Effect of indium doping on transient transport phenomena in semi-insulating GaAs

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(Received 16 December 1999; revised manuscript received 14 June 2000)

The influence of defect structure on transient transport phenomena was investigated in semi-insulating GaAs, undoped and doped with In, grown by the liquid-encapsulated Czochralsky technique. The change in time after a strong laser excitation of the nonequilibrium photo-Hall effect voltage and the photomagnetoelectric effect were used to reveal the influence of In doping in concentrations of up to $\geqslant 2\times10^{20}\,\mathrm{cm}^{-3}$. We did not find additional In levels in the band gap. Nevertheless In doping caused significant changes in the behavior of nonequilibrium carrier mobility in the temperature range of 300–420 K, which were not observed in other crystals, undoped or doped with other dopants. The effect of In becomes pronounced if its concentration exceeds $(6-9)\times10^{19}\,\mathrm{cm}^{-3}$. These changes could not be explained only by the reduction of the dislocation density. We conclude that apart from this the rearrangement of the microscopic inhomogeneities must be taken into account. It is supposed that lattice defects become distributed more homogeneously, and appear more probably as small (short-range) inhomogeneities instead of large accumulations around dislocations. This leads to the diminished role of the percolation phenomena. It was demonstrated that though doping with In reduces the dislocation density, it can intensify the effect of smaller defects on transport phenomena.

I. INTRODUCTION

Semi-insulating (SI) GaAs, a material of constantly growing interest for the needs of modern microelectronics and optoelectronics,[1,2] is a typical representative of binary compensated semiconductors, in which the self-compensation effect is clearly expressed. Investigating and applying such semiconductors one must always face problems, arising not only from the existence of the numerous deep levels in the band gap, but from the existence of a spatially inhomogeneous defect distribution as well (see, e.g., Refs. 1–6). Lately significant progress in the growth technique of bulk GaAs was reached due to an appropriate thermal treatment, which enables relatively good mobility values to be obtained. Nevertheless the dislocation density still remains relatively high especially in liquid-encapsulated Czochralski (LEC) SI GaAs. The problem of inhomogeneities also exists in radiation detectors based on SI GaAs. It is accepted that different defects appear around dislocations, forming a well-expressed cellular structure with different dimensions usually in the regions from tenths of a micron to hundreds of microns.[5,6] Such doping and compensation inhomogeneities occur during the growth process, and cause the appearance of the potential fluctuations of both bands and subsequently of the band-gap potential relief.[7–11] In such materials transport phenomena are directly influenced not only by scattering and recombination centers but by inhomogeneity screening possibilities as well, which drastically depend on the number of charge carriers in the bands. In practice in semi-insulating material carriers are generated mainly by external perturbations, and their concentration usually exceeds a thermal equilibrium value. Thus, effective free-carrier densities are given by a balance between generation and recombination (i.e., excess carrier lifetime), which in its turn depends on the amount of carriers. Therefore, the establishment of equilibrium can last significantly longer compared to a homogeneous semiconductor, and this can lead to a drift of measured parameters with time.[12–14]

Doping by different dopants changes the character of the inhomogeneities and the density of dislocations, and thus the potential fluctuations. In particular doping by isovalent impurities, mainly by In and Sb, can be effective in reducing the dislocation density in LEC-grown SI GaAs. But, on the other hand, such a procedure may lead to the appearance of deep levels in the band gap, furthermore, it causes a redistribution of other defects. These effects reflect themselves in the transport of the charge carriers. We demonstrated this in Ref. 13 on the example of Sb-doped LEC SI GaAs. Here we present an investigation of nonequilibrium carrier transport in undoped and In-doped LEC SI GaAs.

Earlier we demonstrated that extensive information about transport and recombination properties of material, including the influence of its defect structure, can be gained by making simultaneous investigations of the nonequilibrium photoconductivity and the photo-Hall effect voltage decay kinetics[12–14] in a wide time region. This enables one to deduce the type of scattering center and its charge state, as well as its change after excitation. The scattering and recombination centers were found to have different influences at different time intervals. This was explained by the combined influence of point defects and potential fluctuations. We proposed a complex ''island'' model of scattering and recombination centers, consisting of defect clusters and their associations around dislocations, surrounded by potential barriers. At low excitations they are insulating for majority-charge carriers, thus reducing the effective crystal volume and causing percolation transport effects. At temperatures higher than 330–360 K, the main barrier of the ''island'' can be recharged or screened by nonequilibrium carriers, and its fine barrier structure appears as an effective scatterer, causing a sharp decrease of the nonequilibrium Hall mobility. The investigation of the photomagnetoelectric effect (PME) may give additional information, and be helpful in solving

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the problem of the bipolarity of the conductivity, because this effect is caused mainly by minority carriers.[15–25]

In this paper we present an investigation of nonequilibrium transport phenomena in SI GaAs, undoped and doped with In up to concentrations of $\geqslant 2\times 10^{20}\,\mathrm{cm}^{-3}$. We demonstrate that the effect of In doping cannot be explained only by the reduction of dislocation density, the rearrangement of the microscopic inhomogeneities of the band gap must additionally be taken into account.

