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Optically induced long-lifetime photoconductivity in semi-insulating bulk GaAs

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Persistent illumination with photons of energy ranging from 1 to 1.25 eV is known to produce metastable transformations in the photoelectronic properties of GaAs. In this work the generation of a high-photosensitivity state is reported. This state is shown to be associated with a center, labeled C^*A, which is optically created by those photons. These centers are found to have a high hole photoionization, the dominant conduction associated with them upon illumination is p type, and the photoholes remain long-time delocalized in the valence band before their capture by the ionized C^*A centers (persistent photoconductivity effect). This effect is associated with a screening of C^*A centers by ionized shallow donors located nearby. The formation of the C^*A centers is found to occur in two or more stages and is the result of a reordering inside native defect complexes called C, more likely $\mathrm{As_{Ga}}$ aggregates, followed by the association with shallow acceptor levels due to a carbon impurity ($\mathrm{C_{As}}$). The driven force leading to such a defect configuration is assumed to be associated with Coulombic attractive forces appearing upon photoionization of the As antisite defects. This leads to a strong lattice relaxation and hence the formation of the new C^*A centers accounting for the observed photocurrent properties of the samples. The destruction of these centers is accomplished by heating above 135 K; this thermal cycle converts the sample to its normal photosensitivity state.

I. INTRODUCTION

Semi-insulating GaAs is a promising material to be used as a substrate in IC's (integrated circuit) and high-speed FET (field-effect transistor) technologies.[1] Mid-gap levels play a key role in the high-resistivity performance required by the substrate. In the past years a great number of works have been devoted to characterizing both the properties and the physico-chemical nature of these defects.[2,3] This amount of work notwithstanding, there are many yet unanswered questions about those levels. The most important of them is the so-called EL2 in the notation of Martin, Mitonneau, and Mircea.[4] This level is the main compensator of background shallow acceptors in undoped GaAs. Its thermal activation energy is found to be 0.75 eV from the bottom of the conduction band, typical densities are found to be around 10^{16} cm^{-3} and capture cross section lies in the 10^{-14} cm^2 range.[5]

This level changes its photoelectrical properties when illuminated with white light at sufficiently low temperature;[6,7] this fact is usually ascribed to the existence of a metastable state of EL2, which is optically inactive. However, the physical mechanism by means of which the metastable state, EL2*, is created is not yet well understood. This is due to the fact that the chemical nature of the EL2 level itself is poorly known. It is usually assumed that it is a stoichiometric defect, which is observed in horizontal Bridgman (HB), liquid-encapsulated Czochralski (LEC), and vapor-phase epitaxy (VPE) samples grown under excess arsenic conditions, at concentrations of around 10^{14}–10^{16} cm^{-3} depending on the samples.[8,9] A great controversy arose concerning whether EL2 is the anion antisite defect ($\mathrm{As_{Ga}}$) or not.[10] Recent studies about MCD (magnetic circular dichroism) state that EL2 is not likely the isolated $\mathrm{As_{Ga}}$ antisite.[11] However, this point is a matter of controversy now.[12]

Photoconductivity is a quite old technique, which has been largely used for the characterization of semi-insulating GaAs.[13,14] In spite of its relative experimental simplicity, the interpretation of results is often difficult, because the photocurrent signal is a complex function of both the optical emission and capture rates of carriers. However, it provides very useful information about the mechanism giving rise to the photomemory effects in GaAs. Thus, in other previous papers we have described the photoconductivity features of both the optical quenching of the photosensitivity and the photogeneration of a high-photosensitivity state, respectively.[15–18] The observation of these effects is dependent on the sample. This paper deals with another related effect observed in several semi-insulating LEC samples. Basically this effect consists of the photogeneration of a high-photosensitivity state, which is characterized by the long lifetime of the excess carriers. To our knowledge this is the first time that persistent photoconductivity is observed as a bulk effect in semi-insulating GaAs. The electric current level measured after the turning off of the illumination remains significatively higher than the photoconductivity level corresponding to the low-photosensitivity state, even after a long period in darkness.

This phenomenon is known to occur in II-VI compounds[19] and III-V ternary alloys.[20,21] It has also been reported in irradiated silicon[22] and germanium.[23] Furthermore, nonhomogeneous GaAs structures exhibit persistent photoconductivity.[24] It is usually assumed that the slow relaxation of carriers is due to the existence of a repulsive barrier avoiding the capture of free carriers, which then remain delocalized in the bands for a very long time.[25]

In a previous short paper[26] we depicted some phenomenological features of the long-lifetime photoconductivity in semi-insulating bulk GaAs. Our aim in this paper is to give an interpretation of this phenomenon, which can be correlated with the other photomemory effects observed in the photoconductivity of GaAs.[15,18,27,28] The understanding of the persistent photoconductivity can help to understand the unusual physical properties related to the configurational instability of mid-gap levels in GaAs.

II. EXPERIMENTAL SETUP

In this work we study the photoconductivity features of high-resistivity GaAs specimens (10^7—10^9 Ω cm at room temperature) cut from either horizontal Bridgman or liquid-encapsultated Czochralski ingots.

The HB ingots were manufactured by RTC (Radio Technique Compelec-France) and were grown in a quartz sealed container by the horizontal gradient freeze method; different amounts of chromium and/or gallium dioxyde were added to the starting melt. LEC ingots arise from Thomson-CSF (France) and were pulled in a vertical Czochralski system. The starting melt was not intentionally doped and was elaborated in a PBN puller and encapsulated in B_2O_3. The vertical axis coincides with the crystallographic $\langle 100 \rangle$ direction. The ingots present a cylindrical shape. Wafers, 0.5 mm thick, were cut from the ingots along the (100) plane. $5\times2\times0.3$ mm^3 samples were tailored from these wafers, chemically etched in a $[H_2SO_4]:[H_2O_2]:[H_2O]=50:15:15$ solution, cleaned in acetone and mechanically polished. The persistent photoconductivity effect was only observed in several of the LEC samples, whereas the other specimens displayed either optical quenching of the photoresponse or an enhancement of the photoconductivity characterized by the lack of persistency.[15–18] Special care was devoted to the electrical contacts. Several metals and alloys were tested, not revealing any difference from each other for low-bias conditions, so that the results reported in this work were obtained for either silver paste or alloyed indium, annealed at 200 °C during 15 min. These contacts were masked in order to avoid photovoltage effects at the contact barriers. All the measurements were carried out at low bias, in the linear part of the photocurrent-voltage characteristics. On the other hand, the sample configuration (surface cell) allows one to illuminate out of the contact regions, where the nonlinear effects associated with the voltage distribution are negligible.

