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Identification of a second energy level of $EL2$ in n-type GaAs

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A second energy level of the $EL2$ defect has been identified in n-type epitaxial GaAs using junction space-charge techniques. The identification of this second energy level as being due to $EL2$ is established by measurements of the $EL2$-characteristic optical cross section for persistent quenching. The spectral dependence of the optical cross sections for promoting the second electron to the conduction band σ_{n2}^{o} and the corresponding optical excitation of a hole to the valence band σ_{p2}^{o} have been determined in absolute numbers at $T=150$ K and $T=85$ K, respectively.

The identification of the $EL2$ defect and the understanding of its energy structure in GaAs are of vital importance in semiconductor physics. Interest arises, on one hand, from the dominant role the level plays in the compensation mechanism in the technologically important semi-insulating GaAs materials, and, on the other hand, from the peculiar and still unexplained physical properties of this defect, such as its persistent metastability.[1,2] For many years it has been assumed that the $EL2$ defect in GaAs has only one energy level in the band gap. This is the well-known deep donor level at $E_c-0.74$ eV, which is the dominant deep level in vapor-phase epitaxy and bulk-grown GaAs.

From electron paramagnetic resonance (EPR) measurements on the As_{Ga} defect, and in particular from measurements of photoinduced changes of the As_{Ga} EPR signal in plastically deformed GaAs, it was suggested that two As_{Ga}-related energy levels were present in the band gap.[3] This was interpreted in a model where the isolated As_{Ga} defect was acting as a double donor, with the first ionization stage identical to the $EL2$ level. This simple model was, however, questioned when it was realized that the As_{Ga} EPR signal in plastically deformed GaAs showed properties different than the As_{Ga} EPR signal observed in as-grown crystals.[4] The subsequent investigations of the EPR signals in a variety of materials showed clearly that different As_{Ga}-related EPR signals were, indeed, present.[5-8] However, one of the As_{Ga}-related defects observed by EPR in as-grown crystals was found to be a reasonable candidate for the $EL2$ defect, and in the following investigations the properties of this defect were correlated with the properties of $EL2$.[9,10] Since the As_{Ga}-related defect has been observed to have three charge states (indicating the existence of two energy levels in the band gap), the search for a second energy level of $EL2$ has been an important task during recent years.

The first reported attempt (independently of EPR) to observe a second energy level was performed in an n-type liquid-encapsulated Czochralski (LEC) GaAs crystal where a level at $E_v+0.45$ eV was observed using space-charge techniques.[11] The second attempt, using the same technique, was performed in a p-type crystal grown by the horizontal Bridgemen method.[12,13] Here, a hole trap proposed to be associated with the double charge state of the As_{Ga} was observed at $E_v+0.54$ eV. It is, however, clear that the two reported levels are not identical, since the energy position as well as the spectral shape of the ionization cross section for holes differed significantly. It is tempting to believe that the observed defect in p-type material is indeed related to $EL2$ since their experiments indicated that it could be photoexcited to a persistent metastable state, a property characteristic of the $EL2$ defect. The conclusion is, therefore, that the energy level observed in n-type LEC material is probably not $EL2$ related. Since the $EL2$ defect was originally identified via the $E_c-0.74$ eV energy level, which was observed by space-charge methods in n-type GaAs, and since there are no fundamental reasons why a second energy level, if present, should not be observed in such materials, it is very important for the credibility of the identification of $EL2$ as being As_{Ga} related to investigate whether or not there is a second energy level in n-type material.

In this Rapid Communication, we report on the first successful identification of a second $EL2$ level (called $EL2_2$ to distinguish it from the normal $EL2_1$ level) in n-type epitaxial GaAs material. We show that this energy level is, indeed, identical to the energy level previously observed in p-type material. Finally, we present the spectral dependences of the optical cross sections for electron and hole ionization from the second $EL2$ level measured in absolute numbers.

The experimental work was performed on Schottky diodes fabricated on epitaxially grown (metal-organic vapor-phase epitaxy) n-type GaAs layers with free carrier concentrations $\approx 5\times10^{15}$ cm^{-3} and $EL2$ concentration around 5×10^{13} cm^{-3}.[14] The optical cross sections were determined from the analysis of time constants and initial slope values of photocapacitance transients.[15]

In a recent investigation of the optical cross sections of the $EL2_1$ level at low temperatures, it was observed that the optical cross section for electrons, σ_{n1}^{o}, is much larger than that for holes, σ_{p1}^{o}, at $h\nu\gtrsim 1.3$ eV.[16] Consequently, in a sample illuminated with $h\nu=1.38$ eV, the fraction of neutral $EL2$ defects is only around 3%, with the remaining defects being in other charge states (here we use the generally accepted assignment of filled $EL2_1$ levels as being neutral; see Fig. 1). If there is only one level in the gap, this other charge state is singly ionized, while if there

