Solid-State Electronics Vol. 32, No. 12, pp. 1585–1589, 1989
Printed in Great Britain.

0038-1101/89 $3.00 + 0.00

ARE TRANSVERSE PHONONS IMPORTANT FOR $\Gamma - X$-INTERVALLEY SCATTERING ?

Stefan Zollner*, Jens Kircher*, Manuel Cardona*, and Sudha Gopalan**

*Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-7000 Stuttgart 80, FRG
**The University of Western Ontario, Department of Physics, London, Ontario, N6A 3K7

ABSTRACT

We employ the rigid pseudo-ion method to calculate the q-dependence of intervalley deformation potentials for GaP from the Γ-point to the X-valley. We find that the fast transverse acoustic phonon (which cannot couple to the symmetry point X) becomes as important along the XW-direction as the longitudinal acoustic phonon (which is allowed at X). We have measured the temperature dependence of the lifetime broadenings of the E_0-gap of GaP with spectroellipsometry in order to obtain an effective intervalley phonon energy from which the relative contributions of the different phonon branches can be determined, but difficulties arise as intervalley and intravalley (Fröhlich) exciton-phonon interaction both contribute to the broadenings.

KEYWORDS

Intervalley scattering; intervalley deformation potentials; rigid pseudo-ion method; lifetime broadenings; spectroellipsometry; exciton-phonon interaction; exciton-heating; temperature dependence of the dielectric function.

INTRODUCTION

Intervalley scattering (IVS) processes in semiconductors, i. e., the transfer of a carrier (usually an electron) from one valley to a different equivalent or nonequivalent valley in the same (or different) band by a collision with the lattice (phonon or defect) or with another carrier, have been identified as the mechanism causing microwave oscillations (Gunn-effect) and a negative differential resistance. More recently, IVS has also been shown to be important for the cooling of hot carriers after optical excitation. Therefore, IVS has to be considered in the study of fast semiconductor devices operating under high electric fields. An intervalley defomation potential (IDP) formalism (Conwell, 1967) has been developed where the scattering rates are calculated in an effective-mass approximation. The IDP's are usually adjusted in a Monte Carlo calculation (Jacoboni and Reggiani, 1983) to give the best fit to the experimental curves. This approach is unsatisfactory for a number of reasons: (i) The experiments are usually not only affected by IVS, but also by other processes like intravalley phonon or carrier-carrier scattering. Therefore the simulation may not be sufficiently sensitive to yield the IDP with high accuracy. (ii) The IDP is assumed to be constant over the entire valley. (iii) Only one phonon branch is assumed to contribute to IVS.

Calculations of IDPs have been rare and incomplete. The rigid pseudoion method (RPIM), based on parametrized phonon models (Dolling and Waugh, 1965; Price, Rowe, and Nicklow, 1971) and a band structure with local pseudopotential wave functions (Cohen and Bergstresser, 1966), was introduced by Cohen and Tsang (1971) to study the superconductivity in IV-VI-compounds and soon applied to IVS processes in Si, GaAs, and other materials (Fawcett and Herbert, 1974; Pollak and Glembocki, 1985; Krishnamurthy, Sher, and Chen, 1989), but only at a few points in the Brillouin zone. In this framework, the IDP can be written as the scalar product of the phonon eigenvector with the matrix element of the gradient of the pseudopotential (Zollner, Gopalan, and Cardona, 1989b). All existing calculations for GaAs and InP agree on a value of about 3 eV/Å for ΓL- and ΓX-scattering, which is much lower than the results obtained from recent Monte Carlo simulations. Although the accuracy of the RPIM may be questionable (since the eigenvectors of the phonons are not well known, the crystal potential has to be interpolated through only a few values obtained from fitting the band gaps, and the rigid ion model is dubious), it seems appropriate to search for other contributions to IVS not considered so far. One such possibility is IVS via transverse phonons, which will be the contents of this study.

THEORY

The IDPs for scattering from the Γ-point of the conduction band (CB) in the indirect semiconductor GaP (Γ_1-symmetry) to a number of points in the X-valley, obtained with the RPIM (Zollner, Gopalan, and Cardona, 1989a), are shown in Fig. 1. Transitions to most of these points are virtual, of course, as they do not conserve energy, but this does not affect the RPIM calculation, as the IDP's do not depend on the electron energies, only on their wave functions. For scattering to the lowest CB minimum at the X-point (X_1 symmetry, phosphorus at the origin), only the longitudinal acoustic (LA) phonon is allowed to couple, with an IDP of about 1 eV/Å. Figure 1 shows how the IDPs change when the final point moves away from X along the $X\Gamma$- (open symbols, ||) and XW-directions (closed symbols, ⊥). Discontinuities and cusps in the figure are artifacts due to the unsymmetrical truncation of the plane wave set and the cut-off of the pseudopotential form factors for $q > 7.2\pi/a$, where a is the lattice constant.