II. SAMPLES AND EXPERIMENT

We investigated *n*-type SI GaAs samples, undoped and doped with In, and grown by the LEC technique using liquid encapsulation with B_2O_3. To deduce dislocation density by etch-pit-density (EPD) counting, the crystals were etched in KOH at 350 °C for 30 min. The EPD ranged from 5×10^3 up to $8\times 10^4\,\mathrm{cm}^{-2}$. The lowest values, as expected,[26,27] were in the crystals doped with In. At room temperature all samples were n type, with equilibrium concentration $5\times 10^6-3\times 10^8\,\mathrm{cm}^{-3}$, and an effective Hall mobility 3000–7000 $\mathrm{cm}^2/(\mathrm{V\,s})$ in the dark. A series of samples with different In dopings were investigated. They demonstrated similar behavior, depending on the In content. Therefore, in order not to overload the reader with a great deal of experimental data, we analyze further in detail typical results of the investigation of three samples: sample 1 was undoped, sample 2 was doped with In to 6×10^{19}, and sample 3 was doped to $2\times 10^{20}\,\mathrm{cm}^{-3}$. In order to reduce the surface recombination rate, the samples, after initial mechanical polishing, were etched for 2 min in a H_2O_2:H_2O:H_2SO_4 solution (1:1:3), and finally were washed in distilled water. Such chemical treatment reduces the surface recombination rate to $10^3-3\times 10^4$ cm/s, as also reported in Refs. 22–24, and minimizes its influence on transport phenomena. Indeed, to influence the experimentally obtained values of bipolar diffusion coefficient as well as of electron and hole lifetimes, the surface recombination rate should exceed 10^5 cm/s. PME measurements were performed by using He-Ne laser excitation with photon energies of the two harmonics of 1.98 eV ($\lambda=0.63\,\mu$m) and 1.08 eV (1.15 μm), respectively, and a beam intensity of $(1-1.2)\times 10^{17}$ photons/$(\mathrm{cm}^2\,\mathrm{s})$. For high-intensity excitation a pulsed neodymium laser with a pulse duration of 15 ns was used, the photon energy of which was 1.17 eV ($\lambda=1.064\,\mu$m), and the maximum pulse intensity was $\sim 10^{26}$ photons/$(\mathrm{cm}^2\,\mathrm{s})$. The time transients of the Hall mobility were registered from the beginning of the excitation to the end of relaxation to the stationary values. A detailed description of the experimental procedure can be found in Ref. 12.

III. THEORETICAL BACKGROUND

It is generally accepted that a modulation of the band gap (potential relief) takes place in SI GaAs. It is caused by parallel fluctuations of the band edges, appearing due to the inhomogeneity of compensation and doping (mainly by shallow levels), and is influenced by the presence of dislocations as well. The effect of inhomogeneities on Hall and photocurrent data can be summarized qualitatively as follows: (1) The relaxation to the equilibrium state after excitation is slowed down because of the spatial separation of free or localized carriers of different signs by potential barriers. That is prior to the recombination, which occurs mainly via deep recombination centers in SI GaAs, nonequilibrium carriers must overcome the potential barriers of the inhomogeneities. (2) Not all carriers in the bands can take part in the conductivity, because a part of them becomes confined in potential wells. Nevertheless, together with free carriers they screen the field of the barriers, thus reducing their effective height depending on excitation conditions. (3) The inhomogeneous regions scatter charge carriers as neutral or charged scatterers if their effective dimensions are smaller than or comparable to a mean free path of carriers (microscopic and middle-range inhomogeneities), and their density is relatively low. In the case that their dimensions significantly exceed the mean free path (macroscopic inhomogeneities) the Hall mobility depends mostly on the properties of the best conductive regions, and therefore the domains of lower conductivity frequently can be treated as isolating inclusions which reduce the effective volume of the crystal. (4) The influence of bipolarity effects is better pronounced in disordered semiconductors than in homogeneous ones due to the spatial separation of the paths of different carriers. As a consequence, in the presence of microinhomogeneities the photoconductivity and Hall mobility decay after excitation by different laws.[12–14] This situation was described mathematically by introducing the drift and recombination barriers of different height.[7] It must be stressed that due to screening by nonequilibrium charge carriers, the effective heights of the drift and recombination barriers change.[7–11,28] This means that the effective barrier height and its effective space charge depend on the capture probability ω of the single ηth carrier, which is different than that of the $(\eta+1)$th carrier. It depends on two processes, that may be described by probability functions ω_1 and ω_2 (Ref. 28):

$$\omega=\omega_1\omega_2=\exp\left(-\frac{\eta e^2}{4\pi\varepsilon\varepsilon_0 rkT}\right)\times\exp\left[-\frac{2}{h}\int_0^r\left(2m^*\frac{\eta e^2}{4\pi\varepsilon\varepsilon_0 r}\right)^{1/2}dr\right].\quad(1)$$

The first multiplier describes the probability of overcoming the potential barrier Φ of the inhomogeneity by a charge carrier that is situated at a distance r from it. The second one gives the probability of moving in space and getting far enough into the space charge region, where the potential relief is undisturbed, in order to recombine. Here m^* is an effective electron mass. This function has an expressed maximum at $r=R_z$,[28] which stands for the effective radius of the space charge region:

$$R_z=\left(\frac{\hbar^2e^2\eta_{\mathrm{eff}}}{4\pi\varepsilon\varepsilon_0 8m^*k^2T^2}\right)^{1/3}=\frac{\hbar}{kT}\left(\frac{e\Phi}{8m^*}\right)^{1/2}.\quad(2)$$

This corresponds to the effective space charge

$$Z=\eta_{\mathrm{eff}}=\frac{4\pi\varepsilon\varepsilon_0\hbar}{kT\sqrt{em^*}}\left(\frac{\Phi}{2}\right)^{3/2}.\quad(3)$$

Thus both these parameters can be found at every moment of the relaxation if the potential barrier height is known. The

barrier height can be evaluated by analyzing the photoconductivity decay as in Ref. 13, supposing that the instant relaxation time τ is given by:[7]

$$\tau = \tau_0 \exp\left(\frac{E_{\mathrm{rec}}}{kT}\right). \tag{4}$$

Here the height of a recombination barrier E_{rec} is given by $E_{\mathrm{rec}} = e\Phi$. Therefore, recombination causes a change of the effective volume of the charged inhomogeneities and of the drift paths of the carriers. In particular the associations of scattering centers can be divided into single centers, and the effective potential barrier around the clusters may change as well. Thus the disorder leads to the appearance of long-time-scale relaxations of the photoconductivity and Hall mobility, which are caused by the existence of drift and recombination barriers and by the screening of their space charge by nonequilibrium carriers. Furthermore, in the case when excitation is strong, several deep levels in the band gap may be recharged, and this also changes the transport and recombination conditions of carriers.

