Carrier lifetime versus anneal in low temperature growth GaAs

E. S. Harmon, M. R. Melloch, and J. M. Woodall School of Electrical Engineering, Purdue University, West Lafayette, Indiana 47907

D. D. Nolte Department of Physics, Purdue University, West Lafayette, Indiana 47907

N. Otsuka and C. L. Chang School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907

(Received 2 June 1993; accepted for publication 9 August 1993)

The photoexcited carrier lifetimes in *ex situ*-annealed low temperature growth GaAs are measured with a femtosecond transient absorption experiment. The study encompassed two low temperature growth GaAs films with approximately 0.3% and 0.9% excess arsenic incorporated during growth. The observed lifetimes are found to be a function of the spacing of arsenic precipitates formed during the 30 s anneals to temperatures between 650 and 1000 °C. The carrier lifetime for unannealed films was found to be less than ~ 200 fs. The carrier lifetimes increased from ~ 2 to ~ 10 ps as the average precipitate spacing was increased from ~ 400 to ~ 900 Å. These results are in sharp contrast to recent reports of subpicosecond lifetimes in similar GaAs annealed at 600 °C.

Low growth temperature GaAs (LT:GaAs) has interesting electrical, optical, and structural properties due to the incorporation of up to 1.5% excess arsenic during growth.¹⁻⁷ Annealed LT:GaAs has been determined to be a near-ideal material for use as a photoconductive switch.^{3,8} As-grown LT:GaAs is too conductive to be used as a photoconductive switch.^{3,9} However, after annealing to temperatures of 600 °C and higher, the GaAs becomes highly insulating and precipitates of the excess arsenic are observed.^{6,7} Annealed LT:GaAs has the properties of high resistivity, high carrier mobility, and low carrier lifetime, which are all important for high speed photoconductive switches. Here, we report results of femtosecond timeresolved differential transmission spectroscopy on two LT:GaAs films, one incorporating $\sim 0.9\%$ and the other incorporating $\sim 0.3\%$ excess arsenic. These films were annealed to temperatures between 650 and 1000 °C for 30 s. From the decay of the differential transmission we extract carrier lifetimes that are more than an order of magnitude longer than the lifetimes of unannealed LT:GaAs, and, for higher temperature anneals, longer lifetimes are observed. These results are in sharp contrast to recent reports^{3,10} of no significant difference between carrier lifetimes of annealed and unannealed LT:GaAs. We attribute the lack of difference in carrier lifetimes to the low temperature of the anneal used and the consequently smaller precipitate spacing, which results in subpicosecond lifetimes for the annealed as well as unannealed LT:GaAs.

The two LT:GaAs films used in this study were grown in a Varian Gen II molecular beam epitaxy (MBE) chamber at growth temperatures of 250 and 320 °C (as measured by a thermocouple in the sample mount) in order to vary the amount of excess arsenic incorporated into the epilayers.¹¹ Elemental gallium was used for the gallium source and As₂ obtained with a thermal cracker was used for the arsenic source. The As₂/Ga beam equivalent pressure was approximately 20. The film structures consisted of a 0.5 μ m GaAs buffer layer grown at 600 °C, a 500 Å AIAs liftoff layer, a 318 Å GaAs transition region, and a 1 μ m LT:GaAs layer. All layers were grown nominally undoped and no post-growth anneal was performed in the MBE chamber. Samples of each film were annealed to temperatures between 650 and 1000 °C in a Heatpulse rapid thermal annealer for 30 s, which varies the size and density of the arsenic precipitates.^{12,13} The LT:GaAs layer was lifted off of the GaAs substrate^{14,15} and van der Waals bonded¹⁶ to glass slides for the differential transmission measurements.

Transmission electron microscopy (TEM) studies of these annealed films show arsenic precipitates whose average size and spacing depend upon the anneal temperature. A JEM 2000 EX electron microscope with an ultrahigh resolution objective lens pole piece was used to study (011) cross-sectional samples of the film prepared by Ar ion milling. The spherical aberration coefficient of the pole piece is 0.7 mm which yields a point resolution of 2.0 Å. The results of the TEM study showing the average precipitate size and average precipitate spacing versus anneal are presented in Fig. 1 and Tables I and II. The TEM study also indicates that these samples have $\sim 0.9\%$ excess arsenic for



FIG. 1. Precipitate diameter and precipitate spacing vs 30 s anneal for the two LT:GaAs films used in this study.