Illumination was provided by a 150-W halogen lamp through a high-luminosity Bausch-Lomb grating monochromator. A filter system was disposed in order to prevent subsidiary high-order wavelengths. The output monochromatic beam was guided to incite the sample by a light guide through the perforated pole of an electromagnet. The samples were mounted on the copper cold finger of a small liquid-nitrogen cryostat, which was characterized by a weak thermal inertia. The photoconductivity was measured by a logarithmic picoammeter (Keithley Model 26 000); an electrometer (Keithley model 610C) was used for measuring the Hall voltage at a lateral contact on the specimen. Optical absorption tests were carried out in order to ensure that the excitation was homogeneous across the bulk of the sample in the full spectral range scanned in photoconductivity measurements.

III. RESULTS

A. High-photosensitivity state

Time resolved photocurrent measurements showed strong changes in the photosensitivity of samples as a consequence of the illumination. These changes were strongly dependent on the samples. Some of them exhibited a high-photosensitivity state, which was characterized by a high-photoconductivity level, more than two orders of magnitude over the normal photoconductivity level of the samples. This state is created after a long period of illumination with photons of energy ranging from 1 to 1.25 eV at liquid nitrogen temperature (77 K). The 1.13-eV extrinsic photocurrent to the period of excitation is shown in Fig. 1. Firstly, a slow increase of the photocurrent is observed; the rate of this process is henceforth labeled R_c. After a period of excitation depending on both the energy of the incident light and the photonflux a sharp photocurrent enhancement takes place, which follows a near ex-

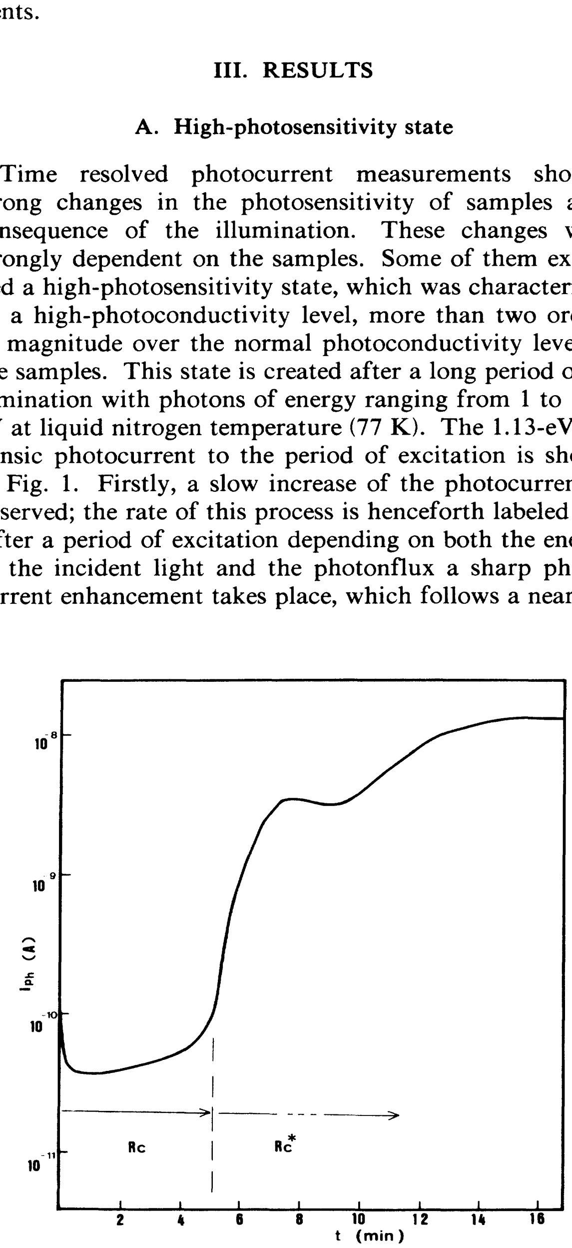

FIG. 1. 1.13-eV photocurrent as a function of the illumination time with 1.13-eV photons. Saturation is obtained by 15 min of continuous excitation, two stages are observed, R_c and R_{c^*}.

ponential law; the rate of this process is denoted as R_{c*} in Fig. 1. The spectral distribution of the generated high-photosensitivity state is shown in Fig. 2, the maximum efficiency is observed at 1.12 eV. It should be noted that not only the steady-state photoconductivity level is a function of the energy of photons but also the kinetics for reaching such a state is dependent on the energy of the excitation light. This suggests that the process of formation of the photosensitivity state is photoionization-rate limited.

B. Persistent photoconductivity

A study of the photoconductivity decay reveals that once the current reaches the saturation level (high photosensitivity), the excess carriers remain delocalized in the free bands for quite a long time after the light is turned off. This behavior is only observed in some LEC samples. The excess carrier concentration, as calculated from photo-Hall data, is, after a long enough time in the absence of light, several orders of magnitude greater than that corresponding to the low-photosensitivity state under illumination. The sample exhibits the persistent photoconductivity phenomenon.[25]

The photoconductivity decays corresponding to several photosensitivity states of the sample, which are associated with different periods of excitation with photons of 1.13 eV, are shown in Fig. 3. It can be observed that the decay becomes slower as the excitation time increases. The photocurrent decay has two components, a fast (inset of Fig. 3) and a slow one, respectively. The fast transient part undergoes a progressive reduction as the specimen is driven into the high-photosensitivity state. The long decay tail, which extends to more than an hour follows a nonexponential law. This decay can be fitted to a time-potential law ($\sim t^n$, $n \simeq -0.5$). Such a behavior has been discussed by other authors in relation with persistent photoconductivity phenomenon (PPC). Thus Stein[22] has reported a similar behavior for the carrier removal rate in neutron-irradiated silicon. Also Queisser[24] used a potential law for describing the decay of the photoinduced excess conductivity in an n-type GaAs layer on a semiinsulating GaAs:Cr substrate. The physical interpretation of such a law is rather difficult and it reveals that there is not a simple capture mechanism involved in the observed phenomena.

