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Deep-acceptor-mediated photoquenching of the midgap donor *EL*2 in semi-insulating GaAs

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The effects of lowering the temperature and/or adding shallow acceptors in semi-insulating GaAs on the photoquenching effect of the midgap donor *EL*2 have been extensively studied. Measurements were made on the near-infrared photoabsorption and the photocurrent at $T=8.6-130$ K for various samples containing different concentrations of carbon acceptors ranging from 1.8×10^{15} to 14.3×10^{15} cm^{-3}. The results indicate a strong influence of the two parameters on the photoquenching; the photoquenching was more enhanced both at lower quenching temperatures and at higher carbon concentrations. The results were consistently explained by assuming a deep-acceptor level located at $E_v+(70-80)$ meV, which triggers the onset of *EL*2 photoquenching when it is neutral, while it triggers the onset of *EL*2 photorecovery when it is negatively ionized.

I. INTRODUCTION

The midgap donor *EL*2 plays an important role in making the undoped GaAs crystals semi-insulating, and its suitable control is undoubtedly an essential part of the inquiry of the GaAs wafer industry. In spite of its history over a decade, however, *EL*2 has not been fully understood as of yet. Not to mention the atomistic structure of *EL*2, some of the elementary optical and electrical properties of *EL*2 have not been given common understandings.

Among them is the photoquenching effect. This is a phenomenon in which all the optical and electrical properties of *EL*2 are extinguished when a GaAs sample is illuminated with a 1-μm light below 130 K. This photoquenched state is metastable because the optical and electrical activities can be recovered when the sample is annealed at around 150 K for a few minutes. This metastable state was originally believed to be optically inert, but recent experiments suggest the presence of optical paths of recovery by illuminations with an extrinsic light (0.9 eV[1,2]) or a near-band-gap light.[2] Various experimental methods have been applied to the study of photoquenching of *EL*2, which include the measurements of near-infrared absorption (NIR),[3] photocurrent,[4,5] photocapacitance,[6-8] or electron paramagnetic resonance (EPR).[9-11] Several models have been proposed therefrom.

The models so far can be categorized into two groups: one that claims that the photoquenching occurs locally at the *EL*2 defect[6] and the other that claims that the photoquenching occurs as a result of interactions of *EL*2 with other defects. Among the latter are the charge-transfer model,[9,10] the actuator-level model,[12,13] or the shallow-donor complex model.[14] The charge-transfer model, developed by Benchiguer *et al.*,[9,10] assumes that the electrons or the holes emitted optically from the midgap $\mathrm{As_{Ga}}^{0/+}$ level are captured by donors or acceptors in the crystal, and they remain trapped at sufficiently low temperatures. The metastability, therefore, is best described by a Fermi-level splitting of the system, which means that the metastability lies in a whole crystal and not at an individual $\mathrm{As_{Ga}}^{0/+}$ defect. The most unique point of this model is that the $\mathrm{As_{Ga}}^{0/+}$ level itself is not annihilated during the "quenching" process. This model is based on its successful reproduction of the temporal behavior of the EPR $\mathrm{As_{Ga}}^{+}$ signal during the quenching light illumination. However, EPR observation alone cannot exclude the possibility of a true annihilation of the $\mathrm{As_{Ga}}^{0/+}$ level, since it brings no information on the concentration of the $\mathrm{As_{Ga}}^{0}$ state. Another problem, within the context of our argument, is that there has been no complete proof for the identification between $\mathrm{As_{Ga}}^{0/+}$ and $EL2^{0/+}$ levels.

The actuator-level model has been proposed by Jimenez *et al.*[12,13] By finding a determinitive role of near-band-gap-light illumination on the optical recovery of the *EL*2 normal state or on the control of the photoquenchable state density, they assumed that the charge state of a certain level, which they called an actuator level, should play a key role in triggering the metastable transition. They named a double acceptor $\mathrm{Ga_{As}}$ as a most probable candidate for this actuator level.

More direct evidence for the possible association of other levels than *EL*2 in the metastable state has been recently reported by Ohyama *et al.*,[14] who observed the behavior of shallow donors by the far-infrared magneto-optical absorption method during the photoquenching process. By finding a simultaneous quenching of a shallow-donor level, they concluded that some shallow-donor levels must be involved in the metastable state of *EL*2.

The nature of the *EL*2 metastable state is also relevant to the identification of the *EL*2 defect. From the very beginning of the *EL*2 history, it has been clear by EPR measurements that *EL*2 at least contains an arsenic antisite ($\mathrm{As_{Ga}}$). Dabrowski and Scheffler[15] calculated the electronic states of a simple $\mathrm{As_{Ga}}$ defect, and showed that the $\mathrm{As_{Ga}}$ at a tetrahedral (T_d) symmetry position, which corresponds to the normal *EL*2, becomes metastable when it is shifted after photoexcitation to a C_{3v} symmetry position to form a vacancy-interstitial ($V_{\mathrm{Ga}}\mathrm{As}_i$) pair.

Therefore, if proof is given that the photoquenching of $EL2$ occurs locally at an $EL2$ defect, it would be good support for the $EL2=\mathrm{As}_{\mathrm{Ga}}$ model.

