ELSEVIER

Physica B 273–274 (1999) 733–736

PHYSICA B

www.elsevier.com/locate/physb

Femtosecond nonlinear optics of low-temperature grown semiconductors

U. Siegner[a], M. Haiml[a,*], F. Morier-Genoud[a], R.C. Lutz[b], P. Specht[b], E.R. Weber[b], U. Keller[a]

[a]*Institute of Quantum Electronics, Swiss Federal Institute of Technology (ETH), ETH Honggerberg HPT, CH-8093 Zurich, Switzerland*
[b]*Materials Science and Mineral Engineering Department, University of California at Berkeley, Berkeley, CA 94720, USA*

Abstract

We investigate the nonlinear optical properties of low-temperature-grown (LT) GaAs. It is shown that the strength of the absorptive nonlinearity is weak in as-grown undoped LT-GaAs with a fast recovery time of the nonlinear absorption. The reason for this behavior is revealed by a quantitative study of the nonlinear optical properties of the most important defect transition from the neutral As antisite to the conduction band. Based on this analysis, we demonstrate two methods for the improvement of the ultrafast nonlinearity of LT-grown semiconductors: post-growth annealing or Be doping of LT-GaAs yields a material with a strong ultrafast nonlinear optical response.

Keywords: Low-temperature GaAs; Optical nonlinearity; Carrier dynamics

Low-temperature (LT) MBE-grown semiconductors will become increasingly important for future femtosecond all-optical switching applications due to the ultrafast recovery time of their optical nonlinearity after above-band-gap excitation. Already now, they are extensively used in optical communication [1] and laser physics [2]. Besides a fast recovery time, these applications require high nonlinear absorption modulation and small absorption losses at high pulse fluences (nonsaturable absorption losses). The ultrafast recovery time of the nonlinear absorption results from trapping of optically excited carriers into defect states introduced by the LT growth [3]. Carrier trapping into defects has been intensively investigated in recent years, in particular for LT-GaAs, which can serve as a model system [4,5]. However, the introduction of defect states may also give rise to new absorption channels, which can affect the strength of the nonlinear optical response [6–8].

In this paper, we present a comprehensive quantitative study of the nonsaturable absorption, the absorption modulation, and its recovery time in different modifications of LT-GaAs. It is shown that as-grown undoped LT-GaAs with a sub-picosecond recovery time suffers from small absorption modulation and large nonsaturable absorption. Therefore, this material is not well suited for ultrafast all-optical switching applications. This experimental result is traced back to the optical properties of the dominating defect transition from the neutral As antisites, As^0_{Ga}, to the conduction band (CB). Combining optical data with measurements of defect densities, we have quantitatively determined the optical absorption cross section and the saturation parameter of this transition for above-band-gap excitation. This data shows that, with reasonable pulse fluences, the As^0_{Ga}–CB transition is difficult to saturate and contributes a major fraction to the nonsaturable absorption losses. Therefore, as-grown undoped LT-GaAs with femtosecond recovery times and high As^0_{Ga} density suffers from high nonsaturable absorption losses. We demonstrate two methods to obtain an optimized material which combines fast recovery times with high modulation and small nonsaturable

* Corresponding author. Fax: + 41-1-633-1059.
E-mail address: haiml@iqe.phys.ethz.ch (M. Haiml)

0921-4526/99/$ - see front matter
PII: S0921-4526(99)00625-0

losses: (i) annealing of undoped LT-GaAs and (ii) beryllium doping of as-grown LT-GaAs. Both methods reduce the density of neutral As^0_{Ga} and the corresponding As^0_{Ga}–CB absorption, but maintain an ultrafast response. Our analysis shows that the Be concentration should be chosen to compensate the material in order to optimize the optical nonlinearity of LT-GaAs : Be.

