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Publication Date

1989-11-01

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

Presented at the 1989 Fall Meeting of the
Materials Research Society,
Boston, MA, December 2, 1989, and
to be published in the Proceedings

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November 1989

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**ABSOLUTE PRESSURE DEPENDENCE OF THE
SECOND IONIZATION LEVEL OF EL2 IN GaAs**

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

ABSOLUTE PRESSURE DEPENDENCE OF THE SECOND IONIZATION LEVEL OF EL2 IN GaAs

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ABSTRACT

We report the results of DLTS experiments under uniaxial stress on the second ionization level of EL2(++/+) in p-type GaAs. We measured the shift in the hole emission rate as a function of stress applied in the [100] and [110] directions. By modeling the valence band with two independently displacing bands and appropriately derived effective masses, we obtain a small absolute hydrostatic pressure derivative for the defect, 39 ± 15 meV GPa⁻¹. The shear contribution is negligible. This result is very different than for the first ionization level, EL2(+/0) with a emission energy pressure derivative of 90 ± 15 meV GPa⁻¹. The difference can be accounted for by the pressure dependence of the electron capture barrier of EL2(+/0), 49 ± 15 meV GPa⁻¹. The absolute pressure derivatives of the two levels are then comparable and in good agreement with simple theory for Ga site point defects.

INTRODUCTION

The fundamentally interesting property of double donor EL2 in GaAs is the metastability of the defect. By illuminating a cooled crystal, $T < 100$ K, with $1.1 \mu\text{m}$ light the EL2 level in its neutral charge state can be removed from the bandgap. This photoquenching property of EL2 has been experimentally well documented, but despite extensive theoretical and experimental studies no commonly accepted microscopic model for EL2 in GaAs exists. Proposals range from very elaborate complexes involving arsenic antisite and vacancies [1] or antisite and interstitials [2] to simple arsenic antisite-like defects [3-6]. Common to all the various microscopic models, the defect metastability is interpreted in terms of a large lattice relaxation of the atoms forming the defect. To investigate the existence of a large lattice relaxation, applied stress can be used in conjunction with other experimental techniques to perturb the position of the atoms and measure the defect properties. The first ionization energy of EL2 is easily accessible by a variety of experimental techniques [7]. On the other hand, properties of the defect in the doubly ionized charge state have been investigated to a lesser extent [8,9]. The difficulty in studying this energy level results from the fact that EL2(++/+) is located in the lower half of the band-gap at $E_v + 0.52$ eV. This requires preparation of p-type GaAs with a sufficient concentration of EL2 so that it is not mistaken for Fe or Cu, which have energy levels close to EL2(++/+). We report on measurements of pressure dependence of the second ionization level of EL2. Using recently determined values of the valence band deformation potential we find the absolute pressure coefficient for this level.

EXPERIMENTAL

This study was carried out on a GaAs crystal grown by the liquid encapsulated Czochralski (LEC) technique. The crystal was doped p-type with Zn, $1.4 \times 10^{16} \text{ cm}^{-3}$ and with In, 0.01%, by weight, to reduce the dislocation density. To prepare samples for stress measurements, $1 \times 1 \times 6$ mm parallelepipeds were cut with the long axes in the [100] and [110] directions. The samples were lapped and lightly etched in 5:1:1 $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ before evaporating Ni Schottky contacts on opposite faces for the DLTS measurements.

To measure the pressure derivative of the ionization energy, the experiment was performed in a DLTS uniaxial stress apparatus capable of applying pressures up to one GPa via a spring and lever arm [10]. The applied stress has been calibrated against the energy splitting of the oxygen thermal donor in Si [11,12] and a correction is made for the thermal dependence of the spring

constant. When stress is applied, endpads are used to cushion the brittle sample. The combination of a long slender sample and endpads produce a homogeneous stress field at the midpoint of the sample where the DLTS measurement is made. To further account for stress inhomogeneities across the sample, DLTS measurements are made on opposite sides of the sample. The sign of the bias is switched to probe under both contacts. The transient time constants of both contacts are then averaged or, if the difference is large, the sample is remounted.

The capacitance of the sample is measured by a one MHz capacitance bridge. The capacitance transient is captured by a digital storage oscilloscope. Multiple transients are averaged by the oscilloscope reducing noise, before the data are transferred to a computer for analysis. The transient is fit to an exponential function determining the time constant of the decay. Figure 1 shows the stress dependence of the transient time constant for stress applied in the [100] and [110] directions. The [100] data extends to higher stress since GaAs is inherently stronger in the [100] than the [110] direction due to stress concentration on the (110) cleavage planes.

When measuring the DLTS peak, it is important to ascertain that the peak is indeed EL2(+++) and is not due to Fe or some other transition metal contamination. Distinguishing this main hole trap from Fe is not necessarily trivial. Identical DLTS energy levels at 0.54 eV have been reported for both Fe [13] and EL2(+++) [9]. Verifying the presence of EL2 by checking for the DLTS signal of the first ionization level, EL2(+/-), at elevated temperatures is not possible in p-type material. The large electron capture cross section of the first ionization transition reduces the magnitude of the DLTS signal in p-type material approximately by two orders of magnitude. To check that the level was not due to Fe contamination, we measured the photon capture cross section of the defect level. Both Fe and EL2(+++) show an initial ionization edge at 0.54 eV but Fe has an additional edge at 0.83 eV [13]. Our sample showed a smooth change in the photon capture cross section over this energy range indicating the level was not due to Fe but rather the second ionization level of EL2.

RESULTS AND DISCUSSION

Ultimately, one would like to know the lattice coupling of a particular charge state of a defect in order to determine the microscopic interaction of the defect wave function with the surrounding atoms, i.e. how does the total energy of a particular charge state change as a function of lattice configuration. Unfortunately, DLTS is an ionization spectroscopy and can measure only the energy difference of initial and final states. It can not measure the pressure dependence of a particular charge state. All pressure dependences are the sum of the pressure dependences of both charge states and the valence band. Thus we determine the pressure derivative of the ionization level. For the stressed DLTS experiment on p-type material we measure the time constant of the thermal emission of holes to the valence band. To interpret the raw emission data as an absolute pressure derivative, several effects must be treated quantitatively. First, the heavy and light hole branches of the valence band split under uniaxial stress complicating the emission process. Second, the carrier capture cross section of the defect can be pressure dependent affecting the DLTS time constant as well. In the following section these complications in the interpretation of the DLTS emission data as a shift in ionization energy will be addressed.

To simplify the problem, the pressure dependent properties of the valence band are approximated by a model which treats the valence band as two independent bands rigidly displacing with increasing stress [14]. The splitting of the light and heavy hole band edge for shear stress is experimentally well known. The normal and shear deformation potentials are $b = -2.0$ eV and $d = -5.4$ eV [15]. The total hole emission probability, is the sum of emission probabilities to both branches of the valence band. This problem has been treated for Si where it has been found that the valence bands can be parametrized in terms of an appropriate effective mass and thermal velocity [14]. One finds in this approach that the effective masses are roughly equal for both bands, $m^* = (m_h + m_l)/2$, and that their values are almost independent of stress. Since the structure of the valence band is similar for GaAs and Si, we can apply the procedure for hole emission in GaAs. To zeroth order we assume a stress independent effective mass. The error introduced by this assumption is only about 5 to 10% of the defect energy shift. Such an error lies well within the sum of other experimental errors.

Figure 1. DLTS hole emission time constant for the second ionization level of EL2 in GaAs versus applied uniaxial stress in the [100] (o) and [110] (Δ) direction. The solid line is the fit for the independent band model.

Figure 2. Shift in defect energy relative to the valence band versus applied uniaxial stress using a rigid two band model for the valence band. (o), [100] applied stress. (Δ), [110] applied stress.

Figure 1 gives the experimental result for the pressure dependence of the DLTS emission time constants for EL2(++/+). At low stress, the time constant increases. The splitting of the valence band is much less than kT at these stresses so hole emission is still occurring to both valence bands. The increasing time constant indicates the level is moving away from the bands. At higher stress, the time constant decreases, even becoming less than the zero stress value. This reflects the large splitting of the valence band. The emission is favored by the Boltzmann factor to the band which is approaching the defect level in energy. Figure 2 shows the calculated energy shift of the level relative to the valence band edge versus applied uniaxial stress using the independent band model. The hydrostatic component of the stress is just one third of the applied uniaxial stress. This slope is $10 \pm 3 \text{ meV GPa}^{-1}$ which corresponds to a hydrostatic pressure derivative of $30 \pm 10 \text{ meV GPa}^{-1}$. The pressure derivative of EL2(++/+) can be expressed as,

$$\left[\frac{\partial E_+}{\partial p} \right]_{R_+} - \left[\frac{\partial E_{vb}}{\partial p} \right]_{R_+} - \left[\frac{\partial E_{++}}{\partial p} \right]_{R_{++}} = 30 \pm 10 \text{ meV GPa}^{-1} \quad (1)$$

where the pressure derivatives are evaluated at the relevant equilibrium positions of each charge state. A value of $a_v = -0.7 \text{ eV}$ [16] for the hydrostatic deformation potential of the valence band, as determined using transition metal deep levels as references, corresponds to a pressure derivative of 9 meV GPa^{-1} . Using this value, the absolute pressure derivative of EL2(++/+) becomes,

$$\left[\frac{\partial E_+}{\partial p} \right]_{R_+} - \left[\frac{\partial E_{++}}{\partial p} \right]_{R_{++}} = 39 \pm 15 \text{ meV GPa}^{-1} \quad (2).$$