2248

TABLE I. Results of 30 s anneals for LT:GaAs layers grown at 250 °C incorporating $\sim 0.9\%$ excess arsenic as determined by TEM cross-sectional analysis and time-resolved differential transmission measurements.

Temperature °C	Spacing (Å)	Diameter (Å)	Lifetime (ps)
700	396	102	2.8
800	509	132	5.1
900	619	167	7.1
1000	769ª	189ª	10.3

^aValues obtained with linear extrapolation.

the sample grown at 250 °C, and $\sim 0.3\%$ excess arsenic for the sample grown at 320 °C.

The transient absorption saturation was measured using the typical pump-probe femtosecond time-resolved differential transmission spectroscopy arrangement.^{17,18} The laser pulses were obtained from a Coherent Mira 900f titanium:sapphire laser producing ~ 125 fs pulses tuned to 866 nm. The wavelength of 866 nm was chosen because it is approximately 10 meV above the band gap of normal GaAs. The pulses therefore probe the states near the conduction- and valence-band edges. The pump beam had an average power of 175 mW and was focused to an ~ 50 μm spot. The probe beam utilized an average power of 4–5 mW and was focused to an $\sim 20 \,\mu m$ spot. The probe beam was perpendicularly polarized to the pump beam in order to remove unwanted coherent effects. We estimate that the excess carrier density generated by the pump pulse is ~ 2 $\times 10^{18} \text{ cm}^{-3}$.

The differential transmission responses of the 0.9% LT:GaAs films annealed to temperatures between 700 and 1000 °C for 30 s are presented in Fig. 2. Also included in Fig. 2 is the response of the LT:GaAs layer with no anneal showing the extremely fast decay (90%-10% falltime < 200 fs) and the characteristic negative response of unannealed material that has not yet been explained.¹⁰ The differential transmission of an Al_{0.3}Ga_{0.7}As/GaAs/ Al_{0.3}Ga_{0.7}As double heterostructure layer grown at normal substrate temperatures with the 1.1 μ m GaAs region implanted with 1×10^{12} cm⁻² protons is also shown. The implant ensures that the "normal" GaAs layer has a short enough carrier lifetime for the layer to return to equilibrium between pump pulses. As expected, the normal GaAs layer exhibits a much longer lifetime than the LT:GaAs layers. The initial fast decay has been attributed to carrier cooling.¹⁸ The carrier lifetime for the annealed layers is estimated by fitting the decay portion of the differential transmission to an exponential. The decay portion of the differential transmission is defined as the portion of the decay that is 1.5 ps after the peak to the point where the decay reaches 10% of the total amplitude in order to ensure that the fit is dominated by carrier recombination rather than carrier cooling or system noise.

The final results of excess carrier lifetime versus precipitate spacing are presented in Fig. 3 and Tables I and II. These results indicate a clear increase of the carrier lifetime with increasing precipitate spacing. These results contrast

TABLE II. Results of 30 s anneals for LT:GaAs layers grown at 320 °C incorporating ${\sim}0.3\%$ excess arsenic as determined by TEM cross-sectional analysis and time-resolved differential transmission measurements.

Temperature (°C)	Spacing (Å)	Diameter (Å)	Lifetime (ps)
650	405 ^a	69 ^a	2.3
700	500ª	86 ^a	3.7
750	595	103	
800	690ª	120ª	6.5
900	880	154	10.0

^aValues obtained with linear interpolation or extrapolation.

with recent differential transmission and differential reflection measurements of similar LT:GaAs films. Gupta *et al.*^{3,10} found virtually no difference between LT:GaAs layers with no anneal and those with a 600 °C anneal for 10 min. The annealed LT:GaAs used in the study of Gupta¹⁰ had a precipitate spacing of <215 Å (density of 1×10^{17} – 1×10^{18} cm⁻³) and an excess arsenic incorporation during growth of ~1%. If we extrapolate from the lifetime measurements presented in this letter (dashed lines in Fig. 3), we see that a precipitate spacing of <215 Å leads to subpicosecond lifetimes, which is qualitatively consistent with the results presented by Gupta.