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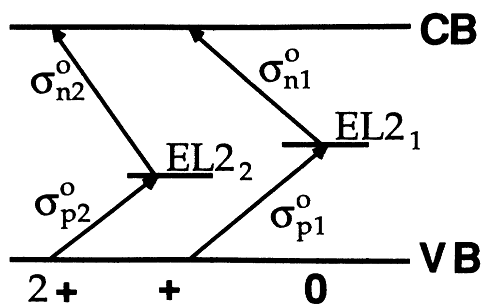

FIG. 1. An energy-level diagram defining the notation of the energy levels, the charge states, and the corresponding optical cross sections for electron, σ_n^o, and hole, σ_p^o, ionization of $EL2$ in GaAs.

are two levels in the gap, the resulting charge states will be singly and/or doubly ionized. The ratio depends on the, hitherto unknown, magnitudes of the optical cross sections of the second energy level. If some of the defects are transformed to the doubly ionized charge state and the second energy level is located in the lower half of the band gap, it should be possible to observe a photocapacitance signal from the hole ionization σ_{p2}^o when the sample is illuminated with $h\nu < 0.75$ eV photons. Performing such experiments, an $EL2_2$-related signal is in fact observed, as will be shown below.

The identification of the signal as being $EL2_2$ related is based on three arguments. The first is the fact that the photon energy used $(0.54 < h\nu < 0.73$ eV) is too low to affect the $EL2_1$ level. The second is the observation that

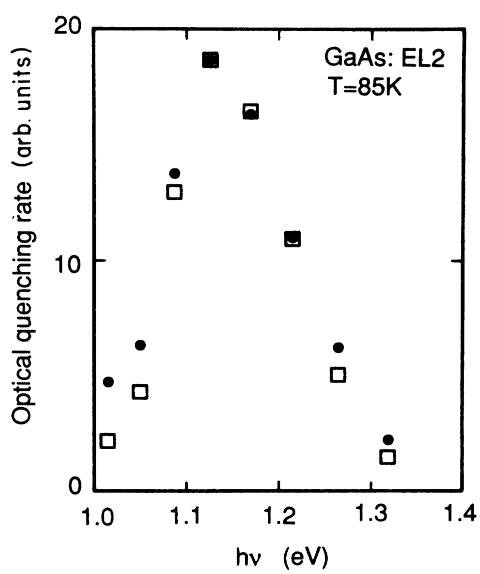

FIG. 2. The optical quenching rates as measured on the $EL2_1$ level (□) and on the $EL2_2$ level (●) in the same measurement sequence. The rates are obtained by measuring the magnitudes of the capacitance signals from 0-+ transitions, using $h\nu' = 1.38$ eV light and $h\nu'' = 0.68$ eV pump light (to prevent centers from being doubly ionized), and for +-2+ transitions, by switching off the pump light, after different periods of quenching illumination with $h\nu$ photons. The deduced rates are plotted here as a function of quenching energy $(h\nu)$.

the signal is persistently bleached when the sample is illuminated with photons in the range $1.0 \leq h\nu \leq 1.3$ eV. The optical cross section for this process is identical to the cross section for the well known[1] quenching of $EL2_1$, as shown in Fig. 2. This shows that the "new" defect (energy level) can be transferred to the neutral-charge state of $EL2$ from where the transfer to the metastable state occurs. The third argument comes from the observation that the ratio of the total capacitance change from the first and second energy levels is always the same. This has been investigated in five different types of epitaxial materials which have been subject to different stoichiometric conditions during growth, resulting in different background dopings as well as different $EL2$ concentrations.[14] It should be noted that the ratios are not, in general, the same if the samples are compared directly, but they are always the same if the signals are measured as the difference before and after quenching of $EL2$, and then compared. The conclusion from these experiments is, therefore, that a second $EL2$ level is present in n-type GaAs.

