

Picosecond absorption dynamics of photoexcited InGaP epitaxial films

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The absorption recovery of a photoexcited InGaP epitaxial film 0.4 μm thick was investigated using the pump-probe laser technique and found to have a time constant of 55 ps at room temperature. Measurements done in the temperature range of 300–50 K show the decay of the photoexcited carrier distribution to be dominated by ambipolar diffusion and surface recombination. The measured absorption recovery time constant corresponds to an ambipolar diffusion coefficient $D > 2.8 \text{ cm}^2/\text{s}$ and a surface recombination velocity of $S > 4 \times 10^5 \text{ cm/s}$ at room temperature.

There has been a considerable amount of research done in characterizing the photoexcited carrier dynamics of GaAs, GaAs surfaces, and AlGaAs/GaAs heterostructures.^{1–10} In contrast, few investigations of the dynamics of photoexcited carriers in InGaP have been reported to date.^{11,12} In this letter we report the first study of the picosecond dynamics of photoexcited carriers in an InGaP epitaxial film grown by gas source molecular beam epitaxy.

The InGaP epitaxial layer utilized in the time-resolved absorption measurements reported here was 0.4 μm thick and was grown on a $\langle 100 \rangle$ GaAs substrate using the technique of gas source molecular beam epitaxy.¹³ First, a 0.5 μm buffer layer of GaAs was grown at a rate of 1 $\mu\text{m/h}$ with a substrate temperature of 600 °C. During the final 5 min of the buffer layer growth, the substrate temperature and the gallium effusion oven temperature were ramped down to the appropriate values for InGaP growth: the substrate temperature was set to 500 °C and the Ga cell temperature was selected to obtain a 1 $\mu\text{m/h}$ growth rate of nominally lattice-matched InGaP. Double x-ray diffraction measurements of the structure showed the $\text{In}_x\text{Ga}_{1-x}\text{P}$ to have a mole fraction x of 0.49. The InGaP layer was unintentionally doped. Films grown under similar conditions have been measured by the Hall–Van der Pauw method to be n type and have carrier concentrations in the range of $(1\text{--}5) \times 10^{16} \text{ cm}^{-3}$.¹³

To create a free-standing film the substrate was entirely removed by attaching the film side of the sample to a glass slide with a crystal bond and etching the GaAs with a commonly used etchant: 2:1:10 solution of ammonium hydroxide-hydrogen peroxide-distilled water. This solution etches GaAs at a rate of 1.6 $\mu\text{m/min}$ at room temperature and is more than 1000 times slower on InGaP. The film was held to the glass slide by Van der Waals forces and no adhesives were required.

The carrier dynamics was studied using the conventional pump-probe picosecond laser absorption technique.¹⁴ The short pulse source was a synchronously mode-locked hybrid dye laser pumped by a frequency-doubled mode-locked Nd:YLF laser. The dye laser has a linear

cavity configuration¹⁵ and two intercavity prisms for the compensation of group velocity dispersion.^{16,17} Using Rhodamine 590 for the gain medium and a mixture of DODCI and DQOCI as the saturable absorber, the laser produces pulses as short as 150 fs, around 600 nm, with an average power of 60 mW. For the absorption measurements, a 20 mW laser beam was split into pump and probe beams with an intensity ratio of 5:1. The two beams were focused on the sample, which was mounted in a closed-cycle refrigeration system, with a 6.38 cm focal length lens. The probe beam exiting from the sample was detected using an EG&G SGD100A photodiode and a lock-in amplifier.

Time-resolved absorption measurements were conducted for several temperatures between 300 and 50 K. The absorption of the sample was measured to be around 60% and the peak modulation in the absorption caused by the pump beam was 0.2%. Figure 1(a) shows typical absorption recovery curves at 300 and 50 K. The recovery of the absorption following the excitation by the subpicosecond laser pulse is a consequence of a decrease of the concentration of the photoexcited carriers, n , due to diffusion and recombination. A semi-log plot of the absorption recovery, Fig. 1(b), shows that its variation as a function of time is monoexponential, having a larger time constant at lower temperatures. This monoexponential behavior is common to all data obtained at the different temperatures.