We have studied 500 nm thick LT-GaAs layers, which were grown by MBE at an As_4/Ga-flux ratio of 4.5 and various growth temperatures ($T_g = 220$–580°C). The undoped layers are either as-grown or have been post-growth annealed at 600°C under arsenic overpressure for 75 min. Some of the as-grown layers are doped with Be at various concentrations. All layers have been grown on $Al_{0.15}Ga_{0.85}As$/AlAs Bragg mirrors and n+GaAs substrates. We have verified that the structural properties of LT-GaAs layers from our MBE system are independent of the substrate type [6]. The concentration of neutral arsenic antisites [As^0_{Ga}] was measured by near-infrared absorption (NIRA) [9] in the epilayers grown on n+ substrates. The Bragg mirror samples have been antireflection (AR) coated on the front surface. These samples have been used for the optical studies in a reflection geometry.

Due to the good quality of the AR coating and the Bragg mirrors, the reflectivity R of the whole structure can be approximated by $R = \exp(-2\alpha d)$ [7] where α is the absorption coefficient, d the physical thickness of the LT-GaAs layer, and $2d$ the effective thickness in the reflection geometry. The linear absorption and the absorptive nonlinearity have been determined from measurements of the reflectivity R versus the pulse energy fluence F in a single-beam experiment [6]. The experimental data are extrapolated to the linear regime and to high fluences using the travelling wave rate equation model for a two-level absorber [10,11]. With respect to the concept of this model, we recall that the reflectivity of an ideal lossless absorber saturates at $R_{ns} = 1$ at high fluences. Here, $R_{ns} = 1$ corresponds to an absorption $\alpha_{ns} = 0$. The model assumes that the reflectivity of a real absorber saturates at $R_{ns} < 1$, corresponding to $\alpha_{ns} > 0$, and explicitly introduces $R_{ns} < 1$ as an additional parameter. R_{ns} (or α_{ns}) accounts for the differences between a two-level absorber and a real semiconductor. Different processes can contribute to α_{ns}: (i) absorption, which only decreases at fluences much higher than the fluences which fully saturate the two-level absorber, and (ii) induced absorption which only occurs in the nonlinear regime, e.g., absorption out of excited states. Very good fits to the experimental data are obtained with this model, see Ref. [6] for an example. From the fits, one determines the linear and nonsaturable reflectivities $R_{lin} = \exp(-2\alpha_{lin}d)$ and $R_{ns} = \exp(-2\alpha_{ns}d)$ (or the linear and nonsaturable absorption α_{lin} and α_{ns}), and the saturation fluence of the two-level absorber. The saturation fluence is a measure of the pulse fluence at which significant changes of the absorption occur. The absorption modulation is given by $\Delta\alpha = \alpha_{lin} - \alpha_{ns}$. With respect to applications, we note that an increase of α_{ns} increases the nonsaturable losses in reflectivity $\Delta R_{ns} = 1 - R_{ns}$ and decreases the reflectivity modulation $\Delta R = R_{ns} - R_{lin}$ of a saturable absorber device. Moreover, ΔR decreases with decreasing $\Delta\alpha$.

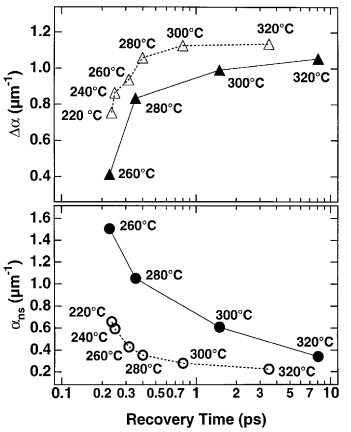

Fig. 1. Absorption modulation $\Delta\alpha$ (△, ▲) and nonsaturable absorption α_{ns} (○, ●) versus recovery times for undoped as-grown (filled symbols) and undoped annealed (open symbols) LT-GaAs. Labels: Growth temperatures. The recovery times have been determined at a carrier density of about 5×10^{18} cm^{-3}.

The time response of the absorption modulation has been determined by pump–probe experiments. We define the 1/e decay time of a pump–probe trace as the recovery time. All optical measurements have been performed at room temperature with 150 fs pulses for excitation above the band gap at 830 nm.

Fig. 1 shows the absorption modulation and the nonsaturable absorption versus the recovery time for undoped as-grown and annealed LT-GaAs. With decreasing growth temperature, the recovery time decreases in as-grown LT-GaAs [4] due to the increasing density of ionized As^+_{Ga} [9], which act as electron traps [5,12]. However, sub-picosecond recovery times in undoped as-grown LT-GaAs are only obtained at the expense of a small absorption modulation $\Delta\alpha$ and large nonsaturable absorption α_{ns}. For a given recovery time, annealed LT-GaAs has a much larger $\Delta\alpha$ and a much smaller α_{ns}. This is because annealing results only in a slight increase of the recovery time for $T_g \leqslant 280^\circ$C and even yields a faster response at higher growth temperatures, but largely increases $\Delta\alpha$ and decreases α_{ns}. The latter point will be discussed in more detail below. Since annealing reduces the density of As^+_{Ga} electron traps [9], we conclude that a fast recovery time is maintained by the As precipitates [13] formed upon annealing.

Fig. 2 provides insight into the microscopic origin of the weak optical nonlinearity in undoped as-grown

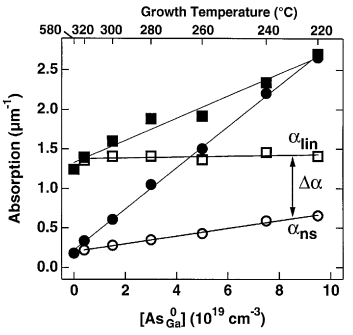

Fig. 2. Linear absorption α_{lin} (□, ■) and nonsaturable absorption α_{ns} (○, ●) for undoped as-grown LT-GaAs samples (filled symbols) and their annealed counterparts (open symbols) versus the neutral As antisite density in the as-grown LT-GaAs samples. The upper horizontal axis shows the growth temperature. The absorption modulation $\Delta\alpha = \alpha_{lin} - \alpha_{ns}$ is indicated by the arrow.

LT-GaAs with a fast recovery time. This figure shows α_{lin} and α_{ns} for the undoped as-grown LT-GaAs samples and their annealed counterparts versus the As^0_{Ga} density in the as-grown samples. It is found that the linear above-band-gap absorption strongly increases with increasing defect density in as-grown LT-GaAs, in agreement with Ref. [14]. We recall that, in undoped as-grown LT-GaAs, more than 90% of the As_{Ga} are neutral while the rest is ionized [9]. For below-band-gap energies, the As_{Ga}–CB transition has a much higher absorption cross section than the transition from the valence band (VB) to the ionized As^+_{Ga} [15] and the second optical ionization of As^+_{Ga} [16]. Consequently, we attribute the excess linear absorption in undoped as-grown GaAs to the As^0_{Ga}–CB transition. We refer to the As^0_{Ga}–CB absorption as to α_T, given by $\alpha_T = \alpha_{lin} - \alpha_{lin}(HT)$ ($\alpha_{lin}(HT)$ linear absorption in high-temperature grown undoped GaAs). Our quantitative data allows for the determination of the absorption cross section σ of this transition at 830 nm. One obtains $\sigma = 1.4 \times 10^{-16}$ cm^2 from $\alpha_T = \sigma[As^0_{Ga}]$ and the linear fit to the data in Fig. 2.

From σ, the saturation fluence $F_{sat} = \hbar\omega/\sigma$ ($\hbar\omega$ photon energy) [11] of the As^0_{Ga}–CB transition can be quantitatively determined: $F_{sat} = 1700$ μJ/cm^2. At this fluence, the absorption of the As^0_{Ga}–CB transition significantly decreases. In contrast, the saturation fluence of the interband transition in GaAs is typically below 50 μJ/cm^2. The comparison shows that α_T is hardly decreased by fluences which almost fully saturate the interband transition. Therefore, the As^0_{Ga}–CB absorption α_T fully contributes to the nonsaturable absorption α_{ns}.

Surprisingly, Fig. 2 shows that the absorption modulation $\Delta\alpha = \alpha_{lin} - \alpha_{ns}$ decreases with increasing As^0_{Ga} density. This decrease cannot be due to the nonsaturable trap absorption α_T since α_T equally contributes to both α_{lin} and α_{ns}. We conclude that there must be another mechanism which gives rise to additional nonsaturable absorption γ_{ns}. The mechanism responsible for the additional absorption γ_{ns} is not yet fully understood. A possible reason for γ_{ns} is free-carrier absorption due to carriers high in the CB. These carriers can be generated by the As^0_{Ga}–CB transition in as-grown undoped LT-GaAs.