On the other hand, Bardeleben *et al.*[16] or Meyer *et al.*[17] proposed an $EL2=\mathrm{As}_{\mathrm{Ga}}-\mathrm{As}_i$ complex model from their EPR,[16,17] deep-level transient spectroscopy,[16] or electron-nuclear double-resonance[17] measurements. A possible presence of a metastable state for this complex has also been theoretically shown by Delerue *et al.*[18] According to the calculation, the normal $EL2$ corresponds to a configuration of this complex with its As_i sitting at a second-neighbor site from the $\mathrm{As}_{\mathrm{Ga}}$. A metastability occurs when the As_i at the second-neighbor site is shifted towards the $\mathrm{As}_{\mathrm{Ga}}$ to a split-interstitial position, which presents no electronic states within the band gap. They further argued the necessity for a presence of negatively ionized $\mathrm{Ga}_{\mathrm{As}}$ in the vicinity of $EL2$, which stabilizes the positive As_i at the second-neighbor position of the $\mathrm{As}_{\mathrm{Ga}}$ against their repulsive interaction.[19] This final picture clearly belongs to the latter category of the photoquenching model.

If the photoquenching of $EL2$ occurs isolatedly at each defect, the phenomenon should not be influenced by the presence or absence of other defects. However, if this is not the case, the photoquenching could be affected by varying the concentrations of other donors or acceptors. This is the strategy of the present study. One thing we have to have in mind is to keep the $EL2$ concentration constant as much as possible. Benchiguer, Mari, and Schwab,[20] who were the first to point out the importance of defects other than $EL2$ in the photoquenching phenomenon, utilized the neutron-transmutation method to introduce shallower donors into the crystal and have investigated the change of the photoquenching phenomenon.[20] Their result indicated a significant enhancement in the time evolution of the $\mathrm{As}_{\mathrm{Ga}}{}^{+}$ EPR signal during the quenching light illumination. This is consistent with their own charge-transfer model, which predicts an enhanced $\mathrm{As}_{\mathrm{Ga}}{}^{+}$ EPR signal during photoexcitation due to enhanced charge transfers to the donors. Their result, however, shows a significant signal increase even before the illumination of the quenching light, which implies a simultaneous introduction of additional $\mathrm{As}_{\mathrm{Ga}}$ or acceptor defects. Aside from their work, to our knowledge no attempts have been made to systematically vary the concentrations of donors or acceptors for the study of the photoquenching phenomenon.

In the present study, we have chosen the carbon acceptor as the defect under control. Carbon, as an extrinsic acceptor, can be rather easily controlled in GaAs, irrespective of the $EL2$ concentration. Our practice[21] indicated a possible variation of the carbon concentration in the range from 10^{14} to 10^{16} cm^{-3}, with the $EL2$ concentration being kept constant at around 1.5×10^{16} cm^{-3}. This fact, together with the rather constant variation of the carbon acceptor within an as-grown wafer as opposed to the dislocation-correlated $EL2$ distribution, suggests a negligible perturbation from carbon acceptors on crystal stoichiometry.

Another requirement for the crystals in the present study is that they should contain a minimum amount of irrelevant intrinsic defects. In this respect, it may be worth commenting that many of the early photoquenching studies in the 1980s were made on insufficiently prepared crystals. In fact, it was not until the development of the ingot annealing technique that the resistivity of GaAs crystals could be systematically described by the concentrations of $EL2$, carbon acceptor, and Si donor.[21] We have therefore utilized a series of liquid-encapsulated Czochralski-grown samples, which have been thermally treated simultaneously with the three-stage annealing method.[22]

Two measurements were made: near-infrared (NIR) photoabsorption and photocurrent (PC). The former detects the $EL2$ defect more directly, while the latter conveys information on the free carriers emitted from $EL2$. After the completion of the photoquenching, NIR and PC indicate the quenching of optical and electrical activity of the defect, respectively. These measurements were performed at various temperatures below 130 K down to 8.6 K, with the aim of obtaining a detailed temperature dependence of the $EL2$ photoquenching effect.

The series of crystals and the measurements employed in the present study not only clarifies the contribution of other defects to the photoquenching, it also suggests a probability order of the three models: the charge-transfer model, the actuator-level model, and the shallow-donor complex model. For instance, NIR measurement is useful in determining the validity of the charge-transfer model because the NIR spectrum conveys information from both the neutral and ionized $EL2$. The present choice of samples is also useful in determining the validity of the actuator-level model. This is so because varying a shallow-level concentration is the best way to change the charge state of an actuator level, if any.