IV. RESULTS

The carrier concentration measured in our samples in the dark was thermally activated. The effective activation energy was about 0.68–0.76 eV, and the highest values were observed in samples doped with In. These values are lower than that of the EL2 level, but they also cannot be attributed to some In-related level. Nor by spectral measurements did we find other closely located shallower levels with high concentrations in the band gap. Such a lowering of the effective activation energy from that of EL2 was attributed in Refs. 9 and 10 to the influence of inhomogeneities with average amplitude of potential fluctuations 90–180 meV. This issue is also supported by the behavior of the equilibrium Hall mobility measured in the dark in our *n*-type samples. The Hall mobility used to decrease slightly in the temperature range of 300–420 K. Such a decrease could be well described using the above model of an inhomogeneous crystal.[9,10] Further we will concentrate on the transient Hall mobility behavior, as directly representing the scattering phenomena of interest. A general analysis of the mobility and photoconductivity decay kinetics after laser-pulse excitation was presented in Refs. 12, 13, and 29. It was demonstrated that photoconductivity and Hall mobility decays after strong excitation usually have long-time-scale tails, which may be longer than 10 ms–1 sec even at room temperature. Furthermore, their relaxation curves are different. This is caused by the influence of complex scattering centers—clusters of impurities and defects. Potential barriers cause a prevailing hyperbolic decay of an excess carrier concentration, which is superimposed by exponential parts due to the influence of deep recombination traps. Meanwhile the nonequilibrium Hall mobility saturates over a wide time and excitation intensity intervals, showing some well-expressed steplike changes (which may also appear as the mobility sign inversion) caused by the recharge of scattering centers. In our case the measured dependencies of the change of Hall mobility on excitation intensity of investigated crystals are presented in Figs. 1–3 for different temperatures. A minimum value in these figures corresponds to the equilibrium mobility in the dark. The curves of mobility kinetics in Figs. 1–3 are sample dependent, though similar tendencies can also be seen. At room temperature [Figs. 1(a)–3(a)] the mobility grows after the laser pulse, depending on the sample and excitation intensity, until saturation is reached. The saturation occurs at lower intensities in samples doped with In, though the saturation values are very similar in all samples and reach 3270 $\mathrm{cm^2/V\,s}$ in sample 1, 3140 $\mathrm{cm^2/V\,s}$ in sample 2, and 2960 $\mathrm{cm^2/V\,s}$ in sample 3. Saturation is reached at intensity of about $6\times10^{23}\,\mathrm{cm^{-2}\,s^{-1}}$ in sample 1, $7\times10^{22}\,\mathrm{cm^{-2}\,s^{-1}}$ in sample 2, and $1\times10^{22}\,\mathrm{cm^{-2}\,s^{-1}}$ in sample 3. Meanwhile the maximal concentrations of generated carriers are $\cong10^{16}\,\mathrm{cm^{-3}}$, and the corresponding change of the level filling can be of up to $5\times10^{15}\,\mathrm{cm^{-3}}$. Thus supposing that the mobility saturation oc-