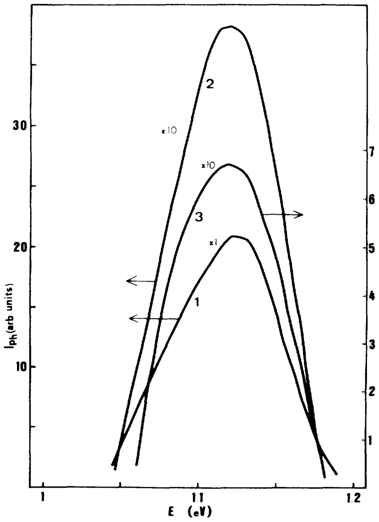

FIG. 2. Spectral distribution of the high-photosensitivity state (curve 1). The spectral distribution of the photocurrent decay for 4 min (curve 2) and 7 min (curve 3), respectively, is also shown after the switching off of the illumination.

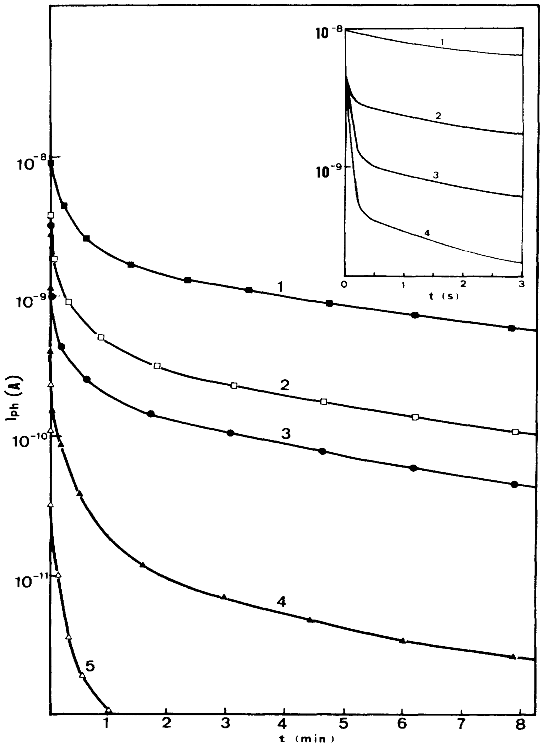

FIG. 3. Photocurrent decays after several different periods of illumination t, with 1.13-eV photons, (1) $t = 13.5$ min, (2) 10.5 min, (3) 9.5 min, (4) 5 min, and (5) 3 min. Each of these curves corresponds to a different photosensitivity of the sample. The decay is slower as t increases. The fast component of the decays are represented in the inset.

It should be noted that once the photocurrent has reached saturation, the photosensitivity of the samples remains in such a state as long as the temperature is kept below 130 K, even after long periods in dark. Thus, when the light is replaced the carrier population characterizing the high-photosensitivity state is quickly restored (several seconds are enought to get the high carrier concentration level instead of the 15 min required in the preliminary illumination). This is a very important result, because it reveals the existence of metastable transformations in the photoelectronic properties of the specimen. Whenever the sample is in such a photosensitivity state, the lifetime of the excess carriers generated by 1–1.25 eV photons will be long.

Because of this, it can be argued that the persistent photoconductivity state is a photomemory effect in semi-insulating GaAs, which exhibits nearly the same spectral distribution of the other well-known photomemory effects observed in the photoconductivity response of this material, i.e., optical quenching and photogeneration of traps.[17,18]

C. Temperature dependence of the photoconductivity

We have performed thermal cycles under illumination when the sample was at its saturation photocurrent level. The thermal evolutions of the steady-state photocurrent for several different excitation light energies are shown in Fig. 4. A strong thermal quenching of the photocurrent occurring in the narrow margin of tempertures ranging from 120 to 135 K is clearly observed. On the other hand, the magnitude of the thermal quenching depends on the photosensitivity state of the sample; this is a well-known result of the other photomemory effects of GaAs.[17,18]

After heating beyond 135 K the sample recovers its normal photosensitivity. Therefore the effect of the temperature increase is not only to quench the photocurrent, but also, it bleaches the high-photosensitivity state itself and the persistent photoconductivity is completely erased. To reproduce this state requires a new persistent illumination with the 1—1.25 eV light at liquid-nitrogen temperature.

As it was stated for other photomemory effects in GaAs the thermal quenching undergone by the high-photosensitivity state may be explained on the basis of an "annealing" of the photogenerated metastable configuration of deep levels. When they transform into their initial equilibrium configuration the photosensitivity of the sample recovers its value before the persistent illumination at low temperature. From this point of view the level leading to this phenomenon may be included in the group of other levels in semiconductors, which display large lattice relaxation characteristics, i.e., EL2 in GaAs (Ref. 7) and $Ga_{1-x}As_xP$ (Ref. 29) *DX* centers in $Al_{1-x}Ga_xAs$ (Ref. 21), *M* centers in e^-- irradiated InP (Refs. 30 and 31), and vacancies in silicon (Ref. 32). The optical and thermal stories of the PPC effect in our sample suggest that the EL2 level could be involved at some stage of the formation of the metastable state displaying PPC characteristics; this item will be discussed later.

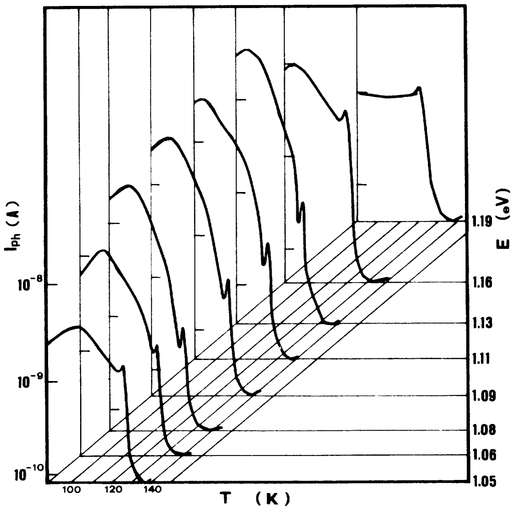

FIG. 4. Three-dimensional representation of the thermal quenching of the photocurrent. A strong quenching occurs between 120 and 135 K for the full spectral range where the high photosensitivity is generated. The magnitude of the quenching is directly related to the photosensitivity state generated. This quenching does not follow a single law versus *T*, but several stages can be observed in the temperature range where the thermal quenching takes place. Special attention must be paid to the sharp peak (2 or 3 K width at half height) observed in these curves, most probably this peak is associated with changes in the kinetics of the physical mechanism restoring the normal photosensitivity.

D. Metastable state. Complementary experiments

1. Photo-Hall measurements

Since we have stated that significative changes are produced by persistent illumination in the photoionization rate, any information about the nature of the transitions involved should be valuable in order to understand this phenomenon. In this way, photo-Hall measurements have revealed that holes are the dominant carriers, when the sample is in the high-photosensitivity state. This change of conduction type under optical excitation has been reported elsewhere by other authors.[13]

The apparent photo hole density $(1/eR_H)$ at saturation to the photon energy is represented in Fig. 5. It can be observed that the spectral distribution of the excess hole

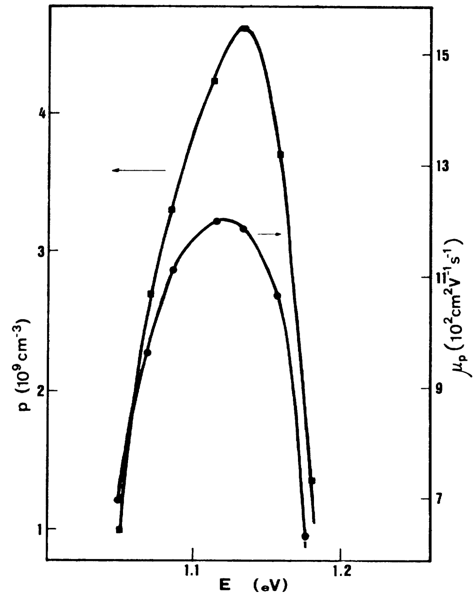

FIG. 5. Spectral distribution of both the photohole concentration and mobility. These values are obtained at saturation in the high-photosensitivity state. These spectral distributions are similar to those of Fig. 2. It is clearly observed that μ_p increases as p does.

density is similar to that reported in Fig. 3 for the generation of the high-photosensitivity state. Also, the spectral distribution of the photohole mobility is reported in Fig. 5, this spectrum is similar to that exhibited by the photohole density. Therefore, it can be stated that the mobility increases as the photohole density does, or in other words, as the high-photosensitivity metastable state concentration is enhanced. This is an important fact to be considered in the following discussion, because it gives additional information about the nature of the centers involved in the observed phenomenon.

2. *Band-edge photoconductivity*

As is well known, photons ranging from 1 to 1.35 eV not only induce the extrinsic photomemory in GaAs but also they are able to produce strong variations in the photoresponse of the band-edge spectral region ($h\nu \geq 1.4$ eV, $E_g \simeq 1.51$ eV at 77 K) of GaAs. We have carried out photoconductivity experiments in this spectral range in order to investigate the evolution of the shallow-level photoresponse in samples exhibiting long lifetime photoconductivity. The same experiments were previously carried out in samples showing photoquenching and photogeneration.[18,33] Recently, band-edge effects have been observed in relation with the striking reversal contrast phenomenon observed in GaAs wafers.[34]

Before persistent illumination with (1—1.25)-eV photons, the near-band-gap photoconductivity spectrum exhibits two peaks, whose maxima are located at 1.45 and 1.507 eV, respectively, in Fig. 6. The last one could be originated by either an excitonic transition or an A^-D^+ transition (at 77 K most of the shallow levels are ionized). It has been claimed by Karel *et al.*[35] that there are bound excitons and they contribute to the photoconductivity as free excitons. In such a case a mixed conduction is expected and the higher mobility of electrons does dominate the conduction type in photo-Hall data. This has been confirmed by our photo-Hall experiments, which demonstrated that *n*-type conduction is the dominant one in the near-band-gap photocurrent. The 1.455-eV band is likely due to an A^--D^+ transition.

Prolonged excitation with photons ranging from 1 to 1.25 eV induces quite noticeable changes in the band-edge photoconductivity spectrum. It can be observed that after long enough excitation with 1—1.25-eV photons an intense photoconductivity peak, whose maximum is located at 1.48 eV, appears. Simultaneously, the bleaching of both the 1.455 and the 1.507 eV peaks occur, see Fig. 6. On the other hand, photo-Hall measurements in this spectral range reveal that the photogenerated 1.48 eV photocurrent peak is associated with a *p*-type conduction, which is more reliably due to the long-lifetime holes.

In order to study the evolution of the band-edge photoconductivity during the extrinsic excitation, measurements in the 1.40—1.51 eV spectral region after different periods of excitation with light of 1.12 eV have been performed. These spectra are reported in Fig. 6, a progressive shift from the initial photoconductivity spectrum (curve 1) to the optically induced spectrum with a peak at 1.48 eV (curve 2), as the period of excitation with 1.12-eV photons increases is observed. This implies a simultaneity between both the building up of the high-photosensitivity state and the evolution of the optical activity of the shallow levels. This result is different from that observed in samples exhibiting photoquenching, for which it was demonstrated that quenching of band-edge photoconductivity takes place after the extrinsic quenching has occurred.[18,33]

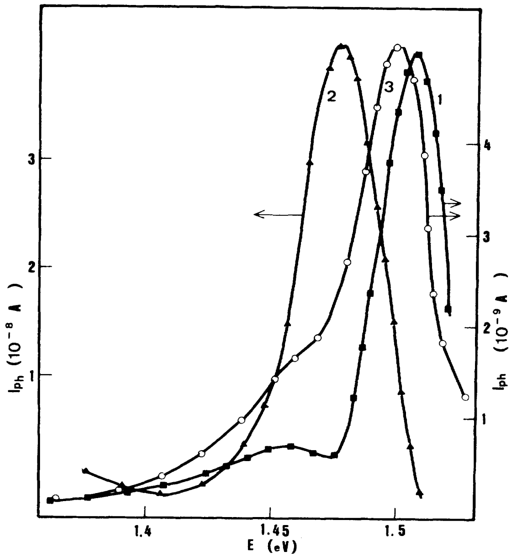

FIG. 6. Near-band-edge photocurrent spectra as obtained for three different photosensitivity states. (1) Nonperturbed spectrum corresponding to the normal photosensitivity state. Showing two bands at ~1.455 and 1.507 eV. (2) Band-edge photocurrent spectrum as obtained after the high-photosensitivity state has been reached by exciting with 1.12 eV, only a band at 1.48 eV is observed. (3) Near intrinsic photocurrent spectrum corresponding to an excitation with 1.12-eV photons intermediate between that of curves 1 and 2.