Since the laser spot size ($\sim 20 \mu\text{m}$) is much larger than the thickness of the sample, the carrier dynamics can be described by a one-dimensional diffusion equation with the boundary conditions set by the nonradiative surface recombination velocity, S , due to surface states. The equations that describe the evolution of the carrier concentration are similar to those discussed in Ref. 10, however, should include a radiative recombination term that depends on n^2 because in our experiment the photoexcited carrier density, $2 \times 10^{18} \text{ cm}^{-3}$, is much larger than the intrinsic carrier density, $n_i \sim (1\text{--}5) \times 10^{16} \text{ cm}^{-3}$.¹⁸ Nevertheless, the single exponential behavior of the measured absorption recovery illustrated in Fig. 1 suggests that the carrier dynamics is dominated by ambipolar diffusion and surface recombination, and that the contribution due to radiative recombination, which would alter the linearity of

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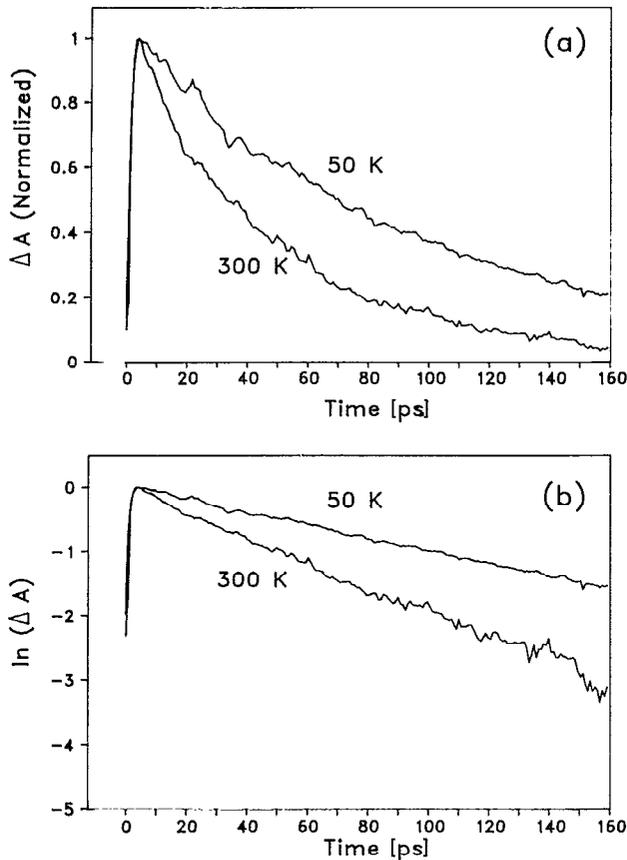


FIG. 1. (a) Temporal variation of the absolute change in absorption of a photoexcited InGaP film 0.4 μm thick at 300 and 50 K, (b) semi-log plot of the data in (a).

the plots in Fig. 1(b), can be neglected. Time-resolved measurements conducted by Fouquet *et al.*¹¹ on metalorganic chemical vapor deposition (MOCVD)-grown InGaP also indicate that the radiative recombination time constants vary from 1.8 ns to $> 1 \mu\text{s}$ depending on growth temperature. In the case where the radiative recombination can be neglected, the solution to the diffusion equation is the same as that discussed by Mayer *et al.*¹⁰ and Crank.¹⁹

Since the sample absorbs 60% of the laser light it should be noted that the initial spatial distribution in the one dimension of interest, is exponential and not a constant as assumed by the solution in Refs. 10 and 19. However, we have determined from numerical simulations that the exponential nature of the initial carrier distribution does not alter the dynamics of the carriers in the time scales of interest here, and the equations given in Refs. 10 and 19 are valid.