II. EXPERIMENT

The samples were liquid-encapsulated Czochralski-grown, semi-insulating GaAs crystals, and were thermally treated following the three-stage annealing method.[22] A thermally stimulated current measurement[23] made on the present samples showed a quite featureless spectrum with significantly fewer trap levels as compared with those in conventional materials.[24] Table I summarizes the specific details of the samples. The carbon concentrations were obtained from Fourier-transformed infrared (FTIR) spectrometry on the local vibrational mode of C_{As} at 580 cm^{-1} at room temperatures with a conversion factor of 8.0×10^{15} cm^{-1}.[25] This quantity, therefore, corresponds to the concentration of the carbon acceptor C_{As}. The $EL2$ concentrations were measured by the multiwavelength NIR method.[26] For NIR measurements, samples with thickness of 3–4 mm with both sides polished were utilized. The carbon concentration was varied from 1.8 to 14.3×10^{15} cm^{-3} while the total $EL2$ concentration stayed unchanged at $(1.5\pm0.1)\times10^{16}$ cm^{-3}. For PC measurements, 10×10-mm^2 samples from wafers of about 500 μm thickness were utilized. The carbon-acceptor concentration for the PC samples varied from 0.7 to 7.1×10^{15} cm^{-3}, while the total $EL2$ concentration was again constant at around 1.5×10^{16} cm^{-3}. Indium

TABLE I. Specifications of SI-GaAs samples.

Sample	$[C_{As}]$[a] (10^{15} cm^{-3})	$[EL2^+]$[b] (10^{16} cm^{-3})	$[EL2]$[b]	Carrier[c] conc. (10^7 cm^{-3})	Mobility[c] (cm^2/Vs)	Resistivity[c] (10^7 Ω cm)	Measurement
K-2	1.8	0.14	1.57	2.8	6810	3.3	NIR
L-2	2.7	0.08	1.46	1.7	6730	5.4	NIR
M-2	6.3	0.24	1.63	0.64	5860	16.7	NIR
N-2[d]	11.0	0.31	1.46	0.49	3320	35.5	NIR
0-2[d]	14.3	0.41	1.49	0.30	3690	45.7	NIR
*L*5-420*A* (*A*1)	0.7[e]			6.7	7140	1.3	PC
*L*3-846*A* (*B*1)	0.9[e]			5.3	7076	1.7	PC
*L*5-318*TA* (*C*1)	7.1[e]			0.57	5288	20.9	PC

[a] As observed with the FTIR localized vibrational mode using a conversion factor of 8.0×10^{15} cm^{-1}.

[b] As observed with the multiwavelength NIR method.

[c] As observed with the van der Pauw method.

[d] Electrical properties were analyzed with an electron-hole bicarrier model.

[e] Estimated from electrical properties.

electrodes with good Ohmic contacts were formed at each of the four corners of the wafer. These samples were mounted in a closed-cycle cryostat for both NIR and PC measurements, in which the sample temperature was varied from 10 to 300 K.

A monochromatized light from a 300-W tungsten halogen lamp was used for either the photoquenching or the measurements of NIR and PC. In the NIR measurements, the transmitted light was detected by a PbS detector. A 1.06-μm light was utilized for both quenching and probing *EL*2 but with different intensities. The bandwidth of the quenching light was 60 nm while that of the probing light was 8 nm, which yielded an intensity reduction for the latter of a factor 40. This intensity of the probing light was weak enough to avoid any modifications of the sample state. In fact, no change was observed in the NIR spectra during the course of the measurements. In the PC measurements, the current flowing under photoexcitation with a bias voltage of 4 or 8 V was detected by an electrometer.

III. EXPERIMENTAL RESULTS

A. Photoquenching of *EL*2 at 77 K

Figure 1 indicates the change of NIR spectrum as a function of the illumination time of the quenching light for a high-carbon sample with $[C_{As}]=6.3\times10^{15}$ cm^{-3} at 77 K. The quenching of *EL*2 is seen in the successive annihilation of the absorption band. At about 45 min of illumination, the relevant absorption band has nearly vanished and further illumination causes no change in the spectrum. If *EL*2 level itself were not quenched, as predicted by the charge-transfer model (CTM) for $As_{Ga}{}^{0/+}$, then the NIR spectrum should present an appreciable absorption band due to transitions from neutral *EL*2. The present NIR result is therefore difficult to understand within the CTM scheme.

Quite contrary to the carbon-rich sample described above, a low-carbon sample with $[C_{As}]=1.8\times10^{15}$ cm^{-3} showed a very weak photoquenching effect (Fig. 2). Most of the *EL*2 absorption band is preserved even after 45-min illumination of the quenching light. A further illumination up to 80 min caused no change in the spectrum. Namely, the effect of lowering the carbon concentration appears to weaken the photoquenching effect at 77 K, which is best represented as a higher residual absorption band after saturation. Measurements on other samples showed a similar tendency.

In order to express the result more quantitatively, the photoquenched fraction of *EL*2 after 45-min illumination of the quenching light was compared as a function of the carbon concentration. Since the photoabsorption coefficient at 1 μm is, to a good approximation, proportional to the neutral *EL*2 concentration, the photoquenched fraction was defined as

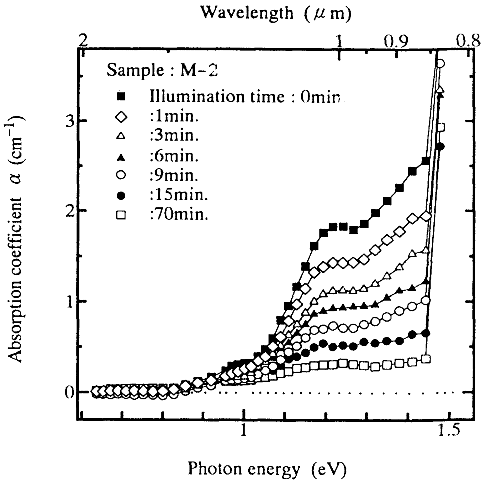

FIG. 1. Near-infrared absorption spectra obtained for a high-carbon sample ($[C_{As}]=6.3\times10^{15}$ cm^{-3}) at $T=77$ K. Quenching of *EL*2 is seen in the annihilation of the absorption band after longer illumination of the quenching light ($\lambda=1.06$ μm).