IV. DISCUSSION

Since we have reported the most relevant phenomenological features characterizing the persistent photoconductivity in semi-insulating GaAs, we ought to explain three aspects of this phenomenon, which would model the problem of persistent photoconductivity in GaAs. We wish to determine (a) the nature of the metastable state, (b) how the metastable state is formed, and (c) the identification of the mechanism accounting for the persistent photoconductivity.

Questions (a) and (b) are of great importance because they are related to the configurational changes of defects, which give photomemory effects in GaAs. The last question is specific of these samples, because the persistency of photoconductivity is only clearly observed in some semi-insulating LEC GaAs samples. On the other hand, this item should provide useful information about both the nature of the metastable state and the mechanisms leading to changes in the defect configuration.

A. The formation of the metastable state

All the reported experimental results qualitatively support the hypothesis of the existence of configurational changes occurring at complex defects, which lead to the high photosensitivity. The nature of the involved defects is unknown, however, the fact that the spectral distribution of the photogenerated state fits to that usually reported for the optical quenching of the EL2 level,[7] suggesting that this defect or someone of its components could be involved in the optically induced metastable state supporting the PPC effect. In this way, it is noteworthy to remember that the nature of EL2 is the subject of a longstanding controversy. Recently, this level has been associated to clusters of $\mathrm{As}_{\mathrm{Ga}}$ antisites.[36,37]

From our experimental results a reliable mechanism giving the high photosensitivity would be the following. Illumination with photons of 1–1.25 eV excites a deep level *C*, which can be related to either EL2 or one of its components, the change in the charge state of the defect introduces an electrostatic driven force which acts on the defect components and therefore there is a competition for the recapture of this electron, restoring the original charge state of the level without any change in its structural configuration and the rearrangement of the defect configuration leading to a distorted defect configuration, which is characterized by emission and capture coefficients different from those of the original defect. Such a model implies a strong influence of the lattice neighboring the defect, which is clearly demonstrated by the influence that the configurational rearrangement has on the shallow-trap photoresponse. In fact, the band-edge photoconductivity experiments reported in Sec. III D 2 can be understood on the basis of the configurational rearrangements. Thus the bleaching undergone by the 1.507 peak cannot be explained by a shortening of excess carrier lifetime, because in the persistent photoconductivity state it has been proven to be quite long. However a configurational arrangement involving the defect to which this transition is related should account for its quenching, because in this case the transition (probably excitonic) is forbidden.

In a similar way we may interpret the quenching undergone by the 1.455-eV acceptor-donor transition, as well as the apparition of the 1.48-eV peak. A tentative explanation of this is the dissociation of the donor-acceptor pair originating the 1.455-eV band, which should produce the quenching of the 1.455-eV peak, then only one of its components (donor or acceptor) remains optically active yielding the 1.48-eV peak as a consequence of the shallow-level free-band transition which is more efficient than the previous *A*-*D* transition. The shallow levels involved in these transitions would be located approximately at 26 (*A*) and 35 meV (*D*), respectively, from the bands. After the metastability had been reached, the optical transitions operating from level *A* should be blockaded and only transitions through level *D* would be active. From the data reported in literature about shallow levels, the *A* level seems to be the carbon acceptor ($E_A - E_v \simeq 0.026$ eV) which is abundant in LEC samples and *D* should be related to an unknown shallow donor, whose binding energy would be approximately 30 meV.[38]

So that the rearrangement undergone by the lattice in the proximity of *C* level should be different depending on the impurities surrounding it, recent works by van Vechten state the influence the impurities have on the local arrangement of the $\mathrm{As}_{\mathrm{Ga}}$ antisite defect molecule.[39] Thus, it should be noted that shallow donors and acceptors are preferably located surrounding EL2 family levels.[40] In conclusion, EL2 must likely appear at different configurations depending on both the local arrangement of the lattice surrounding the main component of EL2 (likely the $\mathrm{As}_{\mathrm{Ga}}$ antisite) and the distribution of impurities in this region. One of the most important characteristics of the ground defect arrangement is that it exhibits configurational instability below 140 K as a consequence of the variation in the charge distribution during the optical excitation. The new configuration is unable to transform in the equilibrium arrangement as long as the sample is kept below 120 K; by heating above 135 K the initial defect configuration is restored. This process yields strong thermal quenching of the photoconductivity contrarily to the photoconductivity enhancement associated to the thermal recovery of the unquenched EL2 level in samples exhibiting photoquenching.[13,18]

The recovery of the unilluminated configuration occurs at nearly the same temperature range as that typically observed for the recovery of the EL2 level from the metastable EL2* configuration.[7] This fact, together with the similarity of the spectral distribution of photons producing this effect and the previously reported photomemory effects,[7,18] suggest that different states or configurations of the same defect should originate in each of them. This agrees with a cluster model. Their different arrangement possibilities which would be dependent on both the sample growth conditions and the impurity distribution, should lead to the different defects giving photomemory effects. Such a model is very adequate to explain the optically induced configurational changes. Indeed, such a kind of "photochemical" transformation seems to be more easily accomplished in disordered clusters, where defect association and/or dissociation and/or rearrangements of some parts of the cluster may occur during the illumination, when the charge distribution is strongly modified.[37] It should be noted, that although the spectral distribution and the temperature dependence are similar to those of the photoquenching, usually ascribed to EL2, the level involved in the high-photosensitivity state does not correspond to the same configuration as EL2. In fact other samples exhibit simultaneously both the photoquenching and the high photosensitivity as a consequence of the excitation with 1–1.25 eV.[41] It should be noted that the thermal recovery of the normal state occurs at a slightly lower temperature for the thermal quenching of the photoconductivity (high photosensitivity) than it does for thermal recovery of the photoconductivity (optical quenching), which allows to distinguish between the metastable states of both phenomena.