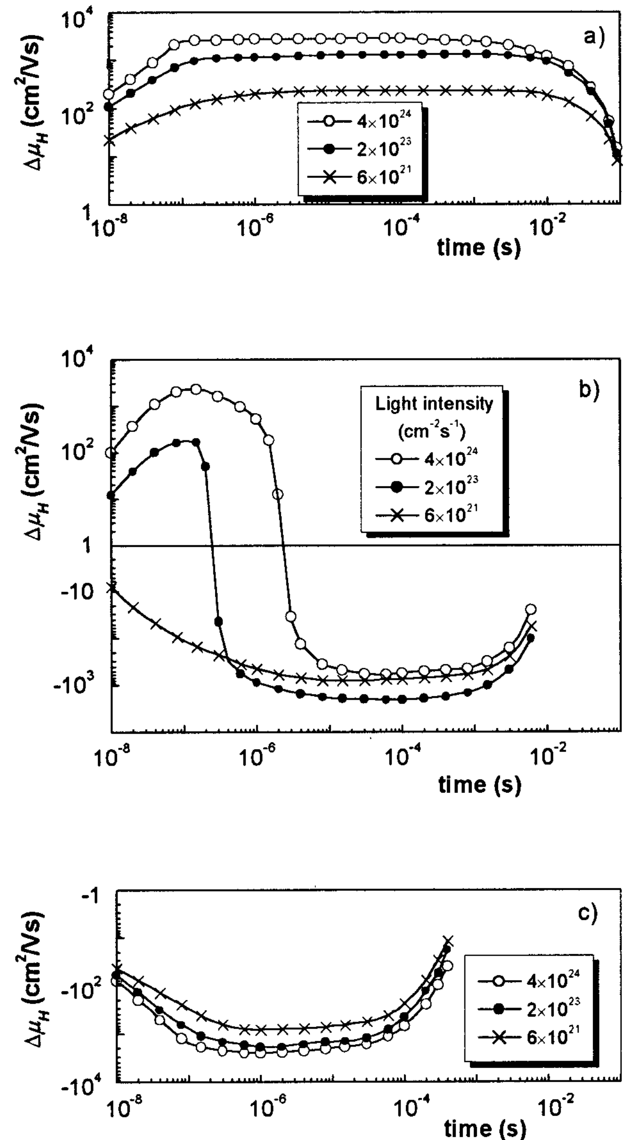

FIG. 1. Temporal changes of the nonequilibrium Hall mobility in sample 1 at 300 K (a), 350 K (b) and 420 K (c). These and further mobility changes are plotted with respect to the stationary values. The increase of the Hall mobility is plotted upward from the minimum value, and decreases downward from it. The laser pulse intensities are given in the figures. Points on the curves are plotted for the sake of convenience, and represent only a minor part of the experimental data.

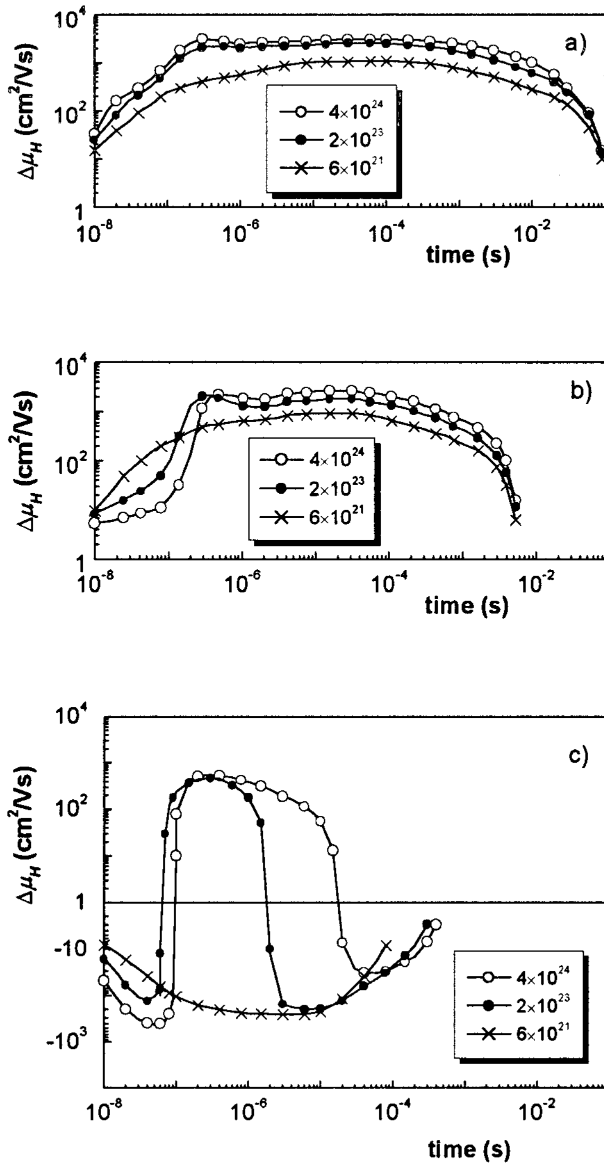

FIG. 2. Temporal changes of the nonequilibrium Hall mobility in sample 2 at 300 K (a), 350 K (b), and 420 K (c).

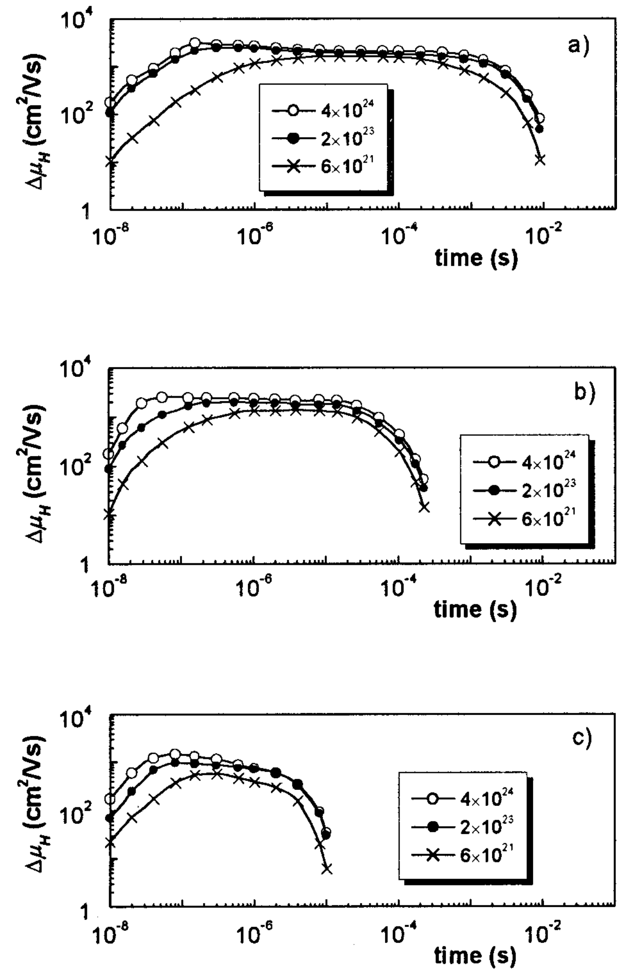

FIG. 3. Temporal changes of the nonequilibrium Hall mobility in sample 3 at 300 K (a) 350 K (b), and 420 K (c).

