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Oscillatory behavior in the photoluminescence excitation and photoconductivity spectra of GaAs-AlAs superlattices

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Oscillations due to the emission of confined LO GaAs phonons by photoexcited electrons have been observed in the ($\sim$4 K) excitation spectra of both the photoluminescence and photoconductivity of GaAs-AlAs superlattices. The period of the oscillations, which is increased over that observed in bulk GaAs, allows us to determine the in-plane heavy-hole mass which gets progressively heavier as the AlAs thickness is reduced. For one sample, a 60-period 25-Å–8-Å GaAs-AlAs superlattice, we estimate the heavy-hole exciton binding energy to be $\sim$8.5 meV. Measurements on the pseudodirect 23-Å–19-Å GaAs-AlAs sample indicate that the electron-phonon interaction in the GaAs initially dominates over transfer into the AlAs X valleys.

INTRODUCTION

Excitation spectra of both the photoluminescence[1] (PLE) and photoconductivity[2,3] (PC) of thick, epitaxial GaAs layers exhibit well-understood oscillatory behavior. The origin of the oscillations lies in the strong interaction between electrons and LO phonons so that electrons excited high above the conduction-band edge preferentially lose energy through the emission of LO phonons.[4] Similar oscillatory structure has recently been observed in the 4-K PLE spectrum seen from a GaAs-$Al_{0.3}Ga_{0.7}As$ superlattice where the binary and alloy components were both only 10 Å thick.[5] In this paper we present low-temperature ($\sim$4 K) measurements of the PLE and PC excitation spectra from a set of three GaAs-AlAs superlattices. In two of the samples the AlAs is sufficiently thin that the lowest conduction-band state is built from the Γ state of the GaAs while the remaining sample has a so-called type-II band alignment with the lowest conduction-band state being at the folded X point in the AlAs.[6] Clear oscillatory features are seen in either the PLE or PC of all the samples studied. The oscillatory period has a spacing enhanced over just ω_{LO}, indicating that in the GaAs-AlAs superlattice system the simultaneous creation of excitons with phonons can be ruled out as an explanation for our observations. The period of the oscillations has been used to yield information on the ratio of the Γ electron mass to the in-plane heavy-hole mass of the GaAs layers. Additionally, for one sample we are able to extract an estimate of the heavy-hole exciton binding energy. The period of the oscillations in the PLE from the type-II sample indicates that the kinetics of the photoexcited electrons is dominated initially by electron relaxation via phonon emission in the GaAs rather than any competing transfer into the X valley in the AlAs. For this sample, at least, transfer to the X valley becomes favored when the electrons are within $\sim$75 meV of the lowest GaAs heavy-hole exciton energy.

Before proceeding to a description of the experimental results and discussion we should bear in mind the important quantities that influence the period of the oscillations and note the differences between the expectations for the three-dimensional and quasi-two-dimensional cases. In the bulk, if an electron is excited high up into the conduction band then it cascades downward in energy emitting LO phonons, the period of oscillations seen in either the PLE or PC being given by[2]

$$\Delta=\hbar\omega_{\text{LO}}(1+m_e/m_h)\ . \tag{1}$$

Here m_e is the electron effective mass and m_h could be either the heavy-hole or light-hole effective mass depending on the origin of the electron-hole pair created by the photoexcitation. In the quasi-two-dimensional situation the same formula describes the period of oscillation but with the following provisos: In the case of quantum wells and superlattices the lowest subband energy is someway above the bottom of the GaAs conduction-band edge so the nonparabolicity of the electron band needs to be considered when calculating m_e. The enhancement factor of $(1+m_e/m_h)$ reflects the creation of electron-hole pairs away from $\mathbf{k}=0$ so that the appropriate hole masses to consider in this factor would be those in the plane of the quantum wells.[7] Finally we should note that there is a modification to the bulk phonon modes due to the layered nature of the structures. In particular, the LO phonon branch of GaAs is at such an energy that the states do not map onto any propagating phonon states in the AlAs. The matching to evanescent states alone means that the GaAs phonons are "confined" to the GaAs layers with a subsequent quantization of their energy.[8]

EXPERIMENTAL DETAILS, RESULTS, AND DISCUSSION

The growth details of the samples we have studied have been described previously.[6] All the samples were prepared by molecular beam epitaxy on (001) oriented GaAs substrates at a growth temperature of ~630 °C. In the context of the present study one should bear in mind that the superlattice region of each sample is bounded by ~1000 Å of GaAs between it and the "free" surface and ~1 μm of GaAs "buffer" layer between it and the substrate. PLE spectra were recorded either using an Ar-ion pumped tunable dye laser (DCM or pyridene) or lamp and scanning monochromator while the PC spectra were recorded using the lamp and monochromator combination.

