide a means to determine the site symmetries of localized centers in cubic crystals.[21] In particular, polarized excitation photocapacitance under uniaxial stress allows symmetry studies of centers which are observed using capacitance transient methods.[22] It has previously been used to verify the site symmetry of the divacancy in Si (Ref. 22). In this Rapid Communication, we report the photocapacitance behavior of the $EL2$ center in GaAs under uniaxial stress and with polarized-light excitation. These measurements confirm that $EL2$ is in fact a defect complex, and yield the first direct information on its site symmetry.

Samples were prepared from two Se-doped liquid-encapsulated Czochralski-grown GaAs crystals with $n \sim 1\times10^{16}$ cm^{-3} and $[EL2]=(2\text{-}4)\times10^{15}$ cm^{-3}. Samples were cut to dimensions $1.3\times1.5\times7.0$ mm^3 with the long axis parallel to the $\langle 001\rangle$, $\langle 110\rangle$, or $\langle 111\rangle$ direction. Ti/Au Schottky diodes were fabricated on each sample near the center of one face. The stress apparatus consisted of an air cylinder and piston arrangement which provided compressive stress parallel to the long axis of the sample. The apparatus was attached to a cold-finger liquid-He Dewar, but could be demounted and placed in an annealing furnace without interruption of the applied stress. A Nd-doped yttrium aluminum garnet (Nd:YAG) laser operating at 1.06 μm was used to illuminate the diodes through the opposite face of the sample. The incident light direction was in all cases $\langle 1\bar{1}0\rangle$. Light polarization was controlled by means of a Glan-Thompson prism and $\frac{1}{2}$-wave plate. An internal verification of equal light intensities for both polarization orientations was always provided because the initial trap-emptying transients were identical within experimental error for both orientations at zero stress, and continued to be so with applied stress, as discussed below.

Two kinds of experiments were performed. In the first kind, stress was applied at low temperature ($T < 100$ K). Photocapacitance transients were then recorded for polarization vector orientations both parallel and perpendicular to the stress axis. In the second kind, high-temperature anneals were performed where 200 MPa of stress was applied for 1 h at 425 K with no bias applied to the diode. This temperature was chosen because changes in the photoquenching properties of $EL2$, attributed to mobility of the arsenic interstitial, have been observed in this temperature range.[16] The sample was then cooled to $T < 200$ K before the stress was removed. The photocapacitance behavior at zero stress was then recorded at 80 K for both polarization orientations. The effects of stress at room temperature were also investigated. Samples were cooled under stress from room temperature to $T < 100$ K where measurements were made at zero stress.

A typical photocapacitance transient recorded in a low-temperature stress experiment is shown in Fig. 1. The stress axis is parallel to $\langle 111\rangle$. The photoquenching behavior characteristic of $EL2$ is seen where the initial trap-emptying transient is followed by a quenching transient which returns the capacitance to nearly its original value.[18]

The initial trap-emptying transients were identical within experimental error for both polarization orientations. This is seen more clearly in the inset of Fig. 1 where the light intensity ϕ has been reduced by a factor of 10. In

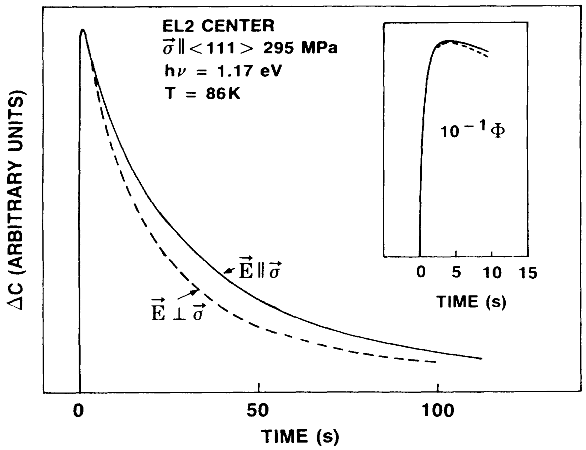

FIG. 1. Photocapacitance transients of the $EL2$ center under uniaxial stress, with the polarization vector **E** parallel and perpendicular to the stress axis. In the inset, the light intensity ϕ has been reduced by a factor of 10 to more clearly show the initial trap-emptying transient.

fact, even with further slowing of the emission rate, no measurable dichroism was seen for the emptying transient in any experiment under any of the stress and temperature conditions used.