Figure 2 shows the calculated dependance of the absorption recovery time constant, τ_{gi} , as a function of the ambipolar diffusion coefficient, D , with the surface recombination velocity, S , as a parameter. The horizontal line represents the measured value of τ_{gi} at 300 K, 55 ps, determined from averaging the results of several measurements. The confidence interval was chosen as one standard deviation and is shown with broken lines. Figure 2 also shows that the measured absorption recovery time con-

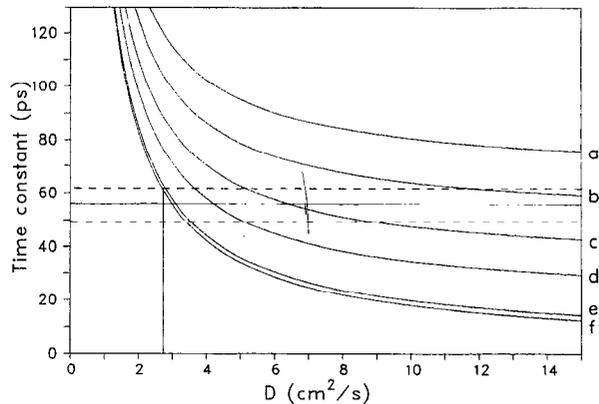


FIG. 2. Calculated values of the absorption recovery time constants as a function of ambipolar diffusion coefficient, D , for several values of surface recombination velocity, S : (a) $3 \times 10^5 \text{ cm/s}$, (b) $4 \times 10^5 \text{ cm/s}$, (c) $6 \times 10^5 \text{ cm/s}$, (d) $1 \times 10^6 \text{ cm/s}$, (e) $5 \times 10^6 \text{ cm/s}$, and (f) $1 \times 10^7 \text{ cm/s}$. The horizontal line represents the measured time constant at 300 K and the dashed lines correspond to the standard deviation.

stant sets a lower limit for the ambipolar diffusion coefficient as $D > 2.8 \text{ cm}^2/\text{s}$, identified by the vertical line, and the surface recombination as $S > 3.8 \times 10^5 \text{ cm/s}$. It should be noticed that the ambipolar diffusion coefficient might be determined by measuring the absorption recovery time constants for samples of different thicknesses. However if the carrier decay is not diffusion limited it is required that the samples have the same surface recombination rate, which for chemically etched InGaP samples described above was found not to be the case.

We have estimated the values of D and S from the measurements of absorption recovery as a function of temperature. The variation of the absorption recovery time constant as a function of temperature is shown in Fig. 3. Each data point again is the result of averaging several measurements and the error bars correspond to one standard deviation. The variation of τ_{gi} as a function of temperature can be described considering the temperature dependance of the ambipolar diffusion D , and surface recombination velocity S , which are given by

$$S = S_0 T^{1/2}$$

$$D = 2 \frac{KT}{q} \frac{1}{1/\mu_{al} + 1/\mu_{ac} + 1/\mu_{po}}$$

$$= 2 \frac{KT}{q} \frac{1}{1/a_1 T^{-1/2} + 1/a_2 T^{-3/2} + \frac{1}{a_3 (\theta/T)^r}}$$

where μ_{al} , μ_{ac} , μ_{po} are the mobilities due to alloy scattering, acoustic phonon scattering and polar optical scattering, which are the dominant scattering mechanisms contributing to the mobility of carriers in InGaP for the temperature range investigated. The constants a_2 and a_3 can be calculated using known parameters of the material.²⁰⁻²⁶ The parameter r depends on the ratio of the Debye temperature, θ , to the absolute temperature, T , and is given in Ref. 18. The parameter a_1 , on the other hand, depends on the de-