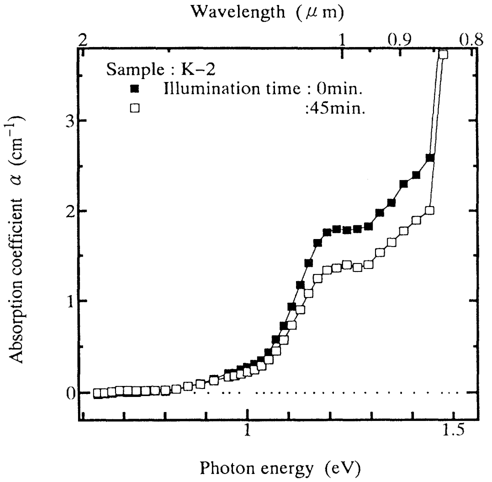

FIG. 2. Near-infrared absorption spectra obtained for a low-carbon sample ($[C_{As}]=1.8\times10^{15}$ cm^{-3}) at $T=77$ K. Most of the original absorption band of $EL2$ is preserved after 45-min illumination of the quenching light.

$$R_{PQ}=\frac{\alpha_0-\alpha}{\alpha_0}\times100\ (\%)\ , \tag{1}$$

and was plotted in Fig. 3. Here, α_0 and α denote the photoabsorption coefficient at 1 μm before and after the 45-min illumination, respectively. The figure indicates a clear positive correlation between the quenched fraction and the carbon concentration for $[C_{As}]<6.3\times10^{15}$ cm^{-3}, proving the carbon's contribution in the $EL2$ photoquenching effect. The negative correlation seen in the region $[C_{As}]>6.3\times10^{15}$ cm^{-3} is currently considered to be spurious. From a feature in the spectrum in this region and from the PC results shown later, this negative correlation is most probably associated with a state other than $EL2^0$, which arises during the photoquenching procedure.

A somewhat more complicated behavior was observed for the PC measurements. Figure 4 is a time evolution of the PC under the quenching light illumination for a high-carbon sample with $[C_{As}]=7.1\times10^{15}$ cm^{-3}. The figure presents a separation into three phases: (I) The initial rapid increase, (II) the subsequent decrease, and (III) the second increase after 600 s. Hall measurements indicated an n-type conduction in (I) and (II), while a p-type conduction was observed in (III). The n-type conduction in (I) and (II) can be understood from the photoexcitation of electrons from the neutral $EL2$ to the conduction band. The decay in (II) can also be given a natural explanation from the photoquenching of the neutral $EL2$. The p-type conduction in (III) is discussed in detail below, but its presence alone can reject the CTM interpretation of the $EL2$ photoquenching. The CTM, when applied to the metastable $EL2$, assumes an almost 100% occupation of the $EL2$ by electrons, which should lead to an n-type conduction.

The rapid increase of the p-type conduction after 600 s suggests a presence of a hole emission from a certain level. Carbon acceptors cannot be a source for these holes although it seems quite natural to expect a hole emission from this level in the absence of $EL2$. The holes from the carbon acceptor should present a persistent photocurrent,[27] which flows steadily even after switching off the quenching light. Quite the contrary, the observed p-type conduction is an enhanced photocurrent (EPC),[27] which rapidly falls off after switching off the illumination as shown in the figure. Additionally, this observed EPC corresponds to a hole concentration of the order of 10^{11} cm^{-3}, which is about four orders smaller than that of the carbon-acceptor concentration (7.1×10^{15} cm^{-3}). These results indicate that the holes that are responsible for this

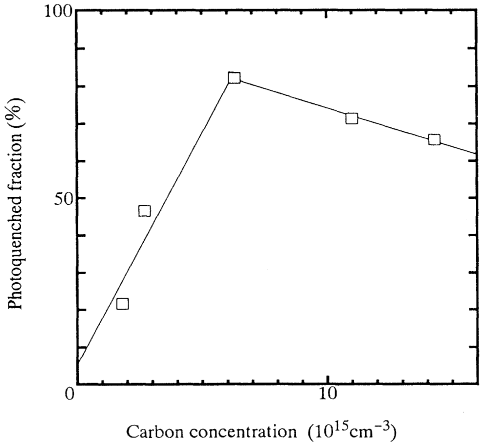

FIG. 3. Carbon concentration dependence of the photoquenching rate at 77 K, which is defined as the fractional photoquenched $EL2$ after 45-min illumination of the quenching light. Essentially, the photoquenching effect is more enhanced at higher-carbon concentrations. The origin of the negative correlation at higher carbon concentrations is discussed in the text.

