Enhanced electro-optic properties of low-temperature-growth GaAs and AlGaAs

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

M. R. Melloch
School of Electrical Engineering, Purdue University, West Lafayette, Indiana 47907

J. M. Woodall and S. J. Ralph
IBM, Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 13 July 1992; accepted for publication 21 January 1993)

The signal-bandwidth products of excitonic electroabsorption of low-temperature-growth (LTG) molecular beam epitaxial films of GaAs:As and $Al_{0.25}Ga_{0.75}As$:As are larger than in the related stoichiometric materials. The enhanced electro-optic properties of these composites may be caused by increased inhomogeneity of dc electric fields. The differential transmission in LTG $Al_{0.25}Ga_{0.75}As$:As annealed at 750 °C for 30 s is relatively broadband and approaches 60% for dc electric fields of only 1.5×10^4 V/cm.

Electro-optic modulators are used in many important applications including optical fiber communication, free-space interconnects, spatial light modulators, and optical computers. Room-temperature semiconductor modulators have relied on the enhancement of transition strengths and on the reduction of broadening of quantum-confined excitons in multiple-quantum-well (MQW) structures.[1,2] The self-electro-optic-effect device (SEED) is currently one of the leading electro-optic modulator devices.[3] The key to improving electro-optic properties has been to reduce the dimensionality of the excitons by band gap engineering. In this letter, we describe an alternative route to enhanced electro-optic properties in bulk materials based on nanometer-scale metallic precipitates distributed through the material. The material is low-temperature-growth (LTG) molecular beam epitaxy (MBE) GaAs and AlGaAs grown at relatively low temperatures (200 °C), resulting in approximately 1% of excess arsenic incorporated into the material.[4] During post-growth annealing, the excess arsenic precipitates into clusters.[5] The arsenic clusters deplete free carriers from the surrounding material. The multiple overlapping depletion regions fully deplete the material, rendering it high resistivity.[6] LTG GaAs is finding applications as buffer layers for electrical isolation of integrated circuits,[7–10] as materials in ultrafast switches,[11–13] and as material for long-wavelength detectors.[14] Recently, we have demonstrated that the material has unique electro-optic and photorefractive properties.[15,16]

We performed electro-optic measurements on four epitaxial layers grown by molecular beam epitaxy: (1) a 1.1 μm layer of GaAs grown as a reference sample under normal conditions at 600 °C; (2) a 1.0 μm layer of GaAs grown at a low substrate temperatures of 250 °C and annealed at 600 °C for 1 h in the chamber prior to unloading; (3) a 1.0 μm layer of GaAs grown at a low substrate temperature of 250 °C and rapidly annealed at 900 °C for 30 s after unloading; and (4) a 1.0 μm layer of $Al_{0.25}Ga_{0.75}As$ also grown at a low substrate temperature of 250 °C and annealed at 750 °C for 30 s. All layers were grown on a 50 nm layer of AlAs. The AlAs layer is used for an epitaxial lift-off technique that allows us to remove the epitaxial layer from the substrate.

After growth, the LTG wafers were annealed to allow the precipitates to form.[5] The 600 and 900 °C GaAs samples had excess As concentrations of approximately 1% and 0.3%, respectively. Average precipitates sizes for the 600 °C sample[17] are approximately 7 nm with an average precipitate spacing of approximately 23 nm. The AlGaAs sample had an excess As concentration of 0.2%, with an average precipitate size of 8.9 nm and a spacing of 60.4 nm. To be able to support the large electric fields without joule heating, the ordinary GaAs sample was made semi-insulating by proton implantation with a flux of 10^{12} cm^{-2}. Proton implantation is used routinely in photorefractive quantum-well structures without adverse effects on electro-optic properties.[18,19]

To measure transmitted signals through the samples the epitaxial layers were removed from the substrates using an epitaxial lift-off technique and bonded to transparent glass slides.[20] Two gold contacts were evaporated on the sample with a 1 mm separation. Thin wires connected the gold layers to a high-voltage dc power supply that supplies 1.5 kV. The contacts were tested for symmetry and linearity. Long time-constant drift of the dark current was observed in the LTG samples, which is characteristic of trap-filling transport in LTG materials.[21]

The electroabsorption of the thin films was obtained by performing differential transmission experiments using a SPEX 1700 Czerny–Turner spectrometer and an incandescent tungsten light source.[19] We performed our experiments with dc electric fields to remove the different time responses for the three materials. For the large absorption coefficients for interband transitions, it is a reasonable approximation to neglect effects of multiple beam interference from the Fabry–Perot fringes on the measurement of $\Delta\alpha$.[19]

The transmission of the $Al_{0.25}Ga_{0.75}As$:As sample is shown in Fig. 1 as a function of photon energy for increasing electric fields. The relatively sharp feature at 1.730 eV