B. Persistent photoconductivity model

Following the above considerations about the configurational changes induced in the structure of defects by extrinsic light excitation, an important point to be analyzed is the physical mechanism producing the long decay of the excess carrier concentration. The key for understanding this effect is related to the nature of the repulsive barrier avoiding the recombination of the optically generated carriers (holes, in this case).

In our case the holes are photogenerated from the optically generated metastable states which we will call *CA*, then they remain for a long time delocalized in the valence band. The mobility increases as the hole density does, Fig. 5, or more properly, it follows the enhancement of the density of (C,A) centers. This result may be explained on the basis of either a reduction of the ionized impurity concentration or a screening of these impurities by free holes. The latter hypothesis seems to be rather unreliable because at the light intensity used ($\sim 10^{12}$ photons $\text{cm}^{-2}\,\text{s}^{-1}$), the concentration of free holes is rather low ($\sim 10^9\ \text{cm}^{-3}$) comparative to the density of the impurities for providing the screening potential accounting for the increase of the mobility. The former hypothesis seems to agree more reliably with our model of defect association, in fact one of the consequences of this association is to reduce the ionized impurity concentration, and hence an enhancement of the mobility would be expected, as it has been effectively observed in photo-Hall experiments. In fact a study of the ionized impurity scattering conduction must allow us to analyze the evolution of the ionized impurity density as a function of the energy of exciting photons.

1. Ionized impurity scattering analysis

On the basis of a classical treatment[42] the mobility, when ionized impurity scattering is the dominant scattering mechanism in the conduction process, is given by the following relationship.

$$\mu = \left[\frac{C_1 T^{3/2}}{N_I} \right] B \ , \tag{1}$$

where N_I is the ionized impurity concentration, T is the temperature, B is a factor accounting for the screening by free carriers (holes in our case), and C is a coefficient whose value for GaAs is $5.54\times10^{17}\ \text{V}^{-1}\,\text{s}^{-1}\,\text{cm}^{-1}\,\text{K}^{-3/2}$, this value has been calculated taking $0.5m$ for the hole effective mass and $\epsilon_s \simeq 10.9$ for the static dielectric constant of GaAs.[43]

The values of N_I have been calculated for the high-photosensitivity state at different wavelengths. The inverse of the ionized impurity density, N_I, to the photon energy is represented in Fig. 7. The spectral distribution of $1/N_I$ is nearly the same as those reported in Figs. 2 and 5. In fact the increase of the mobility is associated to a decrease of the ionized impurity concentration, which could be due to a defect association.

In summary, the mobility behavior seems to reinforce the idea of a rearrangement of neighbor defects which are able to complex under specific thermal and optical conditions.

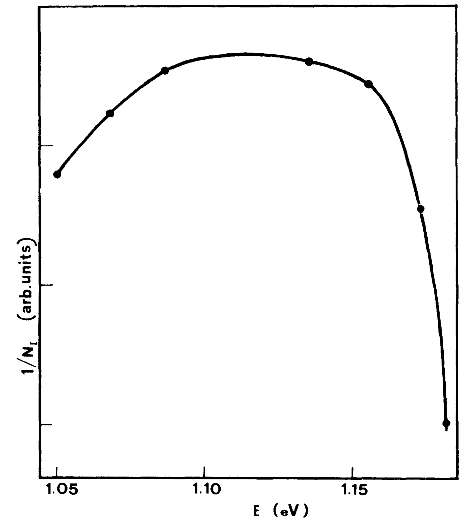

FIG. 7. Spectral distribution of the inverse of the ionized impurity concentration. It is clearly observed the typical spectral dependence already observed in Figs. 2 and 6 correspond to the high-photosensitivity state. The value has been normalized to N_I obtained for 1.18 eV ($N_I \sim 1.2\times10^{16}\ \text{cm}^{-3}$), which corresponds to the maximum value in the spectral range scanned.

2. The repulsive potential barrier

The evolution of the (1.4—1.51)-eV photoconductivity spectrum to the excitation time with extrinsic light (1.12 eV was shown to occur simultaneous to the enhancement of the extrinsic photoconductivity in Sec. III D 2. It can be argued that the progressive transformation of the deep centers induces a simultaneous change in the shallow-trap distribution. The simultaneity observed for the evolution of both the deep *C* and *A* trap population suggests the complexing of these defects under extrinsic light excitation at liquid-nitrogen temperature.

A tentative description of the mechanism leading to the formation of the high-photosensitivity state can be the following. When the deep centers, labeled *C*, are ionized by photons of energy ranging from 1 to 1.25 eV, they undergo a configurational rearrangement involving also the shallow acceptor *A*, which is fully ionized at 77 K. A Coulombic attractive potential working when the charge state of the defects, varied by optical excitation, seems to be the more reliable driven force accounting for the configurational changes in the structure of the defects. On the other hand an important role must be played by the location of the impurities surrounding *C*. The behavior of the shallow-trap distribution[44–46] supports the role played by the impurities in the formation of the (C,A) centers, which are characterized by a high-hole photoemission rate. The repulsive barrier avoiding the recombination of excess holes could be associated to either the (C,A) center itself or a screening barrier due to a space charge surrounding the center. Basically the first hypothesis is formally similar to the typical *DX* center model proposed by Lang *et al.*[21] accounting for the persistent photoconductivity effect in $\text{Ga}_x\text{Al}_{1-x}\text{As}$. The existence of *DX* centers has only been reported in $Ga_xAl_{1-x}As$ $(0.19 \leq x \leq 0.78)$,[47] to our knowledge it has not been reported to exist in GaAs $(x=0)$. On the other hand the observed experimental features of the (C,A) centers are really different from those typically reported for *DX* centers. In fact, the (C,A) center acts as an optically emitting hole level, contrarily to the nature of *DX*.