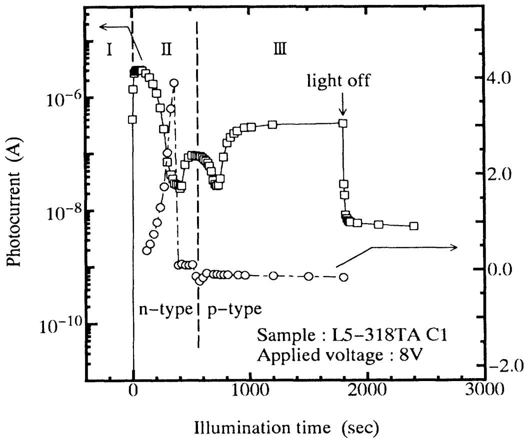

FIG. 4. Time evolutions of the photocurrent (□) and the Hall voltage (○) for a high-carbon sample ($[C_{As}]=7.1\times10^{15}$ cm^{-3}) under illumination of the quenching light at $T=77$ K. The photocurrent displays (I) an initial rapid increase, (II) a subsequent decrease, and (III) a second increase after 600 s. The conduction type is n-type for (I) and (II), while it is converted to p-type in (III).

p-type conduction are not from thermal emission associated with the carbon acceptor but are due to photoexcitation from a deeper level.

Such a level is not necessarily an acceptor. In fact, a certain deep donor must exist after the photoquenching because the crystal is still semi-insulating. Such a deep donor, which compensates the shallow carbon acceptor, can be a good candidate for the source of the holes. One possibility is the $EL2$ itself. The possible presence of $EL2$ levels even after the completion of the metastable transition can be justified as follows. According to conventional understandings,[6] the photoquenching of $EL2$ occurs only at neutral $EL2$. On this basis, an ionized $EL2$ cannot be photoquenched unless it emits a hole to the valence band to become a neutral $EL2$. When no deep acceptors exist in the crystal, however, it is necessary that the emitted hole are recaptured by the neutral $EL2$. Then the ionized $EL2$ survives. This situation happens in carbon-rich samples, for which the amount of the carbon acceptor may exceed the amount of existing deep acceptors. The amount of deep acceptors should be rather sample independent since all the present crystals were grown under similar growth conditions.

This idea also gives a possible explanation to the negative correlation between the photoquenched fraction and the carbon concentration in Fig. 2. As a result of the increase of the carbon acceptor, an increasing fraction of $EL2$ survives as $EL2^+$ after photoquenching, which develops a new absorption band near 1 μm. A support for this model will also be given later by PC measurements at $T < 77$ K.

In spite of its complicated time evolution, the PC measurement brings an identical message with that from NIR: the lower the carbon concentration, the weaker the photoquenching. Figure 5 indicates the PC time evolutions for a pair of low-carbon samples with $[C_{As}]=0.7$ and 0.9×10^{15} cm^{-3}. It is clear from the figure that no photoquenching is occurring for these low-carbon materials.

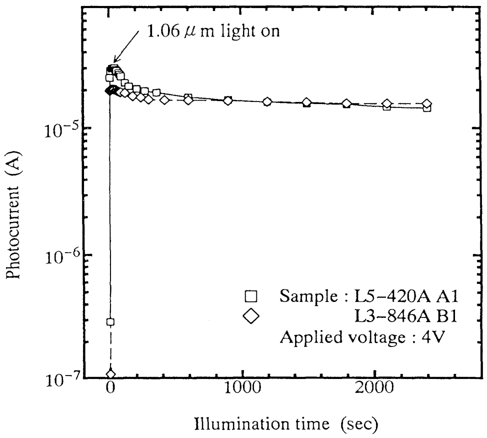

FIG. 5. Time evolutions of the photocurrent for a pair of low-carbon samples, $[C_{As}]=0.7\times10^{15}$ cm^{-3} (□) and $[C_{As}]=0.9\times10^{15}$ cm^{-3} (○), under illumination of the quenching light at $T=77$ K. After the initial increase, both spectra are almost featureless.

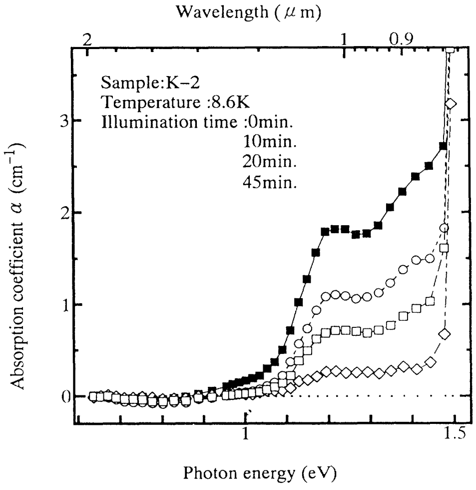

FIG. 6. Near-infrared absorption spectra obtained for a low-carbon sample ($[C_{As}]=1.8\times10^{15}$ cm^{-3}) under illumination of the quenching light at $T=8.6$ K. The sample, which showed virtually no photoquenching effect at 77 K, now presents a photoquenching effect.