curs due to a recharge of low- to medium-range scattering centers,[12,13] it can be concluded that larger inhomogeneities are present in sample 1 or that their number is greater as compared to other samples. The mobility relaxation ends with a final, almost exponential, decay to a stationary value. The longest final relaxation time constant was also in sample 1: 1.8×10^{-2} sec. In sample 2 it was $(1.1-1.4)\times10^{-2}$ sec, and in sample 3 it was $(2.6-2.8)\times10^{-3}$ sec. Such shortening of the time constant supports the previous issue about the character of the inhomogeneities. The more detailed analysis of the decay kinetics enables one to evaluate their parameters according to Eqs. (2)–(4). In Refs. 12, 13, and 29 we demonstrated that after high laser excitation the photoconductivity decay follows the prevailing hyperbolic rule in which different parts can be singled out. Initially, when the carrier concentration is high enough to screen potential barriers, recombination occurs via deep recombination centers, without significant influence of potential inhomogeneities. This initial decay region lasts up to $(0.5-30)\times10^{-6}$ sec at room temperature in different samples. Later recombination rates change, and therefore the pronounced decrease of a slope of the concentration decay curves from 1.2–1.5 down to 0.3–0.8 occurs. The following slower parts of the decrease could not be modeled by taking into account deep levels with realistic parameters. Thus it can be supposed that potential barriers of the inhomogeneities become effective at that moment in time. Therefore, the following decay is effectively influenced by barriers, and thus the instant decay time grows according to Eq. (4). It enables one to evaluate mean recombination barrier heights. In our case we received the inhomogeneity parameters that are plotted in Fig. 4 for all the investigated samples. The values of the final recombination time constants τ, recombination barrier heights $E_{\rm rec}$, effective radii of the space charge regions R_Z, and their charges Z are presented along with their numerical fitting curves. It can be seen that, indeed, inhomogeneities decrease with increasing indium doping. The changes become evident, when the In concentration exceeds the values of about $(6-9)\times10^{19}\,\mathrm{cm}^{-3}$. On the other hand it should be stressed that dimensions of the detected inhomogeneities are much less than those usually obtained by optical and electrical scanning methods. Most probably this is because of the limited spatial sensitivity of the latter. This supports the idea proposed in Refs. 12 and 13 that various inhomogeneities take part in carrier transport in different ways. Greater inhomogeneities, with dimensions according to different authors ranging from

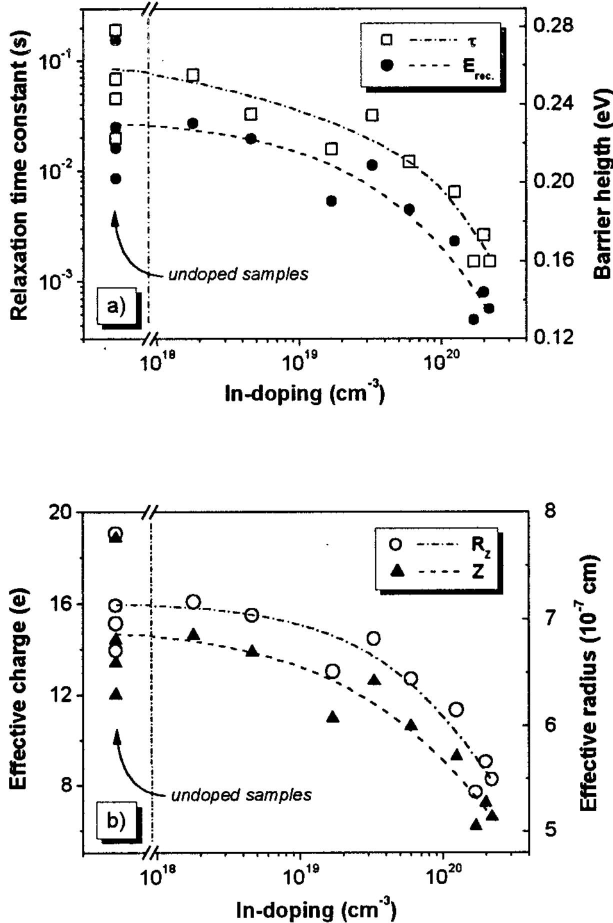

FIG. 4. Values of the final recombination time constants τ, and recombination barrier heights $E_{\rm rec}$ (a); effective radii of the space charge regions R_Z, and their charges Z (b) of the investigated samples. The numerical fitting data are indicated by the dashed and dash-dotted curves. Note that scaling of all vertical axes is different.

some up to hundreds of microns, most probably appear as insulating inclusions for majority carriers in a crystal matrix. The role of such large isolating ''islands'' can be played by clusters of smaller defects and their associations around dislocations. Therefore, such inhomogeneities change current flow trajectory and diminish the effective crystal volume. This keeps the maximum measured mobility (stationary value plus its change after excitation)[12,13] below the phonon-limited value in GaAs. A more homogeneous and defect-free crystal matrix appears between such defect ''islands,'' forming conductive channels for charge carriers. On the other hand, short-scale inhomogeneities which are located within conductive channels also take part in carrier transport acting as charged scattering centers. Our results demonstrate that such submicron inhomogeneities can be effectively recharged or screened by light-generated carriers, which causes significant mobility changes. Nevertheless, if smaller inhomogeneities are screened, then the Hall mobility even in the ''good'' LEC SI GaAs crystals do not exceed maximum values ranging typically from 7000 up to 8000 $\mathrm{cm^2/V\,s}$.[30] This can be explained by the influence of long-range inhomogeneities that remain inaccessible for electrons, e.g., dislocation cores, etc. Their density is relatively high in LEC samples, and therefore they can notably affect the mobility. Evaluation according to the model[31,32] show that in the dark they occupy at least a 0.18–0.43 part of the total crystal volume depending on the sample.