For a final point with coordinates $(1-\epsilon,0,0)$, in multiples of $2\pi/a$, along the $X\Gamma$-direction, the LA contribution (□) rapidly drops, whereas the longitudinal optic (LO) contribution (○) increases, as the final point moves away from X. The effective IDP for both processes, given by the dotted line, is also decreasing. (The meaning of this sum, in the context of Conwell's IVS formula, is questionable for GaP, where the LA and LO energies are not even approximately equal.) Transverse phonon scattering is forbidden by symmetry along the $X\Gamma$-direction, which is reproduced by our calculations. The situation for a final point along the XW-direction is completely different. For a final point with coordinates $(1,\epsilon,0)$ the LA phonon (■) shows a similar behavior as before, the LO phonon (•) contribution, however, turns out to be much smaller. The lower (slow) TA phonon and the lower transverse optic (TO) phonon are forbidden by parity considerations in the diamond structure, as these phonons are odd and the electron states even with respect to a reflection in the xy-plane. Therefore the slow TA and the lower TO branches have negligible IDPs. The upper (fast) TA and the upper TO modes mix with the LA and LO modes and are allowed. Whenever a processes which is forbidden at a high-symmetry point becomes allowed away from that point, it is important to know, at least qualitatively, how strong this process becomes. Our calculations imply that the upper TO contribution remains small, whereas the fast TA (♦) gives the most dominant contribution along the XW-direction. Calculations for GaAs (Fawcett and Herbert, 1974; Zollner, Gopalan, and Cardona, 1989b) have similar results for $X\Gamma$-scattering, but for $L\Gamma$-scattering the contributions of transverse phonons are small.

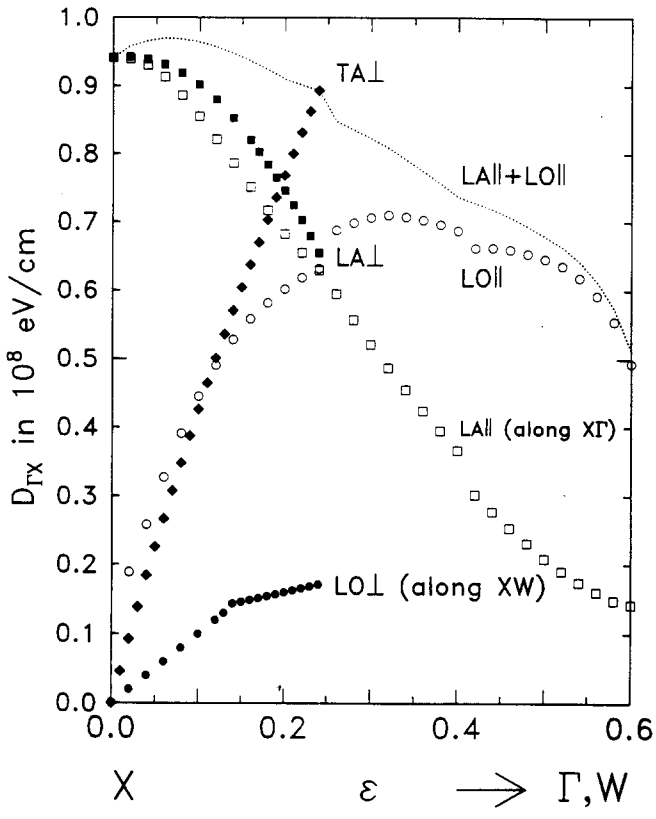

Fig. 1. Intervalley deformation potentials for transitions within the lowest conduction band in GaP from the Γ-point to a final point in the X-valley along the $X\Gamma$-direction (open symbols, ||) for the LA (□) and LO (○) branches and along the XW-direction (closed symbols, ⊥) for the LA (■), LO (•), and TA (♦) branches, calculated with the RPIM from the pseudopotential form factors of Cohen and Bergstresser (1966) and with the 10-parameter overlap valence shell model of Borcherds and co-workers (1979) for the phonons. There is considerable mixing between the longitudinal and transverse modes along the XW-direction.