The small value of the absolute pressure derivative of the second ionization energy must be contrasted with the large pressure derivative of the first ionization energy. From previous DLTS measurements [17] of EL2(o/+) in n-type material, the absolute pressure derivative was found to be,

$$\left[\frac{\partial E_o}{\partial p} \right]_{R_o} - \left[\frac{\partial E_+}{\partial p} \right]_{R_+} \cong 90 \pm 15 \text{ meV GPa}^{-1} \quad (3).$$

This value of the pressure derivative is much larger than those of any other native defect found in GaAs. In general, this indicates a strong coupling of the defect to the lattice. One can deduce from equations (2) and (3) that the coupling occurs for the neutral state of EL2. This is consistent with the fact that the metastability is observed for the neutral state.

When discussing the large difference in pressure derivatives of two different ionization states of EL2 one has to realize that the emission energy, E_e , determined from a DLTS measurement is the sum of two energies: E_T , the energy separation between the minimum of the appropriate band and the fully relaxed defect occupied by a carrier, plus E_b , the energy barrier for the capture of a carrier from the conduction or valence band by the defect level. The pressure dependence will be the sum of the pressure dependences of these two energies. We measured no pressure dependence of the hole capture barrier for EL2(+++) to within $\pm 15 \text{ meV GPa}^{-1}$.

Conflicting results, however, have been reported recently for the pressure dependence of the electron capture barrier of EL2(o/+), with one group reporting no pressure dependence of the barrier [18] and another group finding a large pressure dependence [19] of $dE_b/dp = -49 \pm 5 \text{ meV GPa}^{-1}$. If the pressure dependence of the barrier were indeed this large then, from eq. (3) the absolute pressure derivative of the defect equilibrium energy level would be,

$$\frac{\partial E_T}{\partial p} = 41 \pm 15 \text{ meV GPa}^{-1} \quad (4).$$

Therefore we would find the pressure coefficients for the equilibrium excitation energy, E_T , of the first and second ionization levels of EL2 to be very similar.

One can compare these data with the results of theoretical calculations of pressure dependence of energy levels associated with native defects in GaAs [19]. It is predicted in these calculations that the pressure derivatives of energy levels of native defects involving the Ga-site depend only very weakly on the location of the level in the band gap. In particular, for the As_{Ga} antisite defect the energy levels with A1 symmetry located at $\sim E_v + 0.75$ and at $E_v + 0.57$ are predicted to have pressure derivatives of $\sim 35 \text{ meV GPa}^{-1}$ and 32 meV GPa^{-1} , respectively. Bearing in mind the limited accuracy of the calculations we find that the theoretical values for pressure derivatives of the As_{Ga} levels are in good agreement with the experimental ones determined for the EL2 defect. This result, together with the experimentally found absence of any shear contribution to the pressure dependence of the EL2 energy levels, would appear to be consistent with the As_{Ga} model of the EL2 defect. If, however the capture barrier has little or no pressure dependence then the pressure derivative of the equilibrium energy of EL2(o/+) is large and very different from EL2(+++). In that case the simple theoretical model reported does not predict the pressure dependence of EL2(o/+).

CONCLUSIONS

In conclusion, we have determined the absolute pressure derivative of the second ionization energy of EL2. We find the small value of the pressure derivative and the lack of orientational dependence consistent with the typical values of simple native defects in GaAs. Comparison of the pressure derivatives of the first and second ionization energies of EL2 gives quite different values. However, the lack of consistent data on the pressure dependence of the electron capture barrier of EL2(o/+) does not allow a strong comparison with theory at this point in time. In order to resolve the conflicting data, studies are being undertaken to measure directly the pressure dependence of both the electron capture barrier, E_b and the thermal equilibrium energy, E_T for EL2(o/+).

ACKNOWLEDGEMENTS

The authors would like to thank Jacek Lagowski for his interest in this work and providing the GaAs material. This work was supported by the Director, Office of Energy Research, Office

of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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