In conclusion, we have presented the results of differential transmission measurements on two LT:GaAs films that have $\sim 0.3\%$ and $\sim 0.9\%$ excess arsenic incorporated during growth. After *ex situ* anneals to temperatures between 650 and 1000 °C, a strong dependence between the excess carrier lifetime and precipitate spacing in these LT-:GaAs films is observed and the excess carrier lifetime is more than an order of magnitude longer than that for unannealed material. These results dramatically differ from the results of Gupta, which is directly attributable to the relatively weak anneals used in their study.



FIG. 2. Normalized differential transmission measurements of LT:GaAs layers showing the decay of the differential transmission vs anneal temperature. The normal GaAs film is a normal temperature growth $Al_{0.3}Ga_{0.7}As/GaAs/Al_{0.3}Ga_{0.7}As$ structure implanted with 1×10^{12} cm⁻² protons.



FIG. 3. Carrier lifetime vs precipitate spacing determined by exponential fitting of the differential transmission decay.

This work was partially supported by the Air Force Office of Scientific Research under grants No. F49620-93-1-031 and F49620-93-1-0388. D.D. Nolte acknowledges support by NSF PYI and the Alfred P. Sloan Foundation.

- ¹F. W. Smith, A. R. Calawa, C-L. Chen, M. J. Manfra, and L. J. Mahoney, IEEE Electron. Device Lett. 9, 77 (1988).
- ²M. Kaminska, E. R. Weber, Z. Liliental-Weber, R. Leon, and Z. U. Rek, J. Vac. Sci. Technol. B 7, 710 (1989).

- ³S. Gupta, M. Y. Frankel, J. A. Valdmanis, J. F. Whitaker, G. A. Mourou, F. W. Smith, and A. R. Calawa, Appl. Phys. Lett. **59**, 3276 (1991).
- ⁴A. C. Warren, J. H. Burroughes, J. M. Woodall, D. T. McInturff, R. T. Hodgson, and M. R. Melloch, IEEE Electron. Device Lett. **12**, 527 (1991).
- ⁵D. D. Nolte, M. R. Melloch, J. M. Woodall, and S. J. Ralph, Appl. Phys. Lett. 62, 1356 (1993).
- ⁶M. R. Melloch, N. Otsuka, J. M. Woodall, A. C. Warren, and J. L. Freeouf, Appl. Phys. Lett. **57**, 1531 (1990).
- ⁷A. C. Warren, J. M. Woodall, J. L. Freeouf, M. R. Melloch, and N. Otsuka, Appl. Phys. Lett. 57, 1331 (1990).
- ⁸A. C. Warren, N. Katzenellenbogen, D. Grischkowsky, J. M. Woodall, M. R. Melloch, and N. Otsuka, Appl. Phys. Lett. 58, 1512 (1991).
- ⁹D. C. Look, D. C. Walters, M. O. Manasreh, J. R. Sizelove, C. E. Stutz, and K. R. Evans, Phys. Rev. B **42**, 3578 (1990).
- ¹⁰S. Gupta, J. F. Whitaker, and G. A. Mourou, IEEE J. Quantum Electron 28, 2464 (1992).
- ¹¹K. Mahalingam, N. Otsuka, M. R. Melloch, J. M. Woodall, and A. C. Warren, J. Vac. Sci. Technol. B 9, 2328 (1991).
- ¹²M. R. Melloch, N. Otsuka, K. Mahalingam, A. C. Warren, J. M. Woodall, and P. D. Kirchner, Mater. Res. Soc. Symp. Proc., 241, 113 (1992).
- ¹³ M. R. Melloch, D. D. Nolte, N. Otsuka, C. L. Chang, and J. M. Woodall, J. Vac. Sci. Technol. B 11, 795 (1993).
- ¹⁴F. Stern and J. M. Woodall, J. Appl. Phys. 45, 3904 (1974).
- ¹⁵ E. Yablonovitch, T. Gmitter, J. P. Harbison, and R. Bhat, Appl. Phys. Lett. 51, 2222 (1987).
- ¹⁶ E. Yablonovitch, D. M. Hwang, T. J. Gmitter, L. T. Florez, and J. P. Harbison, Appl. Phys. Lett. 56, 2419 (1990).
- ¹⁷ F. E. Doany, D. Grischowsky, and C.-C. Chi, Appl. Phys. Lett. **50**, 460 (1987).
- ¹⁸J. Kuhl, E. O. Gobel, Th. Pfeiffer, and A. Jonietz, Appl. Phys. A 34, 105 (1984).