B. Photoquenching of $EL2$ below 77 K

The results of the previous section might have given an impression that the carbon acceptor is essential for the onset of photoquenching. This is not, however, the case. By further lowering the quenching temperature below 77 K, even a lowest-carbon sample begins to display the photoquenching effect. Figure 6 is an NIR result at 8.6 K for a sample with $[C_{As}]=1.8\times10^{15}$ cm^{-3}, which at 77 K showed in photoquenching effect (Fig. 2). The absorption band of the normal state is almost extinguished after 45-min illumination of the quenching light. In the same manner, other low-carbon materials, which showed no photoquenching effects at 77 K, also presented a quenching of the $EL2$-related absorption band after being cooled.

Figure 7 shows the temperature dependence of the time evolution of the NIR absorption for the identical sample ($[C_{as}]=1.8\times10^{15}$ cm^{-3}). After each run at a quenching temperature, the sample was annealed at 150 K for 10 min. for a complete recovery of the normal state. This figure clearly indicates that the sample, which exhibits no quenching of $EL2$ at 77 K, begins to present a photoquenching effect after being cooled further. What should be noticed here is that the effect of lowering the temperature appears not only as an increased quenching rate but also as an increased amount of the quenched $EL2$ after saturation. This situation is identical to what is observed for the role of the carbon acceptor on the NIR at 77 K (Figs. 1 and 2).

A similar behavior has been observed also by PC measurements. In Fig. 8, a sample with $[C_{As}]=0.7\times10^{15}$ cm^{-3}, which showed no quenching of PC at 77 K (Fig. 5), now indicates a drastic decrease of PC at reduced temperatures. However, this figure indicates only a monotonic decrease of PC with no EPC's. This absence of

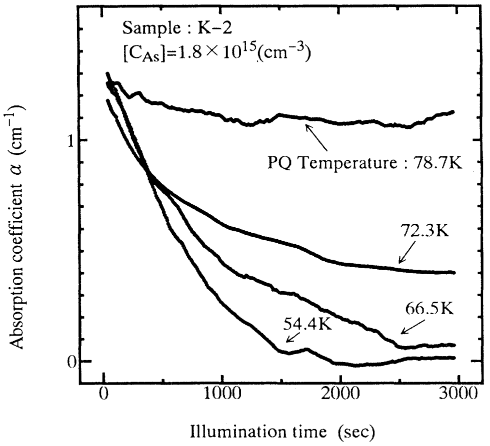

FIG. 7. Temperature dependence of the time evolution of the absorption coefficient at 1 μm for a low-carbon sample ($[C_{As}]=1.8\times10^{15}$ cm^{-3}) under illumination of the quenching light. The effect of lowering the quenching temperature is seen not only in an increase of the quenching rate but also in a lowering of the saturated value.

EPC can also be explained from the model deduced for the high-carbon materials; because the concentration of ionized $EL2$ is low for low-carbon materials, all the holes photoexcited from the $EL2^+$ state can be captured by existing deep acceptor levels. As a result, the conversion of $EL2^+$ to $EL2^0$ is complete, which fully opens the way to quench most of the originally ionized $EL2$. Therefore, after sufficiently long illumination of the quenching light, there should be almost no $EL2^+$, a source of holes for EPC, in the low-carbon materials.

IV. DISCUSSION

From the NIR and PC results presented above, it has been clarified that the $EL2$ photoquenching is more enhanced for higher-carbon materials and at lower temperatures. The former finding suggests that the photoquenching is somehow related to the carbon acceptor. Carbon can be related to the $EL2$ photoquenching either directly or indirectly. The simplest model for the direct correlation should be that the carbon acceptor is a constituent of $EL2$. However, the specifications of the present samples present a reason to reject that idea: the $EL2$ concentration is almost constant while the carbon concentration varies over an order of magnitude. In fact, any model that implies a direct contribution of carbon to the $EL2$ photoquenching effect cannot be compatible with the second finding of the present observation, namely that all the material, irrespective of its carbon content, exhibits a complete $EL2$ photoquenching when they are cooled to enough low temperatures.

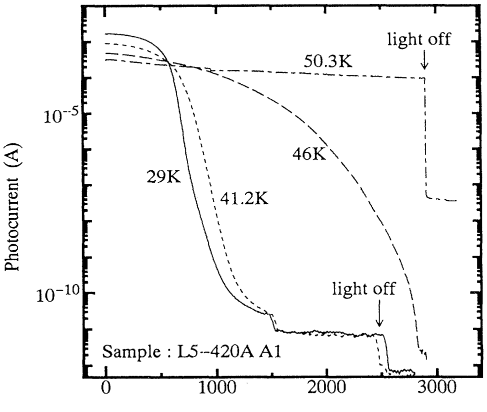

FIG. 8. Temperature dependence of the time evolution of the photocurrent for a low-carbon sample ($[C_{As}]=0.7\times10^{15}$ cm^{-3}) under illumination of the quenching light. By lowering the quenching temperature, the photocurrent begins to display a quenching of a n-type conduction.