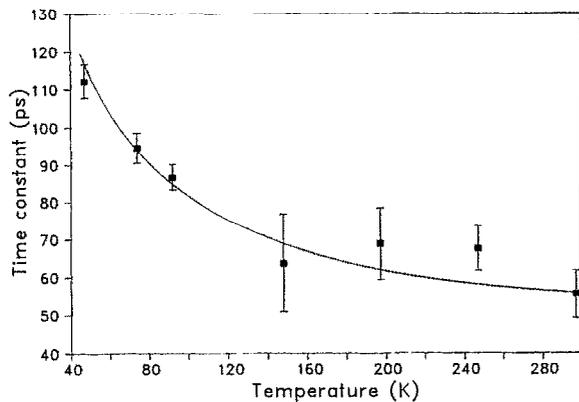


FIG. 3. Temperature dependence of the absorption recovery time constants for the 0.4 μm InGaP film. The squares indicate the mean value of the measurement and the error bars correspond to one standard deviation. The solid line is the best fit predicted by the model. The corresponding values for D and S are $3 \text{ cm}^2/\text{s}$ and $7 \times 10^6 \text{ cm/s}$, respectively at 300 K.

gree of disorder in the material $s(\alpha)$ and the square of the alloy scattering potential, ΔU , which are not precisely known for this sample.

To extract the values of D and S from the absorption measurements, the model equation resulting from the solution of the diffusion equation with the recombination due to surface states as the boundary condition^{10,19} was fit to the data points of Fig. 3 using S_0 and $s(\alpha) \cdot \Delta U^2$ as independent parameters. The best fit to the data is shown as a solid line in Fig. 3 and corresponds to room-temperature values of $D = 3.0 \text{ cm}^2/\text{s}$ and $S = 7 \times 10^6 \text{ cm/s}$. However, since the mobility is dominated by alloy scattering which has the same temperature dependence as S , the uncertainty of the fit is large. It is possible to compare our results with a calculated value of the ambipolar diffusion coefficient obtained from values of Hall mobility, which is usually larger than the actual carrier mobility. A calculated value of $D = 5.0 \text{ cm}^2/\text{s}$ can be obtained from Hall measurements on p -type InGaP reported by Blood *et al.*²⁷ Direct comparison of ambipolar diffusion coefficient with other alloys or InGaP grown by different techniques must take into account the variation of the disorder parameter and the alloy scattering potential.

In conclusion, a photoexcited InGaP epitaxial layer 0.4 μm thick showed a rapid recovery of absorption, 55 ps at room temperature. It was found that in the temperature range investigated, 50–300 K, the carrier dynamics is dominated by ambipolar diffusion and surface recombination.