The total nonsaturable absorption can be written as $\alpha_{ns} = \alpha_T + \gamma_{ns}$. A quantitative analysis of the data in Fig. 2 shows that γ_{ns} makes up about 40% of the total nonsaturable absorption α_{ns} in as-grown undoped LT GaAs. Thus the nonsaturable As^0_{Ga}–CB absorption α_T contributes the major fraction to α_{ns}. With respect to ultrafast all-optical switching applications, we note that the large nonsaturable As^0_{Ga}–CB absorption α_T in as-grown undoped LT-GaAs increases the nonsaturable losses in reflectivity ΔR_{ns} and limits the reflectivity modulation ΔR. Moreover, ΔR can be strongly reduced by γ_{ns} which contributes to the nonsaturable absorption and reduces the absorption modulation.

This analysis shows that LT-GaAs can be optimized for ultrafast all-optical switching applications if the density of neutral As^0_{Ga} is reduced while an ultrafast recovery time is maintained. This goal cannot be reached in as-grown undoped LT-GaAs since the incorporation of a large density of ionized As^+_{Ga} trap states results in the incorporation of even larger densities of neutral As^0_{Ga} [9] which deteriorate the optical nonlinearity.

Fig. 1 has shown that annealing of undoped LT-GaAs yields an optimized material with a strong optical nonlinearity and a fast recovery time due to the presence of As precipitates. In accordance with the guideline for optimization, annealing decreases the neutral As^0_{Ga} density [9] while the fast response is maintained by the precipitates. Due to the reduction of the neutral As^0_{Ga} density, the linear absorption of annealed undoped LT-GaAs in Fig. 2 increases only very slightly with the excess As content, in agreement with the surface plasmon model for precipitates [17]. The absorption α_T is almost totally removed by annealing which substantially decreases the nonsaturable absorption α_{ns}.

An alternative method for the optimization of LT-GaAs for ultrafast all-optical switching applications takes advantage of Be doping. Doping with Be acceptors reduces the neutral As^0_{Ga} density and increases the density of ionized As_{Ga} [18]. The latter insures ultrafast recovery times [6,18].

In order to examine the optical nonlinearity in LT-GaAs : Be, we have plotted the linear and the nonsaturable absorption versus Be doping concentration for as-grown LT-GaAs in Fig. 3. For a given growth temperature, the linear absorption α_{lin} decreases with the Be concentration. As long as α_{lin} is larger than the linear absorption of undoped high-temperature grown

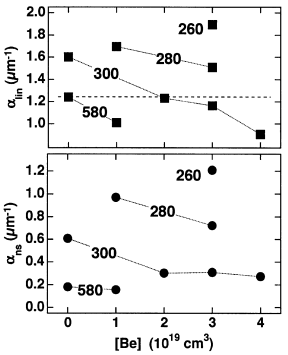

Fig. 3. Linear absorption α_{lin} and nonsaturable absorption α_{ns} versus Be concentration in as-grown LT-GaAs. The growth temperature in °C is indicated. The dashed line marks α_{lin} for undoped high-temperature grown GaAs.

GaAs α_{lin}(HT), this decrease is due to the ionization of the As_{Ga}. Consequently, also the nonsaturable absorption α_{ns} in LT-GaAs is seen to decrease for lower Be concentrations in Fig. 3. The reduced α_{ns} and the ultrafast recovery time [6,18] make LT-GaAs : Be a superior material for all-optical switching applications [6].

For higher Be concentrations, α_{lin} drops below α_{lin}(HT), seen for $T_g = 580°C$ and 300°C in Fig. 3. The reduction of α_{lin} below $\alpha_{lin}(HT) = \alpha_{lin}([As^0_{Ga}] = 0)$ cannot be due to the decrease of the neutral As^0_{Ga} density. We conclude that this reduction results from holes in the valence band, which decrease the VB–CB absorption close to the band edge. The material is p-conductive for higher Be concentrations and all As_{Ga} are ionized. This interpretation is supported by the fact that the nonsaturable absorption stays constant in the Be concentration range in which $\alpha_{lin} < \alpha_{lin}$(HT) where the As^0_{Ga} density cannot be further reduced.