The screening by space charge seems to be the more reliable mechanism accounting for the persistent photoconductivity in our samples. A tentative model for the local charge space surrounding the (C,A) center does consider the role played by shallow levels neighboring the center. Taking into account the results of Sec. III D 2 regarding the band-edge photoconductivity, it may be assumed that as the D^+-A^- pair dissociates, A^- complexes with the ionized *C* level and then only the optically induced transitions from the valence band to the shallow donor level are observed at 1.48 eV. Most of these shallow donors are fully ionized at liquid-nitrogen temperature, which implies that they are positively charged. Taking into account that the distance between *A* and *D* must not be long, this positive charge might screen the (C,A) centers, then the ionized shallow donors would provide the repulsive barrier, which would avoid the capture of excess holes by ionized $(C,A)^-$ centers. On the basis of such a model any neutralization of the positive charge of the shallow donor must result in a decrease of the average screening barrier and hence in a reduction of the excess hole density.

Such a situation can be arrived at by means of a secondary optical excitation with photons of 1.48 eV, which does transitorily change the occupation of the shallow donor level. In fact, by pumping electrons from the valence band to the D^+ level most of these donors are promptly neutralized and therefore it is possible to reduce the average repulsive potential screening $(C,A)^-$ and so far the excess hole concentration decreases by capture at the $(C,A)^-$ centers. In Fig. 8 the decays of the 1.12-eV photoconductivity as recorded for different additional periods of excitation with photons of 1.48 eV are shown. It can be observed that the longer the excitation time with 1.48 eV, the lower the persistent photoconductivity level becomes. It should be noted that the law to which the decays fit $(\sim t^n)$ is nearly the same as that observed for the curves of Fig. 1. This is a very illustrative result, because it reveals that the mechanism itself giving the persistent photoconductivity has not been disturbed, but only the excess hole density has been reduced by the 1.48-eV excitation. In this way it is noteworthy to remark that the capture of the excess holes does not alter the high-photosensitivity state generated by extrinsic light, or in other words the (C,A) center is not destroyed by recombination. In fact, after the enhanced decay produced by 1.48-eV photons, an excitation with 1–1.25 eV quickly restores (several seconds) the initial persistent photoconductivity situation. This fact confirms the metastable character of the (C,A) center; these results rule out the possibility that a doubly charged center could account for the persistent photoconductivity in GaAs, as it has been proposed by Lorenz *et al.*[19] for explaining the long-lifetime photoconductivity in CdSe.

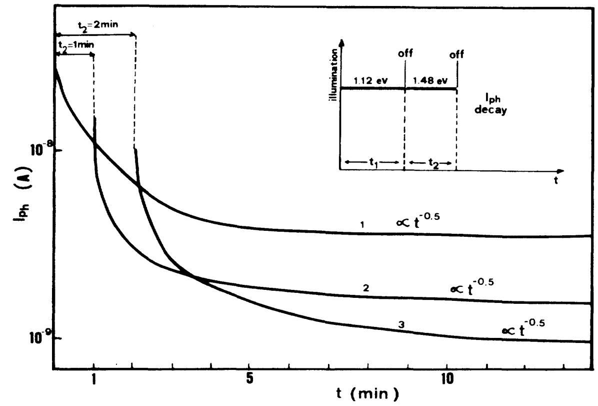

FIG. 8. Photocurrent experiment showing the influence the ionized shallow donors have on the persistent photoconductivity. In the inset is schematically described the experiments. Firstly, the high photosensitivity state is obtained by excitation with 1.12-eV photons during a period t_1. Then this illumination is removed and replaced by 1.48-eV excitation, during a time t_2. The decay is recorded for several t_2: (1) $t_2=0$, (2) $t_2=1$ min, and (3) $t_3=2$ min. The onset of the decay is progressively shifted in the figure in order to correct the time of excitation with 1.48-eV photons. It is clearly observed that the decay is enhanced by 1.48-eV excitation. It should be noted that the fast decay part of curves 2 and 3 is attributable to the 1.48-eV photocurrent decay.

On the other hand, the fact the decay law does not change as the hole density decays suggests that the charge space is associated with each (C,A) center, and there are no macroscopic potential barriers separating the free holes from the ionized $(C,A)^-$ centers as it occurs for semiconducting layers deposed on a GaAs substrate, for which there has been reported a change in the decay law as the carrier density decreases.[24] It is important to say that the shallow donors and (C,A) centers must be sufficiently close together in order to ensure the screening avoiding the hole capture. In this way it has been claimed that shallow traps are located nearby EL2 in GaAs.[40]

C. The kinetics of the metastable state

The observed metastability invokes the role played by EL2 in the generation of the PPC effect and therefore some questions must be answered about the physicochemical nature of level. Although the properties of EL2 have been extensively studied, its nature is not well known. Some evidence has been reported about its complex nature. The existence of several photomemory effects reported in different samples seems to confirm that EL2 might adopt different metastable configurations, or in other words these states would be associated to different structural configurations of the defect.[38,39,48]

Recent calculations have demonstrated that the lattice distortion around the As_{Ga} antisite is rather small,[49] hence is unlikely that it produces such a large lattice relaxation as is predicted elsewhere.[50] On the other hand, experiments on optically detected MCD (magnetic circular dichroism) by Meyer *et al.*[11] stated that EL2 is not likely the As central atom surrounded by four equivalent As ligands. However it is possible that complexes of anion antisites with other defects could account for EL2 properties.[51] On the other hand the broadening of the spectral distribution usually found from each other sample suggests that rather than one level, a family of EL2-like levels exist, which is likely due to a structure containing family of defects. This hypothesis is confirmed by our persistent-photoconductivity results, which demonstrates that there exists a configurational arrangement leading to a metastable state whose photoelectronic properties are thoroughly different from those displayed by the typical metastable state of EL2, i.e., the optical quenching, which is considered as the signature of EL2.

These features suggest that the assertion of Taniguchi *et al.*[38,39] concerning the existence of As aggregates of variable structure is likely a reliable model describing the family of EL2 complex defects. The structure of the aggregates would be strongly dependent on both the growth method and the specific conditions during growth. This would be the reason for the diversity of behavior reported around the $\mathrm{As_{Ga}}$ complexes.