We have also calculated IDPs for scattering from the Γ-point to final points in the neighborhood of the X-points with coordinates $(1-\epsilon,\epsilon,0)$, $(1,\epsilon,\epsilon)$, and $(1-\epsilon,\epsilon,\epsilon)$. The contributions of the lower TA and TO modes have always been negligible, but the upper TA (sometimes also upper TO) modes should be considered. Realistic rates for ΓX-scattering in GaP could be obtained by integrating over the Brillouin zone. For this to be meaningful, more accurate pseudopotential models for the conduction band structure would have to be avalailable.

EXPERIMENT

In order to investigate the relative importance of the different phonon branches experimentally, we have measured the lifetime broadenings of the E_0-gap of GaP as a function of temperature with spectroellipsometry. The optically excited electrons at Γ will be scattered within a few femtoseconds to the lower valleys at X or L via phonon emission or absorption, which results in a lifetime broadening of the E_0 critical point (direct gap) of several meV that can easily be measured with ellipsometry. The temperature dependence of these broadenings should, at least in principle, yield an effective phonon energy for the intervalley transitions of the resonantly excited carriers. The advantage of this method is that the carrier density is very low (cw excitation by monochromatic, linearly polarized light from a 75 W xenon lamp) and carrier-carrier scattering as well as non-equilibrium phonon effects can be excluded. Figure 2 shows the real part of the complex dielectric function (i. e., the square of the refractive index when the absorption is low) of GaP in the vicinity of the direct band gap at liquid helium and room temperatures, as measured with a rotating-analyzer ellipsometer described elsewhere (Lautenschlager and co-workers, 1987; Aspnes and Studna, 1983). Because of the inherent inaccuracy of rotating-analyzer ellipsometry for small absorptions, the imaginary part is not shown. The E_0 and $E_0 + \Delta_0$ critical points can clearly be seen as broadened structures. The arrows in Fig. 2 show their energy positions at 10 K. The transitions shift to lower energies and broaden with increasing temperature (Gopalan, Lautenschlager, and Cardona, 1987).

In order to study these structures in more detail and remove the nonresonant part as well as the background due to higher-energy transitions, we calculate numerically the second derivative with respect to energy E and perform a fit to the appropriate line shape (Aspnes equation, 1980):

$$\Delta\epsilon(E) = -A\exp(i\phi)\ (E - E_g + i\Gamma)^n \tag{1}$$

The four parameters A, E_g, Γ, and ϕ needed to fit each transition are the amplitude, energy, broadening, and phase angle of the transition. The latter was introduced to take into account the possibility of exciton/free carrier interactions. This analysis shows that the data can be fitted best with a broadened Lorentzian ($n = -1$) for each of the two structures. We therefore identify the peaks in Fig. 2 with 1s-exciton states. The broadenings of the E_0 gap for GaP and also GaAs (from Lautenschlager and others, 1987) obtained from the fit are given in Fig. 3.

DISCUSSION

We first discuss the broadenings of the E_0-gap of GaAs, where IVS processes are not possible because of the direct band structure (see Fig. 3a). The broadenings, caused by the heating (Rühle and Polland, 1987) of the resonantly excited (cold) electron-hole-pairs by the warm lattice, are smaller than the experimental resolution (about 0.5 meV) at low temperatures T, which corresponds to a lifetime τ of more than 1 ps, and reach about 20 meV at room temperature (τ=33 fs). Their temperature dependence can be explained well with the absorption of small wave vector (intravalley) LO phonons

$$\Gamma(T) = \hbar N_{\mathrm{LO}}(T)/2\tau_F \tag{2}$$

where N_{LO} is the occupation factor of the LO phonons and τ_F is a combined excitonic Fröhlich scattering time for electrons and holes (see the solid line in Fig. 3a). A calculation of the broadenings for uncorrelated electron-hole pairs (dotted line in Fig. 3a), which includes the Fröhlich interaction, acoustical and optical deformation potential as well as piezoelectric scattering (Conwell, 1967), yields much smaller broadenings. Therefore, the excitonic Fröhlich interaction should be considered, which has also been shown to increase the cross sections in resonant Raman scattering (Trallero-Giner, Cantarero, and Cardona, 1989).