Since the photocapacitance signal (related to $EL2$) is a measure of the redistribution between different charge states of the $EL2$ defect, and since the time derivative of the capacitance signal during illumination is directly proportional to the change in charge concentration, it is useful to study the rate equations describing these processes:

$$\begin{aligned} dn_0/dt &= (-\sigma_{n1}^o n_0 + \sigma_{p1}^o n_+)\phi \,, \\ dn_+/dt &= (\sigma_{n1}^o n_0 - \sigma_{p1}^o n_+ - \sigma_{n2}^o n_+ + \sigma_{p2}^o n_{2+})\phi \,, \\ dn_{2+}/dt &= (-\sigma_{p2}^o n_{2+} + \sigma_{n2}^o n_+)\phi \,, \\ N &= n_0 + n_+ + n_{2+} \,. \end{aligned} \tag{1}$$

Here n_0, n_+, and n_{2+} are the concentrations of $EL2$ defects in neutral, singly ionized, and doubly ionized charge states, respectively. N is the total concentration of $EL2$ defects, σ_{n1}^o the optical cross section for ionization of the neutral state, σ_{p1}^o the optical cross section for transfer from the singly ionized to the neutral state, σ_{n2}^o the cross section for transfer from the singly ionized to the doubly ionized state, σ_{p2}^o the optical cross section for transfer from the doubly ionized to the singly ionized state, and ϕ the photon flux.

The optical cross sections for hole ionization of the $EL2_2$ level were measured at $T = 85$ K using $h\nu = 1.38$ eV light to initially populate the doubly charged state, as described above. Since σ_{n1}^o, σ_{p1}^o, and σ_{n2}^o are equal to zero for photon energies ≤ 0.75 eV, the rate equations [Eqs. (1)] are simplified to

$$\begin{aligned} dn_0/dt &= 0 \,, \\ dn_+/dt &= \sigma_{p2}^o n_{2+}\phi \,, \\ dn_{2+}/dt &= -\sigma_{p2}^o n_{2+}\phi \,. \end{aligned} \tag{2}$$

The σ_{p2}^o cross sections could consequently be obtained from measurements of the initial slope [and also from the time constant $\tau(\tau^{-1} = \phi\sigma_{p2}^o)$] of the photocapacitance signal. Because of the influence from background deep levels, the $EL2$-related photocapacitance signal was measured as the difference between signals obtained before and after bleaching of the $EL2$ defect. As shown in Fig. 3, such subtracted signals are perfectly exponential over two orders of magnitude. Experimental data for σ_{p2}^o could be obtained from the threshold of the signal, around 0.54 eV, to the threshold of the σ_{p1}^o signal of $EL2_1$, around 0.75 eV. The absolute numbers were obtained by measuring the photon flux using a calibrated thermopile detector. Since only a small fraction of the $EL2$ defects are optically converted to the doubly charged state (about 10%), it was only possible to measure the σ_{p2}^o cross section over two orders of magnitude. The measured σ_{p2}^o cross sections are shown in absolute values in Fig. 3.

The optical cross sections for electron ionization of $EL2_2$ were measured at $T=150$ K using the following method. The probe light was used to initially transfer defects from the neutral charge state and a strong pump light at $h\nu=0.68$ eV was simultaneously used to prevent the $EL2$ defects from reaching the doubly charged state. As a result, a certain proportion of the defects was transferred to the singly ionized charge state. The exact amount depends on the energy of the probe light, and at equilibrium the populations of different charge states are given by $n_0=[\sigma_{p1}^o/(\sigma_{n1}^o+\sigma_{p1}^o)]N$, $n_+=[\sigma_{n1}^o/(\sigma_{n1}^o+\sigma_{p1}^o)]N$, and $n_{2+}=0$. If the pump light is switched off (at time $t=t_1$) at equilibrium, a capacitance transient is observed. The rate equations describing this situation at time t_1 are

$$\begin{aligned} dn_0(t=t_1)/dt &= 0\,, \\ dn_+(t=t_1)/dt &= -\sigma_{n2}^o n_+(t_1) \\ &= -\sigma_{n2}^o(\sigma_{n1}^o/\sigma_{n1}^o+\sigma_{p1}^o)\phi N\,, \\ dn_{2+}(t=t_1)/dt &= \sigma_{n2}^o n_+(t_1) \\ &= \sigma_{n2}^o(\sigma_{n1}^o/\sigma_{n1}^o+\sigma_{p1}^o)\phi N\,. \end{aligned} \tag{3}$$