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- ¹C. V. Shank, R. L. Fork, R. F. Leheny, and J. Shah, *Phys. Rev. Lett.* **50**, 124 (1987).
- ²R. F. Leheny, J. Shah, R. L. Fork, C. V. Shank, and A. Migus, *Solid State Comm.* **31**, 809 (1979).
- ³A. Olsson, D. J. Erskine, Z. Y. Xu, A. Schremer, and C. L. Tang, *Appl. Phys. Lett.* **41**, 659 (1982).
- ⁴Y. Silberg, P. W. Smith, D. A. B. Miller, B. Tell, A. C. Gossard, and W. Wiegmann, *Appl. Phys. Lett.* **46**, 701 (1985).
- ⁵A. J. Taylor, D. J. Erskine, and C. L. Tang, *J. Opt. Soc. Am. B* **2**, 663 (1985).
- ⁶D. G. McLean, M. G. Roe, A. I. D'Souza, and P. E. Wigen, *Appl. Phys. Lett.* **48**, 992 (1987).
- ⁷E. Yablonovitch, C. J. Sandoff, R. Bhat, and T. Gmitter, *Appl. Phys. Lett.* **51**, 439 (1987).
- ⁸W. Z. Lin, J. G. Fujimoto, E. P. Ippen, and R. A. Logan, *Appl. Phys. Lett.* **50**, 124 (1979).
- ⁹J. M. Olson, R. K. Ahrenkiel, D. J. Dunlavy, B. Keyes, and A. E. Kibbler, *Appl. Phys. Lett.* **55**, 1208 (1989).
- ¹⁰G. Mayer, B. E. Maile, R. Germann, A. Forchel, P. Grambow, and H. P. Meiner, *Appl. Phys. Lett.* **56**, 2016 (1990).
- ¹¹J. E. Fouquet, V. M. Robbins, J. Rosner, and O. Blum, *Appl. Phys. Lett.* **57**, 1566 (1990).
- ¹²R. Z. Bachrach and B. W. Hakki, *J. Appl. Phys.* **42**, 5102 (1971).
- ¹³J. H. Quigley, M. J. Hafich, H. Y. Lee, R. E. Stave, and G. Y. Robinson, *J. Vac. Sci. Technol. B* **7**, 358 (1989).
- ¹⁴E. P. Ippen and C. V. Shank "Techniques of measurement" in *Ultrafast Light Pulses*, edited by S. Shapiro (Springer, New York, 1977) p. 102.
- ¹⁵M. D. Dawson, T. F. Boggess, and D. W. Garvey, *Opt. Comm.* **60**, 79 (1986).
- ¹⁶J. A. Valdmanis, J. P. Gordon, and R. L. Fork, *Opt. Lett.* **10**, 131 (1985).
- ¹⁷O. E. Martinez, J. P. Gordon, and R. L. Fork. *Ultrafast Phenomena IV*, edited by D. H. Auston and K. B. Eisenthal (Springer, New York, 1984), p. 7.
- ¹⁸C. M. Wolfe, N. Holonyak, Jr., and G. E. Stillman, *Physical Properties of Semiconductors* (Prentice Hall, Englewood Cliffs, New Jersey, 1989) p. 198.
- ¹⁹J. Crank, *The Mathematics of Diffusion*, 2nd. ed. (Oxford University, Oxford, 1975), p. 60.
- ²⁰Shyh Wang, *Fundamentals Of Semiconductor Theory And Device Physics* (Prentice Hall, Englewood Cliffs, New Jersey, 1989), p. 192.
- ²¹Michael Shur, *GaAs Devices And Circuits*, (Plenum, New York, London, 1987), p. 37.
- ²²J. R. Hayes, A. R. Adams, and P. D. Greene in *GaInAsP Alloy Semiconductors*, edited by T. P. Pearsall (Wiley, New York, 1982), p. 189.
- ²³B. W. Hakki, A. Jayaraman, and C. K. Kim, *J. Appl. Phys.* **41**, 5291 (1970).
- ²⁴D. Patel, J. Chen, S. R. Kurtz, J. M. Olson, J. H. Quigley, M. J. Hafich, and G. Y. Robinson. *Phys. Rev. B* **39**, 10978 (1989).
- ²⁵G. Lucovsky, M. H. Brodsky, M. F. Chen, R. J. Chen, R. J. Chicotka, and A. T. Ward, *Phys. Rev. B* **4**, 1945 (1971).
- ²⁶The expressions of mobility due to acoustic phonon and polar optic scattering and the constants used in these expressions were obtained from references: (a) C. M. Wolfe, N. Holonyak, Jr., and G. E. Stillman, *Physical Properties of Semiconductors*, (Prentice Hall, Englewood Cliffs, New Jersey, 1989), p. 198; (b) Shyh Wang, *Fundamentals of Semiconductor Theory And Device Physics*, (Prentice Hall, Englewood Cliffs, New Jersey, 1989), p. 192; (c) Michael Shur, *GaAs Devices And Circuits* (Plenum, New York, London, 1987), p. 37; (d) J. R. Hayes, A. R. Adams, and P. D. Greene, in *GaInAsP Alloy Semiconductors*, edited by T. P. Pearsall (Wiley, New York, 1982), p. 189; (e) B. W. Hakki, A. Jayaraman, and C. K. Kim, *J. Appl. Phys.* **41**, 5291 (1970); (f) D. Patel, J. Chen, S. R. Kurtz, J. M. Olson, J. H. Quigley, M. J. Hafich, and G. Y. Robinson, *Phys. Rev. B* **39**, 10978 (1989); (g) G. Lucovsky, M. H. Brodsky, M. F. Chen, R. J. Chen, R. J. Chicotka, and A. T. Ward, *Phys. Rev. B* **4**, 1945 (1971).
- ²⁷P. Blood, J. S. Roberts, and J. P. Stagg, *J. Appl. Phys.* **53**, 3145 (1982).