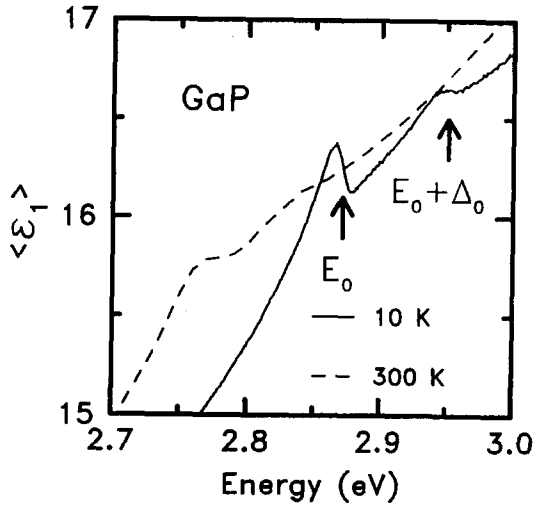

Fig. 2. Real part of the complex dielectric function as a function of energy for GaP at liquid helium and room temperatures. The arrows indicate the energy positions of the E_0 and $E_0 + \Delta_0$ critical points at 10 K.

The situation for the indirect semiconductor GaP (Fig. 3b) is completely different. The broadenings for low temperatures (about 8 meV at 10 K) are much higher than the experimental resolution (2 meV FWHM at 2.844 eV). They are independent of sample and surface quality, hence we believe that they are due to an intrinsic effect, i.e., IVS processes with a time constant of about 40 fs at 0 K. The possible final states are near X (X_1 and X_3) and near L (L_1). For density-of-state considerations, scattering to the X_1-valley is most probable, as the IDPs potentials are about the same for a three types of valleys. The broadenings increase with increasing temperature, but it is difficult

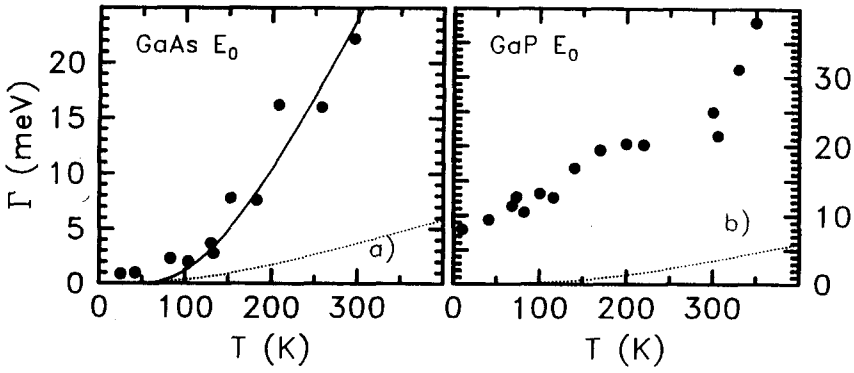

Fig. 3. Lifetime broadenings of the E_0-gaps of GaAs (a) and GaP (b). The dotted lines show the broadenings calculated from Conwell's theory for uncorrelated electron-hole pairs. The solid line in Fig. 3(a) is a fit to Eqn. (2).

to extract IVS times as a function of T, as the excitonic Fröhlich (intravalley) broadenings have to be subtracted for $T > 100$ K (see the broadenings of GaAs).

The broadening at liquid helium temperature can be analzyed approximately with Conwell's (1967) IDP formalism, where the scattering rate for IVS to each of the three possible valleys (near X_1, X_3, and L_1) by phonon emission is expressed by

$$\frac{1}{\tau} = N_V \frac{D^2 m_{\text{eff}}^{1.5}}{\sqrt{2}\pi\hbar^2 \rho E_{\text{Ph}}} \sqrt{\Delta E - E_{\text{Ph}}}. \tag{3}$$

Here ρ is the crystal density, ΔE the energy difference between the initial state at Γ and the minimum of the final valley, E_{Ph} the intervalley phonon energy, D the intervalley deformation potential, m_0 the free electron mass, c the speed of light in vacuum, m_{eff} the effective electron mass for the final state at X_1, X_3, or L_1, and N_V the number of final valleys (3 for X and 4 for L). With a total IDP of about D=1 eV/Å as suggested by the RPIM calculations discussed above and an effective electron mass of m_{eff}=0.68 (Madelung, 1987) at X_1 we obtain an IVS time of about 900 fs for scattering from the Γ-point to the minimum at X_1. This is only a rough estimate, as the density of states-mass is not well known: theoretical, *ab initio* CB structures are inaccurate because of the breakdown of the local density approximation. Scattering rates to X_3 and L_1 are much lower as the energy difference and the effective masses are smaller (Endo and co-workers, 1987; Madelung, 1987). Therefore, a total scattering time of about 700 fs should be expected from the RPIM. The observed broadening of about 8 meV at 10 K, however, corresponds to a much shorter time of only 40 fs, which would correspond to an IDP of about 4 eV/Å. A small part of this discrepancy can be explained if TA-mediated scattering is dominant, but not more than a factor of 2. A similar enhancement of IVS processes (compared to the RPIM theory) has been found by Shah and co-workers (1987) in a femtosecond luminescence study of GaAs. The problem may be in the empirical pseudopotential-rigid ion method (RPIM) used for the calculation of intervalley deformation potentials.

