Ultrafast high-intensity nonlinear absorption dynamics in low-temperature grown gallium arsenide

U. Siegner,[a] R. Fluck, G. Zhang, and U. Keller
Ultrafast Laser Physics, Institute of Quantum Electronics, Swiss Federal Institute of Technology, ETH Hönggerberg-HPT, CH-8093 Zürich, Switzerland

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We study carrier dynamics in GaAs thin films grown by molecular beam epitaxy at 250, 300, and 350 °C by differential transmission experiments at various carrier excitation densities. The differential transmission shows that carrier trapping in point defects is much faster than the recombination of the trapped carriers. As a consequence, the defect states can be saturated at high carrier densities. If the growth temperature is decreased, the initial trapping becomes faster while the subsequent recombination of the trapped carriers becomes slower. We show that this is due to the growth temperature dependent defect densities. © *1996 American Institute of Physics.* [S0003-6951(96)03543-7]

Low-temperature grown (LT) III–V semiconductors have found various applications in optoelectronics and laser science[1–3] due to the short carrier trapping time in these materials. The fast carrier trapping in LT semiconductors is due to the incorporation of excess group-V atoms during LT growth. The excess atoms form point defects,[4] which act as trap states.[5] A short carrier trapping time is essential for fast photoconductive switches with picosecond and subpicosecond response times.[2,5] In laser science, the carrier trapping time in LT semiconductors determines the recovery time of fast semiconductor saturable absorbers, which are used to generate picosecond and femtosecond pulses with solid-state lasers.[3] While the response time of a device after a single optical excitation depends on the time scale of the initial carrier trapping, the maximum repetition rate, at which photoconductive switches or saturable absorbers can be used, is limited by the time in which the LT semiconductor relaxes to the ground state. This time is given by the recombination time of the optically excited electron–hole pairs.

In this letter, we study the growth temperature dependence of carrier trapping and carrier recombination in LT GaAs thin films by differential transmission spectroscopy. In particular, we focus on the nonlinear absorption changes at intermediate and high carrier densities. We find that, at high densities, the point defects can be saturated, leading to a sign change of the differential transmission. Our high-density data also shows that, at lower growth temperatures, the recombination of trapped carriers becomes slower whereas carrier trapping becomes faster. Therefore, careful optimization is required to simultaneously achieve fast response times and high maximum repetition rates in optoelectronic devices.

We study 1 μm GaAs thin films grown by molecular beam epitaxy on GaAs substrates at growth temperatures of 250, 300, and 350 °C, with no subsequent annealing. The As/Ga flux ratio is 30. X-ray diffraction measurements show that all samples are crystalline, as expected. To prepare the samples for transmission experiments, we etch off the substrates and deposit antireflection coatings. Differential transmission experiments are carried out at room temperature with 100-fs pulses from a mode-locked Ti:sapphire laser. In these experiments, we excite and probe above the band gap at 830 nm. The pump and probe pulses are cross polarized, with the probe intensity one order of magnitude lower than the pump intensity.

A schematic level diagram for LT GaAs is shown in the inset of Fig. 1. In LT GaAs, the excess arsenic atoms form As antisites (As_{Ga}) with energies close to the center of the band gap.[1] The As_{Ga} point defect is a double donor, which is generally found in the neutral charge state As_{Ga}^0 and in the single positive charge state As_{Ga}^+. Typical concentrations are $[As_{Ga}^0] \approx 10^{20}\ cm^{-3}$ and $[As_{Ga}^+] \approx 10^{19}\ cm^{-3}$ at the lowest growth temperatures at which crystalline LT GaAs can be grown (≈200 °C). These concentrations decrease with increasing growth temperature.[6,7] The positively charged As_{Ga}^+ defects act as electron traps since the properties of As_{Ga} defects in LT GaAs and EL2 defects in semi-insulating GaAs are very similar[6,8] and since EL2 defects are known as electron traps.[9] The positive As_{Ga}^+ are compensated by native acceptors. Recently, it has been shown that Ga vacancies