The results concerning the shallow levels suggest that impurities play an important role on both the structure of the aggregate and the reordering stage produced during the path to the metastable state by optical excitation with (1–1.25)-eV photon. In fact, we have shown that the complexing between C center and the A acceptor (most likely a carbon acceptor) contributes to the formation of the (C,A) center, which is known as the metastable state of the C center. An important aspect of the problem should be related to the kinetics of the reaction producing the metastable state. Looking at Fig. 1, we see that it is possible that during optical ionization of the complex defect C $(C \xrightarrow{h\nu} CB)$, the defect itself would be reordered C^* $(C^+ + e^- \rightarrow C^*)$ this stage being the rate-limiting process before the complexing between C and A. In Fig. 1 this stage is indicated and labeled by R_c, this rate is dependent on both the light intensity and the energy of incident photons, Fig. 9. This spectral distribution is nearly the same as that reported typically for the photomemory in GaAs, which should indicate that the reordering stage at the complex defect is a common one in the path to the metastable state of the As aggregates. After this reordering and under the optical excitation there is a faster mechanism by means of which C^* and A^- form a dipolar center, which is responsible for the high photosensitivity, due to the ability of dipolar centers to capture an electron optically emitted from the *VB*. This process is simultaneous to the observed shift of the near-band-edge photoconductivity spectrum, which demonstrates the role played by A in the complexing mechanism. Thus, the rate-limiting process is the pairing of C^* and A^-, this rate is labeled as R_{c^*} in Fig. 1. This pairing is responsible for the photohole generation instead of the dominant optical electron emission associated to the C center.

It should be pointed out that at equilibrium the Fermi level is pinned above the C center, due to the electron emission associated to the initial stage of the excitation (R_c in Fig. 1), this implies that this level is electron occupied, so that only a weak hole emission is expected. However, after R_c, hole emission becomes dominant, which implies that the metastable state (C^*,A) is different from that typically associated to EL2, as revealed by photoquenching experiments. On the other hand the intense hole photoionization observed rules out the probability of a single-hole photoionization of EL2, which is known to have a small hole photoionization cross section in the spectral range considered. This process is also energy dependent according to the spectral distribution in Fig. 9.

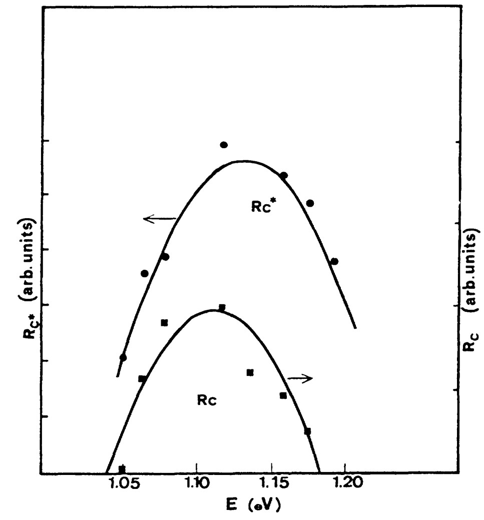

FIG. 9. Spectral distribution of the rates, R_c and R_{c^*}, leading to the formation of the high-photosensitivity state.

This two-stage model agrees with our previous assertion about the complexing between EL2* and shallow levels[18,33] in relation with photoquenching. Recently, photoluminescence experiments by Otsuka *et al.*[51,52] have confirmed the existence of this complexing mechanism.

In Fig. 10 the successive stages of the defect reaction mechanism leading to the formation of the C^*A centers are schematically represented. We have used a new notation for the high-photosensitivity centers instead of the (C,A) symbol used before.

This physical model invokes the motion or the reordering of defects upon variable charge state conditions. It seems that fast diffusors, as interstitials, would enable the structural reordering, on the other hand, the Coulombic

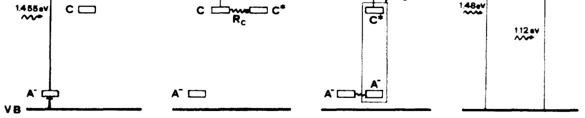

FIG. 10. Single-level sketch showing the path followed to the formation of the metastable state C^*A. The transitions giving photoconductivity are indicated.

potential associated to the ionized atoms would accommodate the atoms composing the defect of the new configuration for which the lattice strain is reduced. This Coulombic attraction when the charge state is varied is basically the dipolar model of Levinson.[53]

The idea of a defect undergoing successive transformations is confirmed by the thermal evolution of the photoconductivity. The nonreversibility of the photocurrent versus T supports the hypothesis of a destruction of the metastable state between 120 and 135 K. Furthermore the thermal quenching of the photoconductivity exhibits several slopes, Fig. 4, which evidences that more than a simple process is occurring. Thus, the sharp peak observed at 130 K (2 or 3 K width at half height) represents an abrupt change in the kinetics of the normal-state recovery, which can denote a change in the ordering mechanism of (C^*,A) defects, which would follow a temperature-dependent hierarchical process. In fact the thermal recovery of the normal state might be considered an annealing of the defect conforming the metastable state.

The fact that the normal configuration is thermally restored implies that the defects involved in the reordering have to be close together in order to ensure the thermal reversibility. It should be noted that some samples exhibit a progressive aging,[54] which seems to agree with the idea of defect rearrangements during the optical excitation.

V. CONCLUDING REMARKS

Photoconductivity studies of undoped semiinsulating GaAs grown by the liquid-encapsulated Czochalski method have revealed the existence of an optically induced high-photosensitivity state of the sample, which is characterized by the persistent-photoconductivity effect (PPC). Photo-Hall experiments have demonstrated that the high-photosensitivity state is associated to a hole conduction, which account for a change of the structure of the complex defects optically active to photons ranging from 1 to 1.25 eV. Optical and thermal properties of the persistent photoconductivity state suggest that the midgap donor EL2 is involved in the observed process. The features displayed by the metastable state (C^*,A) are different from those usually ascribed to the metastable state of EL2, labeled EL2*. From band-edge photoconductivity experiments it has been demonstrated that shallow impurity levels play a capital role in the formation of the metastable state and also in the screening of the (C^*,A) centers, which results in the long-lifetime photoconductivity characterizing these specimens. The kinetics of both the formation and annealing of the (C^*,A) centers implies the existence of several stages, which accounts for the rearrangement mechanisms involving rather disordered lattice regions. The fact that the spectral distribution of the observed effects is always the same invokes the role played by the $\mathrm{As}_{\mathrm{Ga}}$ antisite defect in the formation of the metastable state. Furthermore the idea of the formation of clusters of $\mathrm{As}_{\mathrm{Ga}}$ antisites with other defects which are capable of reordering under specific optical and thermal conditions is confirmed by the results we have reported in this work about the persistent photoconductivity effect.

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