CONCLUSION

We have calculated the q-dependence of intervalley deformation potentials (IDP) in GaP for scattering from the Γ-point to final points in the X-valley along the $X\Gamma$- and XW-directions. We find that not only the LA and LO phonons are allowed to couple away from X, but the fast TA phonon also has to be considered along certain directions. The broadenings of the E_0-gap in GaAs, measured by temperature-dependent spectroellipsometry, are interpreted in terms of heating of the resonantly excited "cold" excitons by a warm lattice via Fröhlich interaction. In order to explain the broadenings in GaP, the intervalley and intravalley (Fröhlich) contributions have to be separated. At low temperatures we obtain an intervalley scattering time of only 40 fs, which yields an IDP of about 4 eV/Å, whereas the RPIM theory gives a value of only about 1 eV/Å.

ACKNOWLEDGEMENT

We would like to thank M. Garriga and A. Cantarero for stimulating discussions, E. T. Heyen for a critical reading of the manuscript, H. Hirt, P. Wurster, and M. Siemers for technical help, and A. Böhringer for the pretreatment of the samples. We are grateful to S. Leibenzeder (Siemens AG, Erlangen, FRG) for providing the GaP crystal.

REFERENCES

Aspnes, D. E. (1980). In M. Balkanski (Ed.), *Handbook on Semiconductors.* North-Holland, Amsterdam. Vol. 2, Chap. 4A, p. 409.

Aspnes, D. E., and A. A. Studna (1983). *Phys. Rev.* B, 27, 985.
Borcherds, P. H., K. Kunc, G. F. Alfrey, and R. L. Hall (1979). *J. Phys. C*, 12, 4699.
Cohen, M. L., and T. K. Bergstresser (1966). *Phys. Rev.*, 141, 789.
Cohen, M. L., and Y. W. Tsang (1971). In D. L. Carter and R. T. Bate (Eds.), *The Physics of Semimetals and Narrow-Gap Semiconductors.* Pergamon Press, Oxford. p. 303.
Conwell, E. M. (1967). *High field transport in semiconductors.* Academic Press, New York.
Dolling, G., and J. T. L. Waugh (1965). In R. F. Wallis (Ed.), *Lattice Dynamics.* Pergamon Press, Oxford. p. 19.
Endo, T., K. Sawa, Y. Hirosaki, S. Taniguchi, and K. Sugiyama (1987). *Jpn. J. Appl. Phys.*, 26, 912.
Fawcett, W., and D. C. Herbert. *J. Phys.* C, 7, 1641.
Gopalan, Sudha, P. Lautenschlager, and M. Cardona (1987). *Phys. Rev.* B, 35, 5577.
Jacoboni, C., and L. Reggiani (1983). *Rev. Mod. Phys.*, 55, 645.
Krishnamurthy, Srinivasan, A. Sher and A.-B. Chen (1989). *Appl. Phys. Lett.*, 53, 1853.
Lautenschlager, P., M. Garriga, S. Logothetidis, and M. Cardona (1987). *Phys. Rev.* B, 35, 9174.
Madelung, O. (1987). *Numerical Data and Functional Relationships in Science and Technology*, Vol. 22a. Springer Verlag, Berlin.
Pollak, F. H., and O. J. Glembocki (1985). In J. T. Devreese and P. Van Camp (Eds.), *Electronic Structure, Dynamics, and Quantum Structural Properties of Condensed Matter.* Plenum Press, New York. p. 451.
Price, D. L., J. M. Rowe, and R. M. Nicklow, *Phys. Rev.* B, 3, 1268.
Rühle, W. W. , and H.-J. Polland (1987). *Phys. Rev.* B, 36, 1683.
Shah, J., B. Deveaud, T. C. Damen, W. T. Tsang, A. C. Gossard, and P. Lugli (1987). *Phys. Rev. Lett.*, 59, 2222.
Trallero-Giner, C., A. Cantarero, and M. Cardona (1989). One-phonon resonant Raman scattering: Fröhlich exciton-phonon interaction. To appear in *Phys. Rev.* B.
Zollner, S., Sudha Gopalan, and M. Cardona (1989a). *Appl. Phys. Lett.*, 57, 614.
Zollner, S., Sudha Gopalan, and M. Cardona (1989b). Unpublished.