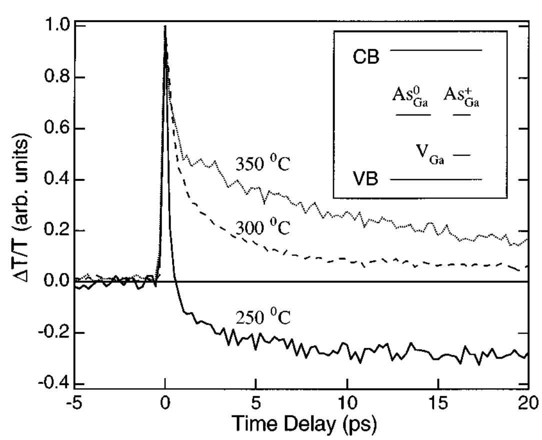

FIG. 1. Room temperature differential transmission signals from LT GaAs grown at 250 °C (solid line), 300 °C (dashed line), and 350 °C (dotted line) at a carrier density $N \approx 5 \times 10^{18}\ cm^{-3}$. All curves have been individually normalized. Inset: Schematic level diagram showing the valence (VB) and the conduction band (CB) as well as the defect states of LT GaAs.

[a]Electronic mail: siegner@iqe.phys.ethz.ch

(V_{Ga}) are the native acceptors in LT GaAs.[10,11] The V_{Ga} states are located in the lower half of the band gap with a concentration equal to the As_{Ga}^{+} concentration.[1]

At the excitation wavelength, transitions between the valence band (VB) and the conduction band (CB) as well as As_{Ga}^{0}–CB transitions form the main contributions to the total population of excited carriers.[12] We can neglect the VB–As_{Ga}^{+} transition since the As_{Ga}^{+} concentration is less than one tenth of the As_{Ga}^{0} concentration.[7] Moreover, the absorption cross section of the VB–As_{Ga}^{+} transition for excitation close to the band gap is about half an order of magnitude lower than the one for the As_{Ga}^{0}–CB transition.[13] Therefore, there are too few VB–As_{Ga}^{+} transitions to significantly reduce the concentration of As_{Ga}^{+} electron traps. We can also neglect optical transitions involving V_{Ga} since infrared absorption spectra from LT GaAs can be well explained without considering these transitions.[6–8] As a consequence, the concentration of the V_{Ga} defects after an optical excitation is essentially given by the equilibrium concentration. If the V_{Ga} defects act as trap states, the concentration of available traps is essentially given by their equilibrium concentration.

Figure 1 shows differential transmission data for an intermediate carrier density of $N \approx 5 \times 10^{18}$ cm^{-3}. After intraband carrier thermalization, the bleaching of the absorption ($\Delta T/T > 0$) in the 350 and 300 °C samples shows an initial decay with time constants of 13 and 4 ps, respectively, due to trapping of carriers in point defects. We will later discuss that the slowly decaying contributions to the bleaching signals reflect the recombination of trapped carriers. As discussed previously, free electrons are trapped by the positively charged As_{Ga}^{+}. Of course, the density of the As_{Ga}^{+} traps created by the optical As_{Ga}^{0}–CB transitions is equal to the density of free electrons excited from the As_{Ga}^{0}. Therefore, in order to avoid saturation of the electron traps, the *equilibrium* concentration of As_{Ga}^{+} has to be larger than the density of electrons excited from the VB.

The differential transmission signal from the 250 °C sample shows a different feature compared to the signals from the 350 and the 300 °C samples. In the 250 °C sample, fast carrier trapping results in a change from the initial absorption bleaching to induced absorption ($\Delta T/T < 0$) within 0.6 ps. Similar behavior has been previously observed in LT GaAs, InP, and InGaP.[14–16] Induced absorption due to VB–CB transitions can result from band-gap renormalization at probe energies around the band gap.[17] However, in our case the probe energy is above the band gap and the induced absorption has to be related to defect-to-band transitions. The reason for the induced absorption signal in LT GaAs is an excess population of trapped carriers, which can build up in the defect states after the fast trapping. The induced absorption is then the result of the reexcitation of trapped carriers. Consequently, the decay of this signal reflects the recombination of the carriers trapped in point defects. Of course, induced absorption is only observed in samples with a high defect concentration.

In Fig. 2 we have plotted the induced absorption signal on a longer time scale. The induced absorption in the 250 °C sample decays with a time constant of 265 ps, i.e., recombination of trapped carriers occurs on a much longer time scale than the trapping.[18] In fact, the observation of induced absorption is a direct consequence of the combination of fast trapping and slow recombination of trapped carriers. We also note that radiative band-to-band recombination takes place on a nanosecond time scale in bulk semiconductors. It can, thus, be neglected compared to the faster recombination via defects in our LT GaAs samples.