In order to investigate the influence of different defects in more detail, we investigated the mobility behavior at temperatures of up to 420 K. A general feature is the shortening of the relaxation kinetics with increasing temperature as Figs. 1(b) and 1(c) to 3(b) and 3(c) demonstrate. At 420 K the final relaxation to equilibrium values occurs $\cong$2.5–3 orders of magnitude faster compared to that at room temperature. This results in an effective activation energy of this process of 0.56–0.67 eV in different crystals and this value also increases along with the In content. Another characteristic feature is the remarkable change of the transient mobility behavior in the temperature region 330–370 K. The mobility increase after laser excitation is changed by a decrease. This feature was observed in most of the investigated samples, undoped and with different doping,[13] except the samples with the highest In doping, as seen from Figs. 1(b)–3(b). In some cases the drop of mobility reached 2000 $\mathrm{cm^2/(V\,s)}$, but the sign of the Hall coefficient remained unchanged. The total mobility (the stationary value plus its change after excitation) is observed to fall from $(5-8.5)\times10^3\ \mathrm{cm^2/(V\,s)}$ down to $(0.9-2)\times10^3\ \mathrm{cm^2/(V\,s)}$ depending on the sample. The decrease ranged from four to nine times, i.e., it was much steeper than could be explained by the phonon scattering. Outside this temperature region the changes of the total mobility were not sufficient. This is clearly seen in undoped sample 1 [Figs. 1(b) and 1(c)]. At high temperatures (420 K) a drop of the mobility occurs at all excitation intensities. A more interesting behavior is observed in this sample at an intermediate temperature of 350 K [Fig. 1(b)], and in sample 2 at 420 K [Fig. 2(b)]. It can be seen that in these cases regions appear where the mobility increase is changed by its decrease, and vice versa. Furthermore, the changes depend on the excitation intensity. Nevertheless in sample 2 the only mobility increase is observed at intermediate temperatures of up to 400 K. In contrast, in sample 3, no mobility drop was observed even at the highest temperature. Such a behavior correlates with the In doping level; nevertheless the effect of In cannot be explained in a simple manner. On the other hand, the influence of some different scattering centers may be supposed, that act differently depending on their charge state and the number of generated carriers.

To explain such mobility behavior the effect of bipolar conductivity must be examined first, because in principle complicated changes of the nonequilibrium mobility could be caused by the generation of excessive holes. Usually the influence of holes was observed only in SI GaAs doped with Cr, while undoped and In-doped material demonstrates electronic conductivity. To prove it on our samples, the photomagnetoelectric effect measurements were carried out as in Ref. 33. Indeed, we obtained that though thermal generation of both sign carriers is intensified with temperature, it does not become decisive at least up to $T=420$ K, and conductivity remains monopolar $(n>p)$. Therefore, the role of excessive holes can be neglected with good accuracy, taking into account that $\mu_n \gg \mu_p$ in GaAs. Subsequently, an additional defect scattering mechanism must be involved to assure the

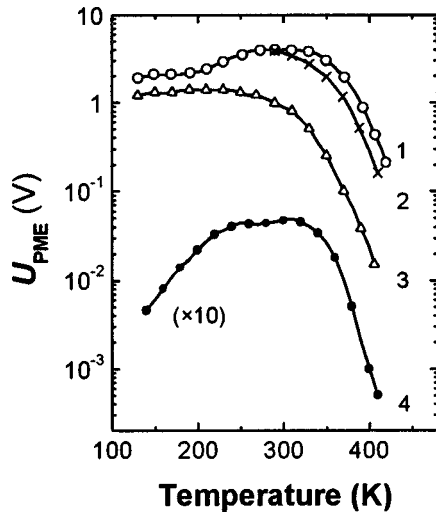

FIG. 5. Temperature dependencies of the photomagnetoelectric effect e.m.f. of the investigated samples. Curves 1–3 represent samples 1–3, respectively. They were measured by using a constant intrinsic excitation, and curve 4 was obtained by exciting sample 1 extrinsically.

described drop of the nonequilibrium mobility, as will be discussed later. Furthermore, we also observed a clear correlation of the photomagnetoelectric effect electromotive force (e.m.f.) (U_{PME}) on In content in our samples. In Fig. 5 the dependencies of U_{PME} on temperature are presented for the same samples by exciting them with light from the intrinsic (curves 1–3) and extrinsic spectral regions (curve 4). It must be noted that values of U_{PME} in the case of intrinsic excitation reach some V for temperatures $T \leqslant 320$ K. Such values exceed their theoretical estimations according to Refs. 15, 17, 19–21, and 25, and, supposing that the crystal is homogeneous, by up to 2–3 orders of magnitude. Probably high values of the PME voltage can be caused by nonhomogeneous defect distribution in the samples due to existence of which the sum of e.m.f. generated on adjacent nonhomogeneities is measured. It was shown[15] that if nonhomogeneities appear as *p-n* type barriers, the PME voltage is proportional to the number of such barriers. In this case photovoltaic effect voltages from neighboring barriers annihilate mutually, and the sum of only PME voltages is measured. The evaluation of a number of effectively acting nonhomogeneities along the samples gives the reasonable value of $10^2 - 10^3\ \mathrm{cm}^{-1}$. It can be seen that in the sample with highest In doping, i.e., with lowest dislocation density, values of U_{PME} are significantly lower (curve 3) than that in undoped sample (curve 1), which confirms the previous issue. It was also possible to measure the U_{PME} signal in an undoped sample (curve 4) by using extrinsic excitation. This was significantly lower than in the case of the intrinsic excitation (curves 1–3). In samples 2 and 3 the sensitivity of the equipment did not allow us to measure U_{PME} in this regime. It is known[20] that in the case of extrinsic excitation, i.e., of low absorption ($\alpha L \ll 1$), PME voltage appears only if generation rates of electrons and holes are different. It takes place if the generation quantum efficiencies of both sign carriers are in general not equal due to the different nature of deep energy levels in the band gap. The existence of the local inhomogeneities in the crystal, that absorb the incident light effectively and separate in space different carriers, assist this mechanism, so the significant values of U_{PME} can be measured.