This analysis shows that compensated LT-GaAs : Be has the optimum nonlinearity. In compensated LT-GaAs : Be, all As_{Ga} are ionized, which minimizes the nonsaturable absorption α_{ns} due to the As^0_{Ga}–CB transition. Moreover, avoiding p-conductivity maximizes the linear absorption α_{lin} and, in turn, the absorption modulation $\Delta\alpha = \alpha_{lin} - \alpha_{ns}$.

In summary, we have investigated the key parameters for ultrafast all-optical switching in LT semiconductors and demonstrated strategies for their optimization.

This work has been supported by the Swiss National Science Foundation and the AFOSR grant no. F49620-98-1-0135. We would like to thank M. Moser, CSEM, Zurich, for the growth of the Bragg mirrors.

References

[1] R. Takahashi, Y. Kawamura, H. Iwamura, Appl. Phys. Lett. 68 (1996) 153.
[2] U. Keller, K.J. Weingarten, F.X. Kärtner, D. Kopf, B. Braun, I.D. Jung, R. Fluck, C. Hönninger, N. Matuschek, J. Aus der Au, IEEE J. Select Topics Quantum Electron. 2 (1996) 435.
[3] G.L. Witt, Mater. Sci. Eng. B 22 (1993) 9.
[4] S. Gupta, M.Y. Frankel, J.A. Valdmanis, J.F. Whitaker, G.A. Mourou, F.W. Smith, A.R. Calawa, Appl. Phys. Lett. 59 (1991) 3276.
[5] U. Siegner, R. Fluck, G. Zhang, U. Keller, Appl. Phys. Lett. 69 (1996) 2566.
[6] M. Haiml, U. Siegner, F. Morier-Genoud, U. Keller, M. Luysberg, P. Specht, E.R. Weber, Appl. Phys. Lett. 74 (1999) 1269.
[7] M. Haiml, U. Siegner, F. Morier-Genoud, U. Keller, M. Luysberg, R.C. Lutz, P. Specht, E.R. Weber, Appl. Phys. Lett. 74 (1999) 3134.
[8] H.S. Loka, S.D. Benjamin, P.W.E. Smith, IEEE J. Quantum Electron. 34 (1998) 1426.
[9] X. Liu, A. Prasad, W.M. Chen, A. Kurpiewski, A. Stoschek, Z. Liliental-Weber, E.R. Weber, Appl. Phys. Lett. 65 (1994) 3002.
[10] G.P. Agrawal, N.A. Olsson, IEEE J. Quantum Electron. 25 (1989) 2297.
[11] L.R. Brovelli, U. Keller, T.H. Chiu, J. Opt. Soc. Am. B 12 (1995) 311.
[12] Z. Liliental-Weber, J. Ager, D. Look, X.W. Lin, X. Liu, J. Nishio, K. Nichols, W. Schaff, W. Swider, K. Wang, J. Wasburn, E.R. Weber, J. Whitaker, in: M. Godlewski (Ed.), Proceedings of the Eight Conference on Semi-Insulating III–V Materials, World Scientific, 1994, p. 305.
[13] M.R. Melloch, N. Otsuka, J.M. Woodall, A.C. Warren, J.L. Freeouf, Appl. Phys. Lett. 57 (1990) 1531.
[14] S.U. Dankowski, D. Streb, M. Ruff, P. Kiesel, M. Kneissl, B. Knüpfer, G.H. Döhler, U.D. Keil, C.B. Sørenson, A.K. Verma, Appl. Phys. Lett. 68 (1996) 37.
[15] P. Silverberg, P. Omling, L. Samuelson, Appl. Phys. Lett. 52 (1988) 1689.
[16] P. Omling, P. Silverberg, L. Samuelson, Phys. Rev. B 38 (1988) 3606.
[17] D.D. Nolte, J. Appl. Phys. 76 (1994) 3740.
[18] P. Specht, S. Jeong, H. Sohn, M. Luysberg, A. Prasad, J. Gebauer, R. Krause-Rehberg, E.R. Weber, Mater. Sci. Forum 258–263 (1997) 951.