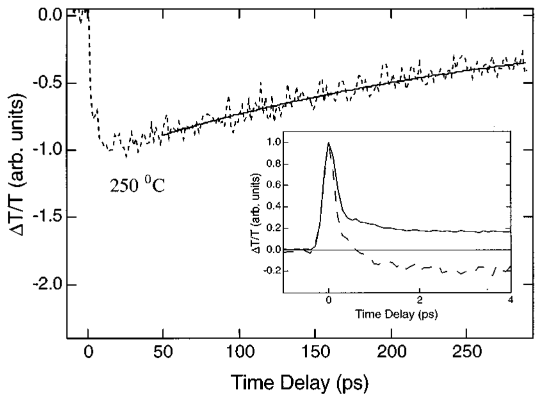

FIG. 2. Room temperature differential transmission signal from the 250 °C sample at $N \approx 5 \times 10^{18}$ cm^{-3} (dashed line) and exponential fit with a time constant of 265 ps (solid line). Inset: Differential transmission from the 250 °C sample at $N \approx 5 \times 10^{18}$ cm^{-3} (dashed) and at $N \approx 5 \times 10^{19}$ cm^{-3} (solid). All curves have been individually normalized.

The inset in Fig. 2 demonstrates that the induced absorption in the 250 °C sample changes to absorption bleaching if the carrier density is increased from $N \approx 5 \times 10^{18}$ cm^{-3} to $N \approx 5 \times 10^{19}$ cm^{-3}. We conclude that the point defects are saturated at the high carrier density. The carriers remaining in the bands lead to strong bleaching of the VB–CB transitions, which masks the induced absorption from the defect-to-band transitions. The slow recombination of trapped carriers acts as a bottleneck for the depopulation of the bands via the point defects if the defects are saturated. As a result, the decay of the bleaching at long time delays reflects the slow recombination of trapped carriers while the initial decay of the bleaching is due to intraband carrier relaxation and carrier trapping. The differential transmission signal from the 300 °C sample in Fig. 1 shows a slowly decaying contribution to the bleaching already at a carrier density $N \approx 5 \times 10^{18}$ cm^{-3}. This part of the signal is due to the saturation of the defects and its decay reflects the recombination of trapped carriers. Thus, saturation of the defects occurs at a lower carrier density in the 300 °C sample than in the 250 °C sample, as expected from the lower defect concentration in the 300 °C sample.

The differential transmission signals from the three samples at the high carrier density of $N \approx 5 \times 10^{19}$ cm^{-3} are plotted in Fig. 3. Surprisingly, the high-intensity data shows that, in the long-time limit, the bleaching decays more slowly in the 250 °C sample than in the 300 and 350 °C samples. It is clear from the data that the recombination of trapped carriers becomes faster at higher growth temperatures. Thus, the recombination time of trapped carriers shows the opposite growth temperature dependence as the carrier trapping time. As expected, trappping becomes faster with decreasing growth temperature[5] due to the increasing defect density.

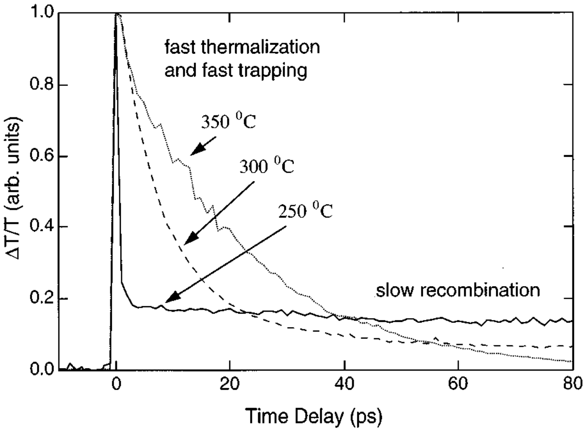

FIG. 3. Room temperature differential transmission signals from LT GaAs grown at 250 °C (solid line), 300 °C (dashed line), and 350 °C (dotted line) at a carrier density $N \approx 5 \times 10^{19}$ cm^{-3}. All curves have been individually normalized.

With respect to the growth temperature dependent recombination time, we will now argue that not only electrons but also holes are trapped in LT GaAs. Without hole trapping, recombination would take place only between trapped electrons and free holes. The density of free holes would be independent of the defect concentrations and of the growth temperature for a fixed excitation intensity. Increasing the growth temperature decreases the concentration of As_{Ga}^{+} electron traps and the density of trapped electrons. Due to the lower density of trapped electrons, the recombination rate would be lower in samples grown at higher growth temperatures. Experimentally, we observe the opposite growth temperature dependence of the recombination rate. Consequently, we conclude that holes are trapped in LT GaAs.