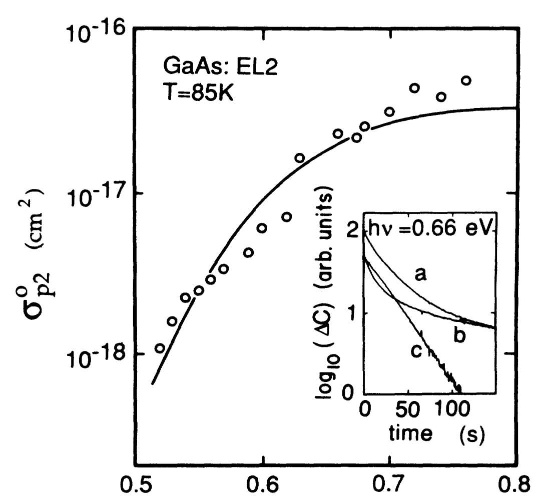

FIG. 3. Hole ionization cross sections, σ_{p2}^o, for $EL2_2$ (rings). The raw photocapacitance data (a in inset) has been corrected by subtracting the signal obtained after persistent bleaching of the $EL2$ defects (signal b), resulting in the perfectly exponential $EL2$ signal (c). The solid line represents the data obtained in Ref. 12 in p-type material.

Since the initial slope of the capacitance signal is directly proportional to the rate of the charge transfer, the σ_{n2}^o cross section of the $EL2_2$ level is readily obtained by dividing the initial slope value by $(\sigma_{n1}^o/\sigma_{p1}^o+\sigma_{n1}^o)N$, where σ_{n1}^o, σ_{p1}^o, and N have been previously measured on the $EL2_1$ level. Also here the $EL2$-related photocapacitance signals were obtained from subtraction of signals measured after quenching of the $EL2$ levels (at $T=80$ K) from signals obtained before quenching (at $T=150$ K). The absolute values were thus directly obtained from a comparison between the initial slope of the well known σ_{n1}^o cross section with the initial slope values for σ_{n2}^o cross section measured in the same experiment. Because of the relative magnitudes of the optical cross sections (σ_{n1}^o, σ_{p1}^o, σ_{n2}^o, and σ_{p2}^o) at the measured photon energies, the dynamic range of the σ_{n2}^o measurements was even more limited than for the σ_{p2}^o measurements. The measured σ_{n2}^o cross sections obtained in this way are shown in Fig. 4 in absolute values.

Since the σ_{n2}^o cross section in Ref. 11 is measured over a very limited energy range (<0.1 eV), it is more rewarding to compare the σ_{p2}^o cross sections. Comparing the σ_{p2}^o cross section from Ref. 11 with that shown in Fig. 3, it is obvious that the spectra originate from different energy levels. Since we have proven that the spectrum shown in Fig. 3 is related to $EL2$, it can be concluded that the defect measured in Ref. 11 is either not related to $EL2$ or, alternatively, that a third $EL2$-related energy level located at ≈ 0.45 eV is present. The latter possibility is, however, quite unlikely since we do not observe any $EL2$-related signal below 0.54 eV in our epitaxial material.

The σ_{p2}^o cross section obtained in p-type material in Ref. 12 is, on the other hand, very similar to σ_{p2}^o obtained in our measurements, as shown in Fig. 3. The persistent quenching of the signals, as is observed in both investigations, provides further evidence for the conclusion that the same energy level is observed in n-type and p-type material. So far, the best estimate of the binding energy of this second energy level of $EL2$ in GaAs is $E_v+0.54$ eV, which was deduced in Ref. 12.

In conclusion, a second energy level of $EL2$ has been identified in n-type epitaxial material. The identification

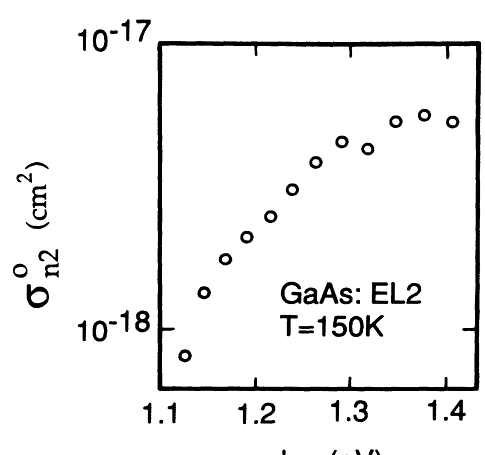

FIG. 4. Electron ionization cross sections σ_{n2}^o for $EL2_2$.

are two levels in the gap, the resulting charge states will be singly and/or doubly ionized. The ratio depends on the, hitherto unknown, magnitudes of the optical cross sections of the second energy level. If some of the defects are transformed to the doubly ionized charge state and the second energy level is located in the lower half of the band gap, it should be possible to observe a photocapacitance signal from the hole ionization σ_{p2}^{o} when the sample is illuminated with $h\nu < 0.75$ eV photons. Performing such experiments, an $EL2_2$-related signal is in fact observed, as will be shown below.

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