A significant dichroism is observed for the quenching transient of Fig. 1. Here the quenching rate for the perpendicular light polarization is greater than for the parallel. A dichroic ratio may be defined as $D = k_\perp / k_\parallel$ where $k_\perp$ and $k_\parallel$ are the rates of change in capacitance with the polarization vector perpendicular to and parallel to the stress axis, respectively. D values observed for the quenching transient in the low-temperature stress experiments are shown in Fig. 2 as a function of stress, σ, at various temperatures for all three stress directions. Significant effects with $D > 1$ were seen for both $\sigma \parallel \langle 110 \rangle$

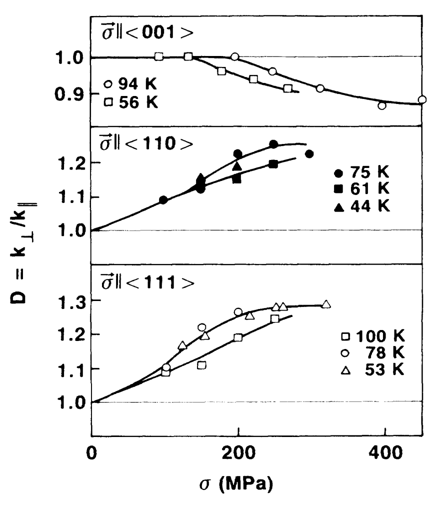

FIG. 2. Dichroic ratios of the photocapacitance quenching transient as a function of stress for the three major stress axes.

and $\sigma \parallel \langle 111 \rangle$. For $\sigma \parallel \langle 001 \rangle$, no dichroism was observed until stresses of 175–200 MPa were applied. D was then observed to decrease with increasing stress. The dichroisms for all three directions were reversible with the removal of the stress in the temperature range of the measurements.

No dichroic effects were observed at zero stress in samples cooled under stress from room temperature. However, zero-stress dichroisms were obtained in the quenching transients after the 425-K stress anneals. The observed values of D were 1.00 ± 0.01, 1.09 ± 0.02, and 1.04 ± 0.01 for $\sigma \parallel \langle 001 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$, respectively.

The absence of any dichroism in the initial trap-emptying transient is consistent with an isolated center of T_d symmetry, but this interpretation is not conclusive because a lower-symmetry center might have an electron density distribution in the relevant electronic state which deviates little from T_d. However, this result has implications with regard to models of $EL2$, as discussed below.

The observed dichroisms in the quenching transient, on the other hand, provide direct information on the symmetry of $EL2$. Indeed, this transient is considered the "signature" of the defect. The model of Vincent, Bois, and Chantre[18] invokes an internal optical excitation of the defect, followed by a lattice relaxation, as the origin of the quenching transient. Stress-induced splittings have been observed in a zero-phonon absorption line attributed to this internal excitation.[6] These splittings were consistent with an isolated center of T_d symmetry. However, it is clear that these zero-phonon line splittings are not related to the dichroisms observed here. The reasons are as follows: First, the high-temperature stress-annealing experiments yield retained dichroisms in the absence of stress. This result is clearly due to a stress-induced preferential orientation of defects which have site symmetry lower than T_d. Second, the dichroic effects observed with low-temperature stress are large compared with those expected to result from the internal excitation splittings. The 1.17-eV photon energy used here is near the center of the absorption band attributed to the internal excitation.[23] The stress-induced splittings of this band should be similar to those of the zero-phonon line. These splittings would be small ($\sim$15 meV or less at 150 MPa)[6] compared to its half-width of $\sim$120 meV.[23] Furthermore, the splittings for $\sigma \parallel \langle 110 \rangle$ and $\sigma \parallel \langle 111 \rangle$ are roughly symmetrical about the zero-stress position,[6] and the intensities of the split components should be equal.[21] The observed dichroisms for stress at low temperature (for example, $D = 1.2$ at 150 MPa for $\sigma \parallel \langle 111 \rangle$) are clearly too large to be consistent with the internal excitation. Third, the sense of zero-phonon line splittings and the dichroisms are inconsistent. With a constant photon energy at the center of the unsplit band, the absorption (and thus the quenching rate) should decrease the most for the split component which moves the farthest from its zero-stress position. The zero-phonon line data[6] would predict $D < 1$ for $\sigma \parallel \langle 001 \rangle$ and $\langle 110 \rangle$, and $D > 1$ for $\sigma \parallel \langle 111 \rangle$. However, the dichroisms observed here show $D \leq 1$ for $\sigma \parallel \langle 001 \rangle$, while $D > 1$ for both $\sigma \parallel \langle 110 \rangle$ and $\sigma \parallel \langle 111 \rangle$. In fact, rather than a decrease in quenching rate, the perpendicular polarizations for the $\langle 110 \rangle$ and $\langle 111 \rangle$ stress axes show *increased* rates relative to zero stress.