Moreover, we note that the spatial overlap between the extended wave function of a free carrier and the localized wave function of a trapped carrier is larger than the overlap between the localized wave functions of two carriers trapped in different, spatially separated, defects. Therefore, we expect the recombination rate between a free carrier and a trapped carrier to be higher than the recombination rate between two carriers trapped in different defects. The overall recombination rate can increase if the density of free carriers increases and the density of the spatially separated trapped electrons and holes decreases. Experimentally, we observe such an increase of the recombination rate for higher growth temperatures and lower defect concentrations when the density of free carriers is increased compared to the density of trapped carriers.[19] This indicates that the above mechanism is effective. Therefore, the growth temperature dependence of the recombination rate suggests that electrons and holes are trapped in *different* point defects. Trapping of electrons and holes in different, spatially separated, defects is also consistent with the relatively large recombination time of several 100 ps. Since electrons are trapped by As_{Ga}^{+}, the most likely candidate for the hole trap is the V_{Ga} defect.

In conclusion, we have performed differential transmission experiments on LT GaAs at various growth temperatures and excitation densities. Our data demonstrates that carrier trapping becomes faster while carrier recombination becomes slower as the growth temperature is decreased. Both effects can be accounted for by the growth temperature dependence of the defect concentration. Here, both electron and hole trapping have been taken into account. For applications where both a subpicosecond trapping time and a picosecond recombination time are required, careful optimization of the growth temperature is necessary.

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[1] G. D. Witt, Mater. Sci. Eng. B **22**, 9 (1993).
[2] J. F. Whitaker, Mater. Sci. Eng. B **22**, 61 (1993).
[3] L. R. Brovelli, U. Keller, and T. H. Chiu, J. Opt. Soc. Am. B **12**, 311 (1995).
[4] M. Kaminska *et al.*, Appl. Phys. Lett. **54**, 1881 (1989).
[5] S. Gupta, J. F. Whitaker, and G. A. Mourou, IEEE J. Quantum Electron. **28**, 2464 (1992).
[6] D. C. Look, D. C. Walters, M. Mier, C. E. Stutz, and S. K. Brierley, Appl. Phys. Lett. **60**, 2900 (1992).
[7] X. Liu, A. Prasad, W. M. Chen, A. Kurpiewski, A. Stoschek, Z. Liliental-Weber, and E. R. Weber, Appl. Phys. Lett. **65**, 3002 (1994).
[8] M. O. Manasreh, D. C. Look, K. R. Evans, and C. E. Stutz, Phys. Rev. B **41**, 10 272 (1990).
[9] M. Kaminska and E. R. Weber, in *Imperfections in III/V Materials*, edited by E. R. Weber (Academic, Boston, 1993), Vol. 38, p. 59.
[10] X. Liu, A. Prasad, J. Nishio, E. R. Weber, Z. Liliental-Weber, and W. Walukiewicz, Appl. Phys. Lett. **67**, 279 (1995).
[11] P. Hautojärvi, J. Mäkinen, S. Palko, K. Saarinen, C. Corbel, and L. Liszkay, Mater. Sci. Eng. B **22**, 16 (1993).
[12] S. U. Dankowsky *et al.*, Appl. Phys. Lett. **68**, 37 (1996).
[13] P. Silverberg, P. Omling, and L. Samuelson, Appl. Phys. Lett. **52**, 1689 (1988).
[14] E. S. Harmon, M. R. Melloch, J. M. Woodall, D. D. Nolte, N. Otsuka, and C. L. Chang, Appl. Phys. Lett. **63**, 2248 (1993).
[15] Y. Kostoulas, L. J. Waxer, I. A. Walmsley, G. W. Wicks, and P. M. Fauchet, Appl. Phys. Lett. **66**, 1821 (1995).
[16] Y. Kostoulas, K. B. Ucer, G. W. Wicks, and P. M. Fauchet, Appl. Phys. Lett. **67**, 3756 (1995).
[17] T. Gong, W. L. Nighan, and P. M. Fauchet, Appl. Phys. Lett. **57**, 2713 (1990).
[18] T. Dekorsy, X. Q. Zhou, K. Ploog, and H. Kurz, Mater. Sci. Eng. B **22**, 68 (1993).
[19] Note that the curves in Fig. 3 have been individually normalized. The absolute signal strength decreases with decreasing growth temperature.