 0003-6951/93/121356-03$06.00 © 1993 American Institute of Physics

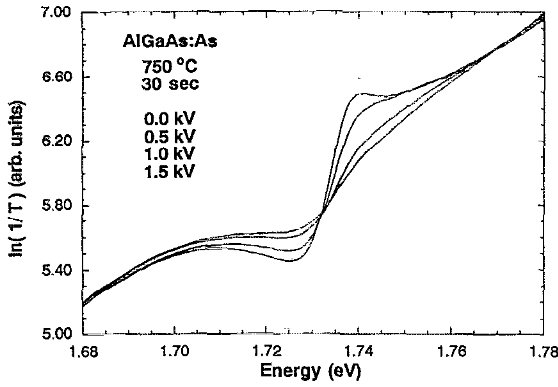

FIG. 1. Transmission of LTG $Al_{0.25}Ga_{0.75}As$:As annealed at 750 °C for 30 s for different dc electric field strengths. The peak modulation approaches 60% for a field of 15 kV/cm.

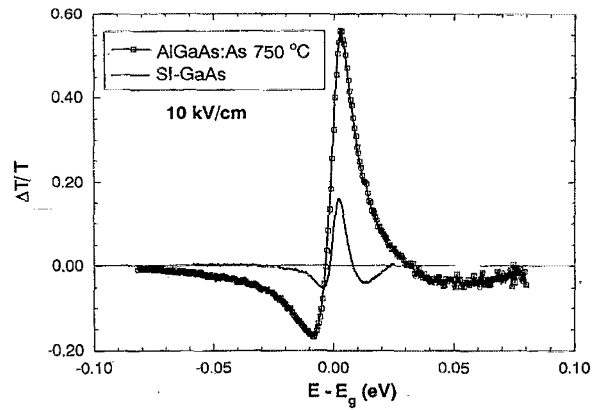

FIG. 3. Differential transmission of LTG $Al_{0.25}Ga_{0.75}As$:As annealed at 750 °C relative to GaAs for an applied dc electric field of 10 kV/cm.

corresponds to room-temperature excitons. A differential transmission approaching 60% is obtained with a dc field of 15 kV/cm. The measurements were taken after the dark current had reached steady state, which typically took several minutes. Our demonstration of 60% differential transmission is comparable to values in electro-optic modulators based on the quantum-confined Stark effect in quantum-well structures.[22] The electroabsorption and electrorefraction data are shown in Fig. 2 for 15 kV/cm. The data were obtained by fitting the differential transmission with smooth functions and performing a Kramers–Kronig analysis. The electrorefraction approaches 0.06 for this electric field.

The differential transmission of $Al_{0.25}Ga_{0.75}As$:As is compared with GaAs in Fig. 3 for a field of 10 kV/cm. The photon energy is plotted relative to the band gap energy E_g. For fields of 10 kV/cm the GaAs sample exhibits a differential transmission of 16% for the same field strength. The width of the LTG differential transmission is significantly broader than for the GaAs sample. This is expected on the grounds of inhomogeneous broadening of the exciton transition in the LTG material because the As precipitates perturb the material homogeneity. The electroabsorption in the LTG GaAs samples were also measured. Peak differential transmissions between 15% and 10% were observed, which are comparable to the GaAs sample, despite the significantly broader linewidth.

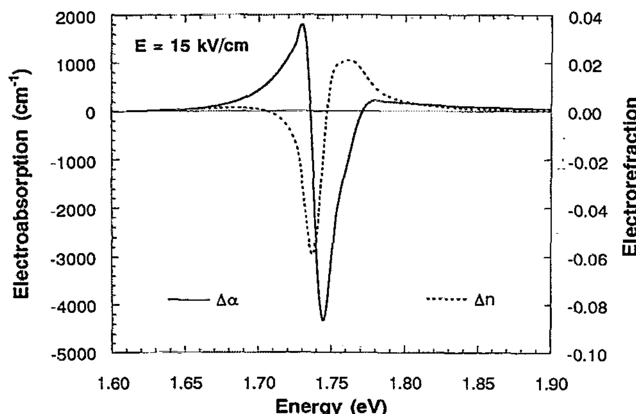

FIG. 2. Electroabsorption and electrorefraction for LTG $Al_{0.25}Ga_{0.75}As$:As at 15 kV/cm.

The large differential transmission values up to 60% in the LTG materials are surprising in view of the severe inhomogeneous broadening that occurs because of the presence of the precipitates. Broad excitonic transitions normally exhibit weak electroabsorption. The product of the linewidth Γ of an exciton transition with the peak absorption α_p is proportional to the exciton oscillator strength. In the case of exciton lifetime broadening, the peak electroabsorption is given by the relation

$$\Delta\alpha_p\Gamma^2 \propto f_{ex}\Delta\Gamma \tag{1}$$

for small lifetime broadening $\Delta\Gamma$, where f_{ex} is the exciton oscillator strength. The large electroabsorption $\Delta\alpha$ in the LTG materials most likely occurs through an enhancement of the exciton sensitivity to internal electric fields, expressed through the broadening $\Delta\Gamma$.