The PLE spectrum from the 25-Å–8-Å, GaAs-AlAs sample is shown in Fig. 1. The detection energy was set in the low-energy tail of the heavy-hole exciton at 1.788 eV. Note that this PLE spectrum does not mimic the expected absorption spectrum but is dominated by a single exciton creation peak with apparently little absorption in the continuum region. The explanation for this is simple;[5,6] PLE as opposed to absorption reflects both the creation of electron-hole pairs and their subsequent relaxation down to the emitting state. The apparent weak continuum absorption means that at least one member of the created carrier pair is lost by some other channel rather than relaxing to the emitting state. In the case of the samples studied here the absence of any confining barriers around the superlattices means that excited carriers would be easily lost to the GaAs capping layer, free surface, buffer-layer or substrate.

The peak in the spectrum at 1.803 eV is the heavy-hole exciton associated with the lowest electron subband. The smaller peak at 1.828 eV is assigned to the lowest light-hole exciton; this assignment having been confirmed by subsequent PLE circular polarization measurements where linearly polarized laser light was electronically chopped by an oscillating stress plate to produce alternating σ^+ and σ^- excitation.[9] At still higher energy are three equally spaced rather broad features; the period of these oscillations is ~48 meV. We believe that these oscillations are due to the emission of confined GaAs LO phonons as the photoexcited electrons relax to the lowest subband edge. Peaks in the PLE spectrum arise since the probability of forming an exciton will be a maximum for an electron at the subband edge and at LO phonon intervals relative to that edge. Excited electrons that relax to within one LO phonon energy of the subband edge proceed to lose energy via the slower process of acoustic phonon emission; increasing the probability of the electron's escape into the outermost GaAs rather than forming an exciton in the superlattice region.

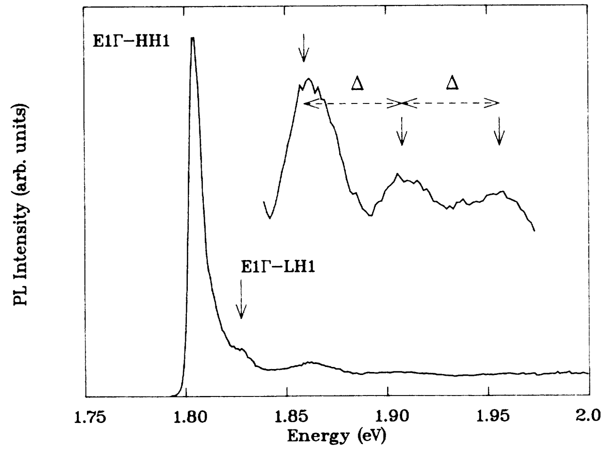

FIG. 1. Low-temperature PLE spectrum from a 60-period 25-Å–8-Å GaAs-AlAs superlattice. The inset shows the higher-energy portion of the spectrum at an increased gain.

The period of the oscillations is greater than the 43 meV observed in bulk GaAs.[1–3] Confinement effects on the phonons decreases their energy in comparison to the bulk[8] so that the increase in period is due to the enhancement of the effective mass ratio (m_e/m_h). Using an envelope function calculation we estimate the position of the lowest electron subband to be about 218 meV above the GaAs bulk conduction-band edge. At such an energy nonparabolicity effects on the electron effective mass cannot be neglected. It has been shown that for isolated GaAs-$\mathrm{Al}_{0.35}\mathrm{Ga}_{0.65}\mathrm{As}$ quantum wells of a similar thickness with a confinement energy of ~178 meV then the in-plane electron mass can be as high as $0.083m_0$.[10] Using the same expression for the nonparabolicity of the electron band as found in Ref. 10 then we estimate the electron effective mass for this sample to be $0.085m_0$.

The confined phonon energies for this sample have been measured[11] by resonance Raman spectroscopy in a backscattering geometry to be $\hbar\omega_{\mathrm{LO}_2}=36.1$ meV and $\hbar\omega_{\mathrm{LO}_4}=35.4$ meV. We anticipate that the LO phonon emission would be predominantly at the frequency of LO_1 (which cannot be observed in the configuration used in Ref. 11) but it is likely that there will be some contribution from the lower frequency phonons which will in part contribute to the broadening of the peaks. A "linear chain" calculation of the confined modes of a 25-Å GaAs layer predicts LO_1 to be about 0.5 meV higher in energy than LO_2. So we use a value of 36.6 meV in Eq. (1). Using our calculated $\hbar\omega_{\mathrm{LO}_1}$ and the estimated m_e we arrive at a value of the in-plane hole effective mass of $0.27m_0$. From this value we infer that m_h refers to the in-plane value of the $m_j=\frac{3}{2}$ particle. The smaller in-plane value, as compared to the bulk, arises due to the light- and heavy-hole mixing at finite wave vectors. The inferred value here is somewhat larger than the calculated value expected near to $\mathbf{k}=0$ but we note that while the "heavy-hole" band starts out from $\mathbf{k}_{\parallel}=0$ with a light mass closer to the decoupled limit,[12] calculations[13] show that the band is very nonparabolic and the in-plane mass rapidly becomes larger. Our derived value reflects this feature of the band structure.

Further information may be gleaned from this particular spectrum. Note that the lowest energy oscillