Optical excitation of the metastable $EL2^*$ level

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Photocurrent studies of optical quenching of the near-intrinsic photosensitivity by 1.1-eV photons in semi-insulating GaAs reveal that this phenomenon is associated with an internal excitation of the metastable $EL2^*$ level, which then relaxes into a second metastable state, which is characterized by both extrinsic (1.1-eV) and intrinsic ($h\nu > 1.4$-eV) photosensitivity quenching. The spectral distribution of the $EL2^*$ excitation is obtained, and the results are discussed. Photoluminescence studies suggest the role played by shallow acceptors in this phenomenon.

I. INTRODUCTION

Midgap levels in semi-insulating GaAs are very interesting in view of the technological applications of this material. These levels are the compensators of residual shallow levels and thus provide the semi-insulating properties required by GaAs as a substrate in integrated-circuit (IC) technology. There is a family of levels commonly labeled $EL2$,[1,2] which possess the ability to relax into a metastable configuration with illumination at low temperature in the energy range from 1 to 1.3 eV.[1-4]

The physics of this defect is a matter of controversy, due to the fact that its chemical identity is not well characterized and also because the nature of the strong relaxation undergone by the lattice leading to the metastability is poorly understood. New insights have led other workers to claim that $EL2$ is a complex involving an arsenic antisite and an arsenic interstitial.[5,6] Such a complex would have different optical parameters depending on the relative position of its components. The first-neighbor arrangement is believed to be the metastable configuration, whereas the normal configuration would be associated with more distant pairs.

It should also be noted that other metastable behavior has been observed in this material; for example, it exhibits a similar photoexcitation spectrum to that of $EL2$, from which we conclude that they are related to the same family of defects.[7] In fact, they are optically induced by 1–1.3-eV photons, and the reverse transition, i.e., the restoration of the initial state, is a thermally activated process. These metastabilities are observed in different experimental ways and can be summarized as follows.

Band-edge effects. Different transformations of the band-edge photoresponse have been reported, i.e., quenching of the optical absorption, far-infrared absorption from residual acceptors,[8] changes in the low-temperature thermally stimulated current (TSC) spectra,[3,10] quenching and enchancement of the photoconductivity,[11,12] and quenching of the photoluminescence excitation (PLE).[13]

Other effects. The main effects to be cited here are the optical enhancement of the extrinsic photocurrent[7,12] and the observation of new EPR signals after excitation with extrinsic light.[14,15]

The enhancement of the photocurrent has been proved to be associated with a defect other than $EL2$, probably the so-called $EL6$.[16-18] Nevertheless, the study of such an effect reveals the existence of some relation between the two as has been suggested elsewhere.[19,20] Indeed $EL6$ seems to involve the As_{Ga} antisite,[16,20] which has been largely described in other papers.[7,11,12]

Contrary to the usual assertion of the nondirect experimental observation of the metastable state, the subsidiary quenching effects seem to account for the possibility of an optical excitation of the metastable state. This possibility has already been considered in relation to the recovery of the normal photosensitivity at low temperature by exciting with 0.8-eV (Ref. 21) or 1.1-eV photons.[22] The aim of this paper is the study of optical quenching of near-band-gap photocurrent and its relation to optical excitation of the metastable $EL2^*$ level.

II. EXPERIMENTAL

A. Samples

The samples used were cut from both horizontal Bridgman (HB) and liquid-encapsulated Czochralski (LEC) ingots. Typical resistivities lie between 10^7 and 10^9 Ω cm at

room temperature; the samples were mechanically polished and etched in a 5:1:1 H_2SO_1:H_2O_2 (30%) solution. Typical sizes of the specimens used for measurements are $5\times2\times0.5$ mm^3.

The HB samples (grown by RTC, France) were intentionally doped with Cr, and different amounts of Ga_2O_3 were added to the melt. Most of the results reported here refer to sample RT 420, for which the weight ratio (Cr to GaAs) in the melt was 0.000 20.

The LEC samples (grown by Thomson Semiconductor, France) were either undoped or In doped. Most of the results reported refer to a sample cut from ingot Ag 70, (which is weakly In alloyed).

The choice of samples RT 420 and Ag 70 for illustrating the results presented in this paper was made because they exhibited a strong photoquenching effect revealing the existence of a high concentration of $EL2$ levels.

Electric contacts were made by different procedures: In dots annealed at 390 °C, silver-paste-painted electrodes, evaporated In, and AuGe-alloyed electrodes. No significant variation of the results was observed between them when the photocurrent was measured at low bias, in the linear part of the I_{ph} versus V plot. The contacts were masked in order to avoid illumination of the space-charge region. Samples were provided of lateral electrodes for measuring the Hall effect.

B. Apparatus

The samples were mounted in the holder of a closed-circuit liquid-helium Air Products cryostat, which allowed temperature regulation from 10 to 300 K. Optical excitation was provided by a 150-W halogen lamp passing through a Bausch & Lomb grating monochromator and a filter system. Light was directed onto the sample by a light pipe transparent to near-infrared radiation. The photon flux was measured by a thermopile and then corrected for incident wavelengths, in order to excite with a uniform photon flux along the scanned spectral range. Photocurrent measurements were made by either a logarithmic picoammeter (Keithley model 26000) or a digital electrometer (Keithley model 616).

III. RESULTS

A. Preliminary results

Here we will consider previous results on near-band-gap persistent phenomena, obtained by ourselves or by other authors.

1. 1–1.3 eV near-band-gap persistent phenomena

We summarize the near-band-gap effects related to extrinsic photoquenching. The observation requires preliminary excitation with bleaching light (1–1.3 eV). This stage shall be implicit in the following description.

The optical quenching of the near-band-gap absorption has been reported by several authors and consists of a persistent quenching of the optical absorption for energies above 1.4 eV. The recovery of the initial optical transmission is thermally activated and occurs between 60 and 120 K depending on the samples.[22–24] This is in agreement with similar observations on thermal recovery of the extrinsic optical quenching effect. This confirms the relationship between the two quenching phenomena.

Optically induced far-infrared absorption from residual acceptors (Fourier transform ir, FTIR) demonstrates the neutralization of the residual acceptors, mainly C and Zn, by holes.[8] This optical absorption is correlated with a decrease in the normal $EL2$ concentration. In this way, the existence of persistent holes, either bound or free, has been detected by electronic Raman spectroscopy (ERS) and Drude-type free-carrier absorption.[25,26]

TSC spectra recorded from 4 K reveal a strong dependence on the excitation conditions and samples. A strong quenching of the trap population, as revealed by TSC, is observed for traps with activation energies below 150 meV under bleaching excitation conditions. This phenomenon has been the subject of a previous study.[9,10]

Photoconductivity. The near-band-gap photoconductivity ($h\nu \geq 1.4$ eV) undergoes significant quenching when the sample is illuminated with quenching light.[11,27]

The occurrence and mechanisms of such band-gap phenomena imply a close relationship between the steps leading to both the extrinsic and the near-intrinsic quenching of the photoresponse. This has been considered to be a check on Levinson's dipolar model of $EL2$.[28] This model consists of the pairing between a deep and a shallow donor, which are driven to a close configuration by a Coulombic force when photoionization places the system into a favorable electrostatic condition. The direct relationship of both quenching effects with such a mechanism has to be proved. In other words, it must be checked whether the appearance of both metastabilities is the immediate consequence of such a pairing or not.

2. Quenching of the near-intrinsic photocurrent

In order to obtain insight into this problem, further information is required on the formation kinetics of both quenching effects as well as the correlation between them in different kinds of samples.

The first question to be answered deals with the simultaneity of the occurrence of both quenchings upon excitation with 1.1-eV photons. All of our studies using the photocurrent technique clearly demonstrated a sequential mechanism; in other words, the extrinsic quenching of the photocurrent took place in the first state, and further illumination with extrinsic photons induced the quenching of the near-intrinsic photocurrent[11,27] (Fig. 1). Therefore, we concluded that the quenching of the near-intrinsic ($h\nu > 1.4$ eV) photocurrent did not correspond to a relaxation of the normal state of $EL2$ but rather seems to be associated with a relaxation of the $EL2^*$ state itself. This is in agreement with results reported by Otsuka *et al.*[25] from far-infrared magnetoabsorption measurements, from which the authors claimed a pairing between $EL2^*$ and a shallow donor. This observation would invoke the possibility of optically exciting the metastable $EL2^*$ level.

The quenching of intrinsic photocurrent with 1–1.3-eV light takes place in the absence of extrinsic photocurrent,[11] which suggests that this transition does not in-

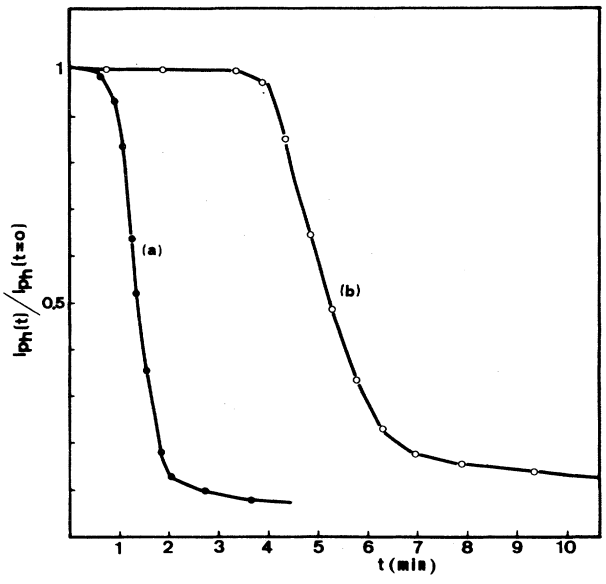

FIG. 1. (a) $I_{ph}(t)/I_{ph}(t=0)$ vs excitation time with 1.1-eV light. ($h\nu=1.1$ eV), (b) ($h\nu=1.45$ eV) $T=80$ K. The extrinsic quenching takes place prior to the intrinsic quenching.

volve the ionization of $EL2^*$; therefore, such an excitation would deal with an intracenter transition of $EL2^*$.

The internal excitation of the metastable state, which has been considered to be optically inaccessible, was also suggested by the piezospectroscopic data of Levinson and Kafalas,[30] who stated that the quenching transient of the photocapacitance would arise from the metastable state itself, which would relax in a sequential charge-state-controlled process in As_{Ga}-containing defects. Other long-term relaxations[22,23] have also been reported in the literature which seem to agree with a rather complex lattice-relaxation mechanism. This would imply that the lattice relaxation leading to the quenching of the near-intrinsic photocurrent does not fit a pure Coulombic model unless the charge redistribution in the complex defect could lead to a Coulombic-like interaction between different parts of the complex.

B. Optical excitation of $EL2^*$

From the above considerations it seems possible to assess the excitation spectrum of $EL2^*$ and thus the following experiment has been carried out (Fig. 2).

The sample is illuminated with quenching light (primary light, $h\nu_1=1.1$ eV) for a time sufficient to produce extrinsic quenching, and then the near-intrinsic photocurrent spectrum ($h\nu>1.4$ eV) is recorded. Next the sample is illuminated for a time t_2 with secondary light, $h\nu_2$, and thereafter the near-intrinsic spectrum is recorded again. The secondary light is tuned to determine the spectral distribution of the quenching of the near-intrinsic photocurrent. The normal state is restored after every cycle by heating above 150 K. It is clearly observed that the near-intrinsic quenching is a long-term process in relation to the extrinsic quenching and depends on the secondary light's wavelength. The obtained spectral distribution is shown in Figs. 3 and 4 for a LEC and a HB sample, respectively.

It seems reasonable to assume that this spectrum is associated with the excitation of the $EL2^*$ state. Indeed, the observation of the near-intrinsic quenching of the photocurrent is only possible if the extrinsic quenching has occurred in the first stage as shown in our experiments. Furthermore, the secondary light does not transfer free carriers to the free bands, because transitions from $EL2$ were previously quenched by the primary light; therefore the electronic transition leading to the quenching of the near-intrinsic photocurrent would be related to an intracenter transition of the metastable $EL2^*$ state. The maximum of the $EL2^*$ excitation spectrum is around 1.1 eV, and the full width at half maximum (FWHM) is 110–120 meV, which agrees quite well with the value reported by Kaminska *et al.*[31] for the intracenter transition of $EL2$. If we compare the spectrum of the near-intrinsic quenching with that of the extrinsic quenching, a slight shift to the low-energy side is observed, more markedly in the HB sample, which might

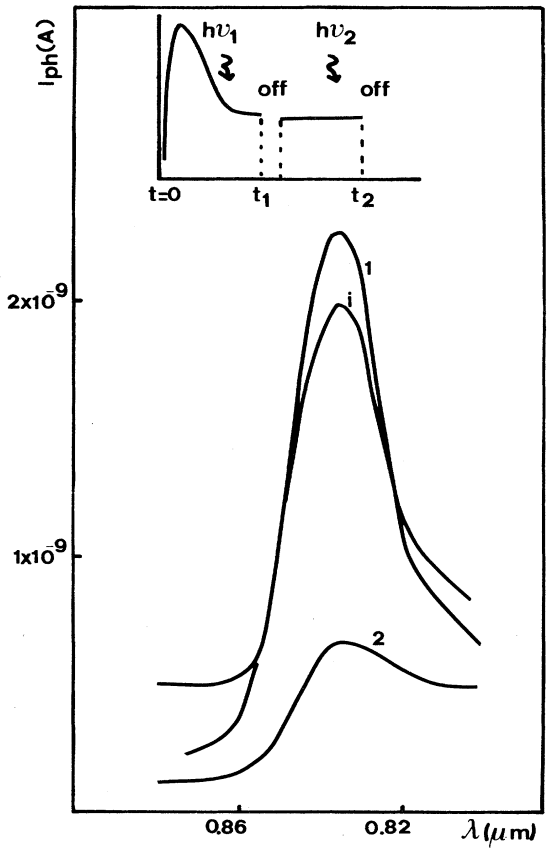

FIG. 2. Experiment for determining the spectral distribution of $EL2^*$. Curve i is the initial near-intrinsic photocurrent spectrum. Curve 1 is the near-intrinsic photocurrent spectrum after primary light excitation. Curve 2 corresponds to the near-intrinsic photocurrent spectrum after secondary light excitation (see text).

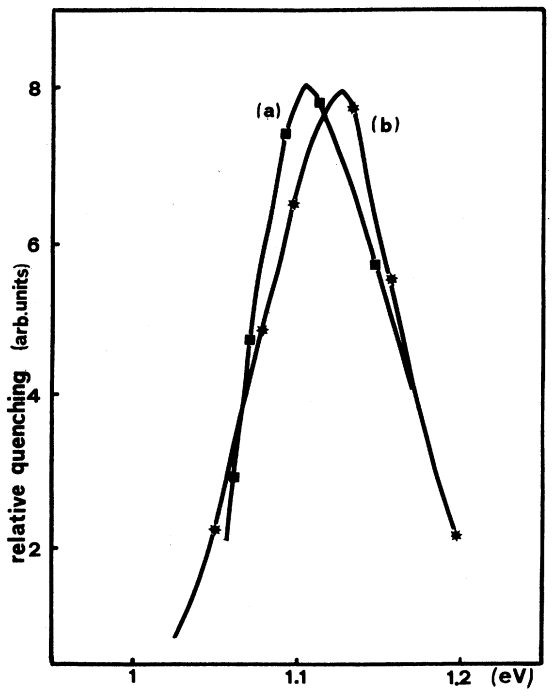

FIG. 3. (a) Spectral distributions of near-intrinsic quenching and (b) extrinsic quenching for a low-ln-doped LEC sample.

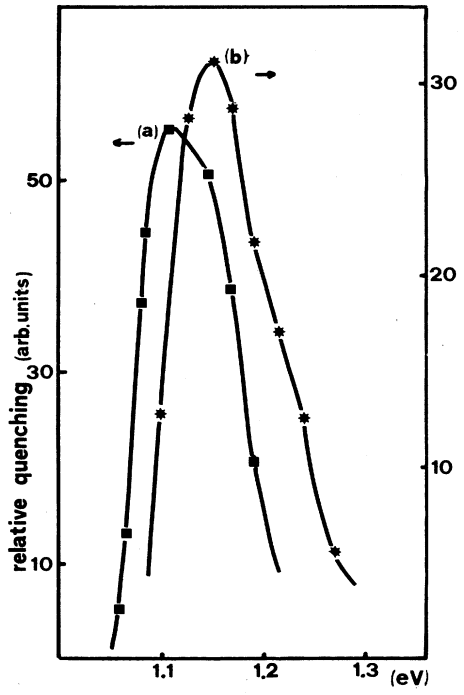

FIG. 4. (a) Spectral distribution of the near-intrinsic quenching and (b) extrinsic quenching for a Cr-doped HB sample.

reveal a different arrangement of the complex defect involved in the photoquenching phenomenon.

IV. DISCUSSION

Two interpretations could account for the observed quenching of the band-edge photocurrent.

1. The near-intrinsic quenching occurs as a consequence of sequential relaxation of a complex defect involving both $EL2^*$ and the corresponding shallow donor or acceptor, which are generated or neutralized during the relaxation.

2. The excitation of $EL2$ to $EL2^*$ transforms the properties of other levels, which then show a metastable behavior, as has been proposed by Bray *et al.*[25] for describing the existence of free holes and acceptorlike ERS signals.

In other words, the relaxation might produce a change in the location and concentration of levels or only a change in their occupation due to the shift of the Fermi level, when the extrinsic quenching is achieved.

It is worth noting that experiments on temperature recovery of the photocurrent[11] demonstrated that the restoration of the near-intrinsic photocurrent took place a few degrees (~ 10 K) below the recovery of the normal extrinsic photocurrent. This observation, in addition to the delayed near-intrinsic photocurrent quenching, supports the hypothesis of a sequential lattice relaxation under 1–1.3-eV light excitation. This is in agreement with the thermal recovery of normal sensitivity observed at 60 K for n-type samples.[22,23] Nevertheless, the fact that the intrinsic quenching could also reflect a change in the occupation of such levels as a consequence of the metastability of $EL2$ is a non-negligible possibility, which could coexist with the sequential mechanism.

The lattice relaxation would occur in the following stages.

1. Initially the $EL2^0$ and $EL2^+$ populations are in equilibrium depending on the location of the Fermi level, which implies the existence of ionized shallow acceptors A^-. The excitation with extrinsic light has two consequences: (a) the $EL2^+$ are converted into $EL2^0$ and (b) the $EL2^0$ are ionized and then transformed at a low rate in metastable $EL2^{0*}$ states. Point (a) corresponds to the short-time regime in Fig. 5, and the second is associated with the long-term quenching of Fig. 5. It should be noted that the short-time regime can be strongly modified, even erased if excitation with 0.9 or 1.4 eV is performed before the 1.1-eV illumination. This is achieved by the corresponding shift in the Fermi-level position produced by such excitation. It is quite interesting that in a first stage, before the extrinsic quenching takes place, the intrinsic photocurrent increases relative to the initial intrinsic photocurrent level. This may be due to a decrease of the $EL2^+$ population, with a corresponding decrease in the recombination rate of the electrons excited from shallow acceptors. In fact, the $EL2^+$ level is the main recombination center for the e^- excited from the ionized shallow acceptors (<0.03 eV for LEC samples and <0.08 eV for HB samples above the valence band), as is deduced from the short-time response of the I_{ph} (1.1 eV) versus t plot before and after the 1.4-eV excitation (Fig.

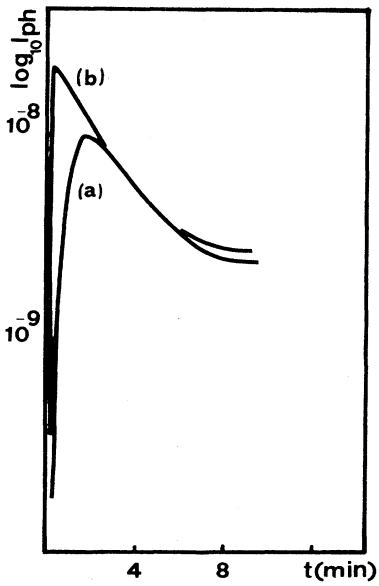

FIG. 5. (a) $I_{ph}(1.1\ eV)$ vs t, before 1.49-eV excitation and (b) after 1.49-eV excitation.

5).

2. The excitation and subsequent relaxation of the $EL2^*$ levels leading to the intrinsic quenching begins at the moment they are created, in other words when the extrinsic quenching begins to be observed. Nevertheless, this relaxation is produced at a low rate and is only clearly observed in the final stages of the extrinsic quenching, for which the dominant process is the excitation of $EL2^*$. A major point of this relaxation is to know the role played by the shallow levels, that is to say, whether the shallow levels participate in the final metastable state, which will be labeled $EL2^{**}$, or are not optically active only because they are emptied due to the $EL2^{**}$ metastability. The hypothesis that the shallow levels should undergo a lattice relaxation leading to a shift of the energy levels is non-negligible and is supported by changes in the trap energies observed in TSC experiments.[9,10] However, the study of In-doped samples (sample Ag70) reveals the existence of quenching, both extrinsic and intrinsic, without noticeable shifts in the TSC spectrum, contrary to what happens for undoped LEC samples.

In relation to this, it should be worth studying the behavior of the band-edge photoluminescence under quenching conditions. The 1.49-eV band, associated with C^0_{As} acceptors, exhibits significant quenching after bleaching light excitation at 4 K.

This observation could be associated with either a decrease of the radiative recombination yield or a decrease of the excitation efficiency. These experiments were carried out with the 514-nm line or an Ar^+ laser as the source of excitation. No shift of the PL band is observed, showing that the radiative recombination efficiency was reduced as a consequence of the existence of nonradiative recombination competitive processes. On the other hand, this result also indicates that at least a part of the carbon acceptors keeps their identity after quenching. In order to obtain insight into this problem, it should be valuable to have data on (PLE) under quenching conditions.

The band-gap absorption is also quenched,[24] which suggests that the excitation of carriers from shallow acceptors becomes less efficient after quenching. In other words, in view of the reported experimental data, it seems to be a reliable hypothesis that the intracenter excitation of the metastable state of $EL2^*$ leads to a lattice relaxation that induces changes in the acceptor population, resulting in changes in the charge state of the shallow acceptors. This could be a consequence of the formation of deep acceptor levels associated with the metastability, which would lock in the electrons initially trapped at shallow acceptors. Therefore other remaining residual shallow acceptors are led to exhibit metastable behavior as a consequence of the above-mentioned metastabilities, without undergoing a lattice relaxation themselves.[25] Another possibility would be that a part of the shallow acceptors shifts to a deeper position in the band gap as a consequence of the lattice relaxation.

The metastable acceptor levels should lie between 0.03 and 0.4 eV above the valence band as deduced from TSC experiments.[9,10] EPR measurements demonstrate the appearance of these acceptors during the metastability of $EL2$[15].

V. CONCLUSION

For the first time the intracenter excitation spectrum of $EL2^*$ has been determined. The results reported in this paper indicate that deexcitation of the excited $EL2^*$ level induces a low-probability nonexponential relaxation. The relation between shallow acceptors and $EL2$ has been discussed, this being an important aspect for understanding the $EL2$ level in GaAs.

In our opinion time-resolved measurements can help one to understand the complexity of $EL2$ metastability. New work on this problem is now in progress and is planned to be the subject of forthcoming papers.

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