Therefore, we conclude that the internal transition which has been assigned to *EL*2 is not directly responsible for the quenching transient. Furthermore, the dichroisms observed here result from a center of less than T_d symmetry. However, the isolated As_{Ga} antisite is not expected to undergo any symmetry-lowering distortion.[24,25] These results indicate unambiguously that *EL*2 is not an isolated antisite defect, and so it must be a complex.

The symmetry properties of noncubic centers in cubic crystals subjected to uniaxial stress have been tabulated by Kaplyanskii.[21] The lack of dichroism after the 425-K stress anneal for $\sigma \parallel \langle 001 \rangle$ while $D>1$ for $\sigma \parallel \langle 110 \rangle$ and $\sigma \parallel \langle 111 \rangle$, and only be consistent with C_{3v} (trigonal) symmetry. We interpret this behavior to be the result of a normal thermally activated stress-induced reorientation of a center of C_{3v} symmetry.

An assignment of C_{3v} symmetry for the defect is also supported by the low-temperature stress results. The lack of a dichroism for $\sigma \parallel \langle 001 \rangle$ at lower stress levels is again consistent with C_{3v} symmetry. The fact that a dichroism does appear at higher levels of stress may indicate that the defect is slightly distorted from C_{3v}, perhaps by second- or third-nearest-neighbor constituents of the complex. There is in fact evidence that *EL*2 consists of an extended cluster rather than a simple point-defect complex.[12,15,26]

The low-temperature dichroisms are obviously not due to the same kind of atomic reorientations which occur at high temperatures, as these are frozen in at low temperatures. These effects are also unlikely to result from reorientations among different Jahn-Teller configurations of the defect because, at least at low stress levels, they correspond to the same C_{3v} symmetry as the nominal atomic arrangement. They may be the result of stress-induced lattice relaxations which are dependent on the orientation of the defects with respect to the stress axis, and which affect their optical cross sections.

Our determination of C_{3v} symmetry for the *EL*2 center is in agreement with the EPR-related experiments of Meyer, Hofmann, and Spaeth.[20] They observe a As_{Ga}-As_i complex with the As_i on a $\langle 111 \rangle$ axis from the As_{Ga}. The present results are also in excellent agreement with the *EL*2 model of von Bardeleben *et al.*,[16] which also involves an As_{Ga}-As_i complex. Here the "normal" state (i.e., the singly ionized paramagnetic state of *EL*2 which is observed in EPR) has the As_i in a second-nearest-neighbor position from the antisite. It is expected that at this separation the two species have little electronic overlap, and each behaves essentially as if isolated. This assumption has both experimental[20] and theoretical[27] support, and explains the apparent T_d symmetry deduced for the antisite from the internal excitation splitting experiments. It is also consistent with our observation of no dichroism in the trap-emptying transient.

For the "metastable" configuration, which results from the photoquenching process, this model has the interstitial in a first-nearest neighbor position. Here, the interaction between the two As atoms is large enough to significantly alter the electronic structure.[27] Such an interaction is consistent with our observation of large dichroic effects together with C_{3v} symmetry for the quenching transient. The most consistent interpretation is then that the quenching transient arises from the metastable state.

The origin of the quenching transient has implications as to the mechanism of the configurational transformation. If the optical transition which produces the quenching transient occurs when the defect is in the metastable configuration, then this transition occurs *after* the transformation to that configuration has taken place. However, in the original model of Vincent, Bois, and Chantre[18] an internal excitation of the defect in the "normal" state is responsible for the transformation, and the quenching transient should thus reflect the symmetry properties of the normal state. As noted above, the experimentally observed internal excitation, which arises from the normal state and shows apparent T_d symmetry is not directly related to the quenching transient, which shows strong dichroic effects with C_{3v} symmetry. The present data therefore do not support this model, but are consistent with a charge-state controlled relaxation model where the quenching transient arises from an optical transition of the defect in the metastable state.[19]

In conclusion, the photocapacitance quenching behavior of the *EL*2 center under uniaxial stress indicates directly that *EL*2 is a complex with C_{3v} (trigonal) symmetry. These results are in agreement with the model of von Bardeleben *et al.*[16] and recent EPR-related observations of an As_{Ga}-As_i complex which has been attributed to *EL*2 (Ref. 20). These experiments also show that the intracenter excitation of *EL*2 is not directly related to the photoquenching effect.

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