We use a figure of merit based on moments of the electroabsorption that allow direct comparisons among electro-optic properties of different materials. The first and second moments are defined by

$$M^{(1)} = \frac{2}{\pi}\frac{nc}{\omega_p^2}\int_0^\infty \Delta\alpha(\omega)d\omega \approx 0$$

$$M^{(2)} = \frac{\pi}{2}\left(\frac{nc}{\omega_p^2}\right)^2 \frac{\omega_0}{\Delta\alpha_p}\left(\int_0^\infty [\Delta\alpha(\omega)]^2 d\omega\right) \approx \frac{2}{\pi} f_{ex}\frac{\Delta\Gamma}{\Gamma}, \tag{2}$$

where n is the refractive index, $\Delta\alpha_p$ is the peak change in the absorption, ω_p is the ionic plasma frequency, and ω_0 is the transition frequency. The first moment of the electroabsorption of an isolated transition vanishes because of conservation of oscillator strength. The second moment of the electroabsorption is equivalent to the signal-bandwidth product for the electroabsorption, valid for $\Delta\Gamma \ll \Gamma$. The figure of merit expressed in Eq. (1) is obtained through the relationship

$$f_{ex}\Delta\Gamma = \left(\frac{\pi}{2}\right)^2 \omega_0 \frac{[M^{(2)}]^2}{\Delta\alpha_p}. \tag{3}$$

TABLE I. Ratios of electroabsorption figure of merits relative to bulk GaAs.

Ratio to GaAs[a]	LTG $Al_{0.25}Ga_{0.75}As$ 750 °C 30 s	LTG GaAs 600 °C 3600 s	LTG GaAs 900 °C 30 s	AlGaAs MQW[b]
$M^{(2)}$ [c]	6.0	2.1	1.8	1.4
$f\Delta\Gamma$	12.7	6.0	3.1	1.6

[a] $E = 10$ kV/cm.
[b] Exciton lifetime broadening only.
[c] Second moment: equivalent to signal-bandwidth product.

Equation (3) is used rather than Eq. (1) to obtain experimental values, because the linewidth Γ cannot be measured directly. This figure of merit cannot be used for direct measurements of oscillator strength, because the electric-field dependence of electroabsorption is included through the lifetime broadening $\Delta\Gamma$.

The $f_{ex}\Delta\Gamma$ figure of merits of LTG GaAs and $Al_{0.25}Ga_{0.75}As$ are given in Table I relative to GaAs for electric fields of 10 kV/cm. In the table, LTG GaAs:As annealed at 600 °C for 1 h exhibits an enhancement over GaAs by a factor of 6. LTG AlGaAs:As also shows a dramatic enhancement by a factor of 13. The oscillator strength in stoichiometric $Al_{0.25}Ga_{0.75}As$ is enhanced over GaAs because the effective mass and the dielectric constant in AlGaAs vary with Al fraction. For $\{Al\} = 25\%$ the oscillator strength is increased by approximately a factor of 3 relative to stoichiometric GaAs. This leaves an enhancement of a factor of approximately 4 for $Al_{0.25}Ga_{0.75}As$:As relative to stoichiometric $Al_{0.25}Ga_{0.75}As$. We conclude from this analysis that there is an enhancement of the sensitivity in the LTG GaAs and LTG AlGaAs samples several times larger than in stoichiometric materials for our annealing conditions. Different annealing conditions may produce further enhancements.

We include in Table I the ratio of an $Al_{0.3}Ga_{0.7}As$/GaAs MQW sample[19] with 75 Å wells and 100 Å barriers relative to GaAs for the field applied in the plane of the quantum well. It is interesting to note that the figure of merit of the electroabsorption is considerably smaller in the MQW than for the LTG materials. The quantum-confined excitons have an oscillator strength approximately an order of magnitude larger than for bulk excitons. However, by increasing the oscillator strength of the quantum-confined excitons, the sensitivity of the exciton to an electric field is decreased. Therefore, the exciton lifetime broadening $\Delta\Gamma$ of quantum-confined excitons is weaker than for bulk excitons, *for a given electric field strength.* The net result is only a moderate enhancement of the electro-optic properties of quantum-confined excitons relative to bulk excitons. The chief advantage of quantum-confined excitons only comes at high field strengths.