The important fact is that the increase in temperature above 320 K leads to a sharp drop of U_{PME}, which occurs in the same temperature region as the change of the total Hall mobility as described above, and therefore is probably caused by the same mechanism. In order to find the activation energy of the nonequilibrium conductivity caused by the PME effect, we also measured the short-circuit current I_{PME} of the PME effect. Then the conductivity could be calculated as $\Sigma_{PME} = I_{PME}/U_{PME}$. This again gave us similar activation energy values of about 0.64–0.76 eV that were highest in the doped samples. Thus, it can be supposed that the shortening of the Hall mobility kinetics and the drop of U_{PME} with increasing temperature are caused by the electrons released from the EL2 level. Indeed, usually the effective thermal generation from this level starts above 300 K. The reduced values of the activation energy are most probably caused by potential fluctuations according to the model.[9,10] Furthermore in the course of recombination these fluctuations can change conduction paths in a complicated way, so lower activation energy values may be obtained by transient methods. The thermal generation of the carriers diminishes the effects of potential fluctuations by reducing the effective number and barrier heights of the inhomogeneous regions. It is caused by a filling of the band tails of the potential relief by thermally activated carriers and an increase of the average electron energy. This results in a decrease of the potential barrier heights. Subsequently the increase in temperature facilitates the recombination of the nonequilibrium carriers via deep levels.

V. DISCUSSION

To explain the role of In doping on carrier transport, the contradictory complex effect of this impurity in SI GaAs should be stressed. It was reported that In can cause additional energy levels in the band gap.[34,35] In Ref. 36 an assumption was made that isovalent impurities such as In, Sb, and P in concentrations higher than $10^{19}\ \mathrm{cm}^{-3}$ may form electrically active complex defects (probably undergo nonradiative transitions). These acceptors and donors may play an important role in compensation mechanisms. In Ref. 37 a Fermi level stabilization in the region of 0.5–0.67 eV was observed in SI GaAs with indium concentrations $10^{19} - 1.3 \times 10^{20}\ \mathrm{cm}^{-3}$. In contrast in Ref. 38 a thermal activation energy of 0.77 eV was reported in Si GaAs with an indium content $1 \times 10^{20}\ \mathrm{cm}^{-3}$. In Ref. 39 it was also reported that isovalent doping of GaAs up to concentrations of $\sim 10^{19} - 10^{20}\ \mathrm{cm}^{-3}$ does not result in an effective defect creation. Rather it causes the state change of the whole defect ensemble, due to the interaction between intrinsic defects with each other and with the doping atoms and increase of a crystal lattice period.[40] The related change in the concentration ratio of intrinsic and associated point and more complicated defects, were reported in Refs. 37 and 41. Apart from these, a general conclusion was drawn that isovalent impurities, such as In, Ga, and Sb, have been remarkably effective in reducing the dislocation density because of lattice hardening effects, especially if their concentrations are high enough

$>(10^{19}-10^{20}\,\mathrm{cm}^{-3})$.[35,40,42–45] Moreover, isovalent doping, together with a reduction of dislocation density, can reduce or increase the concentration of other point defects and their associations.[46] Point defects are bound if the concentration of the isovalent dopant is lower than the critical value, and their interaction energy is negative. Otherwise the generation of point defects can be intensified. In the case of In the critical concentration was evaluated to be of the order $(1.6-2)\times10^{20}\,\mathrm{cm}^{-3}$.[45,46] It can be seen that these values coincide with that of the effective suppression of dislocations. Additionally, the reduction of dislocation number facilitates the manifestation of existing point and microdefects. It is well known that usually dislocations getter the smaller defects,[47–52] particularly EL2 (see, e.g., Refs. 47–51) and In atoms in In-doped material,[52] and therefore the main matrix of the crystal around dislocations remains relatively defect free.[49,52] Therefore, the reduction of dislocation density results in a redistribution of these smaller and/or point defects,[53,54] thus causing an increase of their apparent concentration.[55,56] This conclusion is supported by other data.[57] It was reported in Ref. 57 that despite the significantly improved uniformity of the sheet carrier concentration in completely dislocation-free and striation-free In-doped GaAs, the Hall mobility values as well as their spatial fluctuations remained nearly unchanged as compared to conventional LEC dislocated samples. This effect should be reflected then on the transport and recombination phenomena. Thus, in Ref. 35 the EL2 deep level transient spectroscopy (DLTS) peak broadening was observed in vapor-phase-epitaxy GaAs:In at In concentrations as high as $5\times10^{20}\,\mathrm{cm}^{-3}$. The authors measured the change of compensation ratio by increasing In concentration, and found a drop of about four times at an In concentration of $5\times10^{20}\,\mathrm{cm}^{-3}$, which was explained by the drop of the EL2 concentration. Nevertheless, from our point of view it could be caused by the change of the concentration of other shallower levels as well. It is supported by the fact that the DLTS indicated no increase of the EL2 peak height.[35]