Thus, the role of carbon in the photoquenching phenomenon should be more indirect. The only model that seems to be compatible with the two findings above is the actuator-level model developed by Jimenez *et al.*[12,13] This model suggests a presence of an acceptor level as an actuator level (AL), whose particular charge state is assumed to trigger the onset of the photoquenching. Here we assume more specifically that the AL enables the $EL2$ photoquenching when the AL is capturing a hole and is thus electrically neutral. This model is based on the fact that the photoquenching is more enhanced at higher-carbon materials and that most of the levels other than $EL2$ are ionized before the quenching procedure. In our model, the hole neutralizing the AL originates from the carbon acceptor, is next captured at $EL2$ as $EL2^+$ before quenching, and finally is photoexcited to the valence band to be captured by the AL.

By assuming a deeper acceptor as the AL, we can consider a competition between the hole capturing and hole emission processes of the AL and the valence band. The amount of neutral AL, and hence the rate of the photoquenching, is then determined from a balance between the two processes. According to this model, low-carbon materials present no photoquenching effect at 77 K, not because they contain an insufficient amount of AL, but because they lack in free holes in the valence band due to the shortage of $EL2^+$. When the samples are cooled to low enough lower temperatures, then, the thermal emission of holes from the AL can be suppressed. The result is an increased amount of neutral AL and hence an enhanced photoquenching effect Thus, all the results obtained in the present work can be consistently explained by the AL model.

This model gives a quantitative explanation for the temperature-dependent NIR time evolutions shown in Fig. 7. As mentioned at the figure, a feature of this figure is that the effect of lowering the quenching temperature appears as an increase in the amount of quenched $EL2$ at its saturation. This fact implies a presence of a thermally activated reverse process, whose balance with the quenching process eventually determines the saturation value. This reverse process, however, is not identical with the one known as the thermal recovery of the $EL2$ normal state. Figure 9 illustrates the typical thermal recoveries of $EL2$ for an identical sample, which indi-

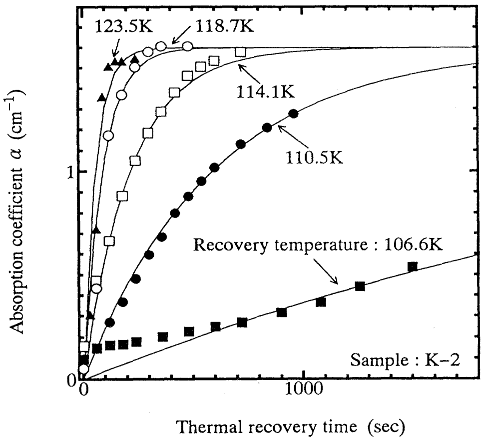

FIG. 9. Thermal recovery of the normal $EL2$ as observed from the photoabsorption coefficient at 1 μm for a sample with $[C_{As}]=1.8\times10^{15}$ cm^{-3}.

cates that the thermal recovery is highly temperature sensitive and virtually no recovery occurs below 100 K. The activation energy is 0.24 eV, which is about three times larger than the one obtained later for the recovery process during the photoquenching. Therefore, the recovery process that is of concern here is not purely thermal but is thermally activated only under illumination with a quenching light. Now we assume here that the thermal activation part of this photorecovery process is also related to the change of the charge state of AL, i.e., the photorecovery occurs when the AL is ionized. Therefore, our final model can be summarized as a statement that the charge state of the AL controls both the quenching and the recovery of $EL2$ under illumination of the quenching light.

Following this model, the time evolution of the $EL2^0$ concentration is given as follows:

$$\frac{dN_{EL2^0}}{dt} = -\sigma^0_{PQ} N_{EL2^0} \frac{N_{AL^0}}{N_{AL}} \phi + \sigma^0_{RC} N_{EL2^*} \frac{N_{AL^-}}{N_{AL}} \phi , \qquad (2)$$

where ϕ is a photon flux and σ_{PQ^0} and σ_{RC^0} are the optical cross sections for the photoquenching and recovery processes, respectively. The denominator N_{AL} was introduced to express the fractional activity of $EL2^0$ or $EL2^*$. This choice *a priori* implies a statement that all $EL2$ defects are accompanied by the AL, which should be checked in the future studies. However, the present choice is not crucial in the following discussion, where only stationary states are argued.

The AL^0 concentration, N_{AL^0}, is determined from a balance between emission and trapping of holes between the AL and the valence band:

$$\frac{dN_{AL^0}}{dt} = \sigma_{p,AL} p v_{th,p} N_{AL^-} - e_{th} N_{AL^0} , \qquad (3)$$

where $\sigma_{p,AL}$ is the thermal capture cross section of the AL for the free holes, p the free-hole concentration, $v_{th,p}$ the thermal velocity of the holes, and e_{th} the thermal emission rate from the AL to the valence band:

$$e_{th} = A \exp\left[-\frac{E_{AL}}{kT} \right] . \qquad (4)$$

The saturation value of N_{EL2^0} is calculated by equating the left-hand side of Eqs. (2) and (3) to zero as

$$N^{\infty}_{EL2^0} = N_{EL2} \left[1 + \frac{\sigma^0_{PQ} C_{p,AL} p}{\sigma^0_{RC} e_{th}} \right]^{-1} , \qquad (5)$$