At this time, we cannot ascribe a definite mechanism for the enhanced electro-optic properties of LTG material. However, it is likely that excitonic electroabsorption in the LTG material is sensitive to local electric fields caused by the inhomogeneous distribution of arsenic precipitates. The slow response time of the LTG material raises questions concerning the role of transport in the enhancement mechanism. More work is necessary to discover the precise mechanisms for the enhancement.

D.D.N. would like to acknowledge support by NSF Grant No. ECS-9008266, the Presidential Young Investigator Program, and the Alfred P. Sloan Foundation. M.R.M. would like to acknowledge support by the Air Force Office of Scientific Research under Grant No. F49620-93-1-0031.

[1] D. S. Chemla, T. C. Damen, D. A. B. Miller, A. C. Gossard, and W. Wiegmann, Appl. Phys. Lett. **42**, 864 (1983).
[2] D. A. B. Miller, D. S. Chemla, T. C. Damen, A. C. Gossard, W. Wiegmann, T. H. Wood, and C. A. Burrus, Phys. Rev. Lett. **53**, 2173 (1984).
[3] D. A. B. Miller, Opt. Quantum Electron. **22**, S61 (1990).
[4] M. Kaminska, E. R. Weber, Z. Liliental-Weber, and R. Leon, J. Vac. Sci. Technol. B **7**, 710 (1989).
[5] M. R. Melloch, N. Otsuka, J. M. Woodall, A. C. Warren, and J. L. Freeouf, Appl. Phys. Lett. **57**, 1531 (1990).
[6] A. C. Warren, J. M. Woodall, J. L. Freeouf, D. Grischkowsky, D. T. McInturff, M. R. Melloch, and N. Otsuka, Appl. Phys. Lett. **57**, 1331 (1990).
[7] F. W. Smith, A. R. Calawa, C. Chen, M. J. Mantra, and L. J. Mahoney, IEEE Electron. Device Lett. **EDL-9**, 77 (1988).
[8] M. R. Melloch, D. C. Miller, and B. Das, Appl. Phys. Lett. **54**, 943 (1989).
[9] B. Lin J.-F., D. P. Kocot, D. E. Mars, and R. Jaeger, IEEE Trans. Electron. Devices **ED-37**, 46 (1990).
[10] L.W.-. Yin, Y. Hwang, J. H. Lee, R. M. Kolbas, R. J. Trew, and U. K. Mishra, IEEE Electron. Device Lett. **EDL-11**, 561 (1990).
[11] F. W. Smith, H. W. Lee, V. Diadiuk, M. A. Hollis, A. R. Calawa, S. Gupta, M. Frankel, D. R. Dykaar, G. A. Mourou, and T. Y. Hsiang, Appl. Phys. Lett. **54**, 890 (1989).
[12] S. Gupta, P. K. Battacharya, J. Pamaulapati, and G. Mourou, Appl. Phys. Lett. **57**, 1543 (1990).
[13] A. C. Warren, N. Katzenellenbogen, D. Grischkowsky, J. M. Woodall, M. R. Melloch, and N. Otsuka, Appl. Phys. Lett. **58**, 1512 (1991).
[14] A. C. Warren, J. H. Burroughes, J. M. Woodall, D. T. McInturff, R. T. Hodgson, and M. R. Melloch, IEEE Electron Device Lett. **EDL-12**, 527 (1991).
[15] D. D. Nolte, R. M. Brubaker, M. R. Melloch, J. M. Woodall, and S. E. Ralph, Appl. Phys. Lett. **61**, 3098 (1992).
[16] M. R. Melloch, D. D. Nolte, J. M. Woodall, and S. E. Ralph, IEEE Trans. Electron. Device **ED-39**, 2654 (1992).
[17] A. C. Warren, J. M. Woodall, P. D. Kirchner, X. Yin, F. Pollak, and M. R. Melloch, Phys. Rev. B **46**, 4617 (1992).
[18] D. D. Nolte, D. H. Olson, G. E. Doran, W. H. Knox, and A. M. Glass, J. Opt. Soc. Am. B **7**, 2217 (1990).
[19] Q. N. Wang, R. M. Brubaker, D. D. Nolte, and M. R. Melloch, J. Opt. Soc. Am. B **9**, 1626 (1992).
[20] E. Yablonovitch, D. M. Hwang, T. J. Gmitter, L. T. Florez, and J. P. Harbison, Appl. Phys. Lett. **56**, 2419 (1990).
[21] B. Wu, A. Verma, J. Gamelin, H. Sohn, and S. Wang, in *Low Temperature (LT) GaAs and Related Materials* (Materials Research Society, Pittsburgh, PA, 1992), Vol. 241, p. 45.
[22] M. Whitehead, P. Stevens, A. Rivers, G. Parry, J. S. Roberts, P. Mistry, M. Pate, and G. Hill, Appl. Phys. Lett. **53**, 956 (1988).