To explain the mobility kinetics presented in Figs. 1–3, we again refer to the proposed ''island'' model. The role of the large isolating ''islands'' can be played by clusters of smaller defects and their associations around dislocations as described above. Their nonhomogeneous distribution implies that a more defect-free and relatively homogeneous crystal matrix appears between them. Therefore, the inhomogeneities change a current flow trajectory and reduce the effective crystal volume. The evaluation according to the model[31,32] shows that in the dark they occupy at least the 0.18–0.43 part of the total crystal volume depending on the sample. It was shown in Ref. 12 that the maximum mobilities reached in the samples correlate with their defectiveness, thus confirming the previous issues. Thus, it might be proposed that at lower temperatures optically excited carriers screen the inhomogeneous regions, thus reducing their effective volume. This causes an increase of the mobility, though the inclusions remain inaccessible for electrons. With an increasing concentration and energy of thermally generated carriers, the effective screening and/or the recharge of the main potential barrier of such accumulation ''islands'' can occur, and they become transparent for the carriers. Subsequently their internal fine barrier structure, consisting of smaller defects, starts to act effectively in the scattering, reducing mobility. Qualitatively the same possibility was predicted also in the early works of L. R. Weisberg.[58] A somewhat similar effect could be involved in Refs. 59 and 60, where the drop of equilibrium Hall mobility from about 7000 down to 1000 $\mathrm{cm}^2/(\mathrm{V\,s})$ was observed in a range of equilibrium carrier concentration $10^9-10^{11}\,\mathrm{cm}^{-3}$ in n-type GaAs. It was explained by the localization of carriers in the conductive channels interrupted by the smaller inhomogeneities, which appear because of the specific compensation conditions in the samples when the Fermi level is located between the EL3 and EL2 levels.

In our samples, ''steplike'' mobility changes were observed, which included the mobility decrease as well as increase in different time intervals at higher temperatures as Figs. 1(b) and 2(c) demonstrate. These peaks were demonstrated to be caused by the charge-state change of the deep levels,[13] the recharge of which is reflected on the scattering as well. This is supported by the fact that such temporary changes take place only at the highest excitations, and not at the lowest ones. Actually a significant change of the scattering center concentration N or their scattering cross section S should occur to influence mobility notably. Indeed, when evaluating the change of their product $\Delta(SN)$, according to Ref. 12, we obtained values ranging from 10^5 to $10^6\,\mathrm{cm}^{-1}$. Such great values cannot be obtained for single point defects by taking into account the real values of scattering cross sections and concentrations of point defects in GaAs.[12,13] This implies that indeed their associations or complexes play a role, and therefore a relatively great excitation is necessary to change their charge state. Subsequently the change $\Delta(SN)$ can be treated only as an effective value, which represents the scattering by complex scatterers. Thus it may be supposed that due to the laser pulse, donors become exhausted from electrons, which screen potential barriers, thus causing the mobility drop as in Fig. 2(b). Later nonequilibrium electrons are trapped by the ionized level, making it neutral and diminishing its scattering cross section. When the recharge is finished, the role of inhomogeneities again becomes major. This is supported by the fact that curves 3 in Figs. 1(b) and 2(c), measured at higher temperatures by using a relatively low excitation intensity which was not high enough to change the level filling significantly, does not demonstrate steep mobility changes in the intermediate time intervals. On the other hand, it is noteworthy that such mobility ''steps'' were observed at a higher temperature in sample 2, but not in sample 3 with the highest In doping. We suppose that this could be explained by the change of the character of inhomogeneities with changing doping conditions. Indeed, if inhomogeneities appear around dislocations, the measured values of $\Delta(SN)$ under light excitation may be great. On the other hand, the dislocation density in In-doped crystals is usually reduced, and therefore smaller defects become distributed more homogeneously. Thus it may cause the fact that in sample 3 only smaller potential fluctuations appear, that may be simply screened by relatively low concentrations of generated carriers. This results in an increase of mobility after laser excitation even at higher temperatures because of the smoothing of potential relief.

VI. SUMMARY

We investigated the effect of In doping up to a concentration $\geqslant2\times10^{20}\,\mathrm{cm}^{-3}$ on transient transport phenomena in

semi-insulating LEC-grown n-type GaAs. The changes in time after a strong laser excitation of the nonequilibrium photo-Hall-effect e.m.f. were analyzed at different temperatures up to 420 K. We did not find additional energy levels caused by indium. Nevertheless In doping causes significant changes in the behavior of nonequilibrium carrier mobility in the temperature range of 300–420 K that were not observed in other undoped crystals or in crystals doped with other dopants. The observed peculiarities could not be explained only by a reduction of the dislocation density. We propose that, apart from this, a rearrangement of the microscopic inhomogeneities takes place, which causes a change of the potential barrier structure of the band gap. This issue is also supported by the high values of the photomagnetoelectric effect e.m.f., that clearly correlate with the In content in the samples. We demonstrated that lattice defects are still present in the crystal volume of the doped samples, but they become distributed more homogeneously. Therefore, they appear more probably as small (short-range) inhomogeneities in contrast to the large defect accumulations around dislocations in weakly doped crystals. This effect becomes pronounced if the In concentration exceeds $(6-9)\times10^{19}\,\mathrm{cm}^{-3}$. This leads to the diminished role of the percolation phenomena. The mean recombination barrier height was evaluated to range from $\geqslant$270 meV in undoped crystals to about 120 meV in highly In-doped samples.

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