where

$$C_{p,AL} = \sigma_{p,AL} v_{th,p} . \qquad (6)$$

On the other hand, to a good approximation, the photoabsorption coefficient α at 1 μm is proportional to N_{EL2^0}, which yields

$$\frac{\alpha_0}{\alpha_\infty} - 1 = \frac{\sigma^0_{PQ} C_{p,AL} p}{\sigma^0_{RC} A} \exp\left[\frac{E_{AL}}{kT} \right] , \qquad (7)$$

where α_0 and α_∞ are the photoabsorption coefficient before and after the saturated illumination of a quenching light. In deriving Eq. (7), we have assumed that the total $EL2$ concentration ($N_{EL2} = N_{EL2^0} + N_{EL2^*}$) is constant throughout the quenching process. The right-hand side of Eq. (7) suggests an Arrhenius-type temperature dependence, which is actually verified in Fig. 10. The activation energy is 76 meV for this figure, which in our model corresponds to the one for the hole emission process from the AL. Similar analyses on other samples also indicate activation energies between 70 and 80 meV. These values are about one-third of the activation energy for the thermal recovery of $EL2$.

From this result, a most probable candidate for the AL is Ga_{As} as suggested by Jimenez *et al.*[12,13] It is a double acceptor possessing levels at 78 and 200 meV.[28,29] Al-

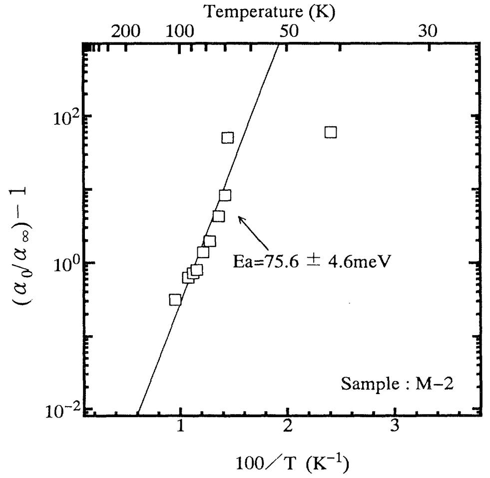

FIG. 10. Arrhenius plot of $(\alpha_0/\alpha_\infty)-1$ for a sample with $[C_{As}]=1.8\times10^{15}$ cm^{-3}, where α_0 and α_∞ denote the photoabsorption coefficient at 1 μm before and after the saturated illumination of the quenching light, respectively. A good linear correlation is obtained, which yields 76 meV for the activation energy of the hole emission process from the actuator level.

though the defect is related to Ga-rich stoichiometry, its presence in crystals grown from As-rich melt stoichiometry is theoretically predicted[30,31] or experimentally suggested by EPR measurements.[11] This level, when illuminated at low temperatures, presents enhanced EPR signals, which suggests its involvement in a kind of a charge-transfer process.

The nomination of $\mathrm{Ga_{As}}$ as a possible candidate for the AL seems to give a strong support for the $EL2=\mathrm{As_{Ga}}+\mathrm{As}_i$ complex model proposed by Bardeleben and co-workers.[19,32] According to the complex model, this double acceptor acts as a glue to combine electrically positive $\mathrm{As_{Ga}}$ and As_i ions. One problem with this model, however, is that it seems to be inharmonious with the present finding on the AL charge state. When the $\mathrm{Ga_{As}}$ acceptor is neutral as is required in our model for triggering the metastable transition, it loses its power as a glue, while the complex model requires a more attractive force between $\mathrm{As_{Ga}}$ and As_i ions to shift As_i even closer to the nearest-neighbor position of $\mathrm{As_{Ga}}$. Although a complex model $EL2=\mathrm{As_{Ga}}+X$ seems to be still the strongest candidate, its detailed specification is open to further studies.

Finally, a brief comment should be made on the simple $EL2=\mathrm{As_{Ga}}$ model. The present result, indicating clearly a strong influence of the carbon acceptor on the $EL2$ photoquenching, does not necessarily deny the isolated antisite model. There is still a possibility that the deep acceptor AL is located in the proximity of an isolated $\mathrm{As_{Ga}}$. For instance, if an ionized $\mathrm{Ga_{As}}$ is located in the nearest-neighbor site along the $\langle 111 \rangle$ direction of an $\mathrm{As_{Ga}}$, then its transition from the ionized state to the neutral state would naturally explain the shift of $\mathrm{As_{Ga}}$ from the T_d symmetry to the C_{3v}-symmetry position. The authors, however, consider the isolated antisite model implausible. From our recent EPR experiments[33] on the present samples, the $\mathrm{As_{Ga^+}}$ signal intensity was quite insensitive to the carbon concentration as opposed to the NIR measurement. Response to the quenching light illumination was also very sensitive as compared to those from NIR or PC.

To summarize, by use of the carbon acceptor as a probe, we have clarified that a deep-acceptor defect, which is most probability the $\mathrm{Ga_{As}}$, plays an important role in controlling the transition to and from the $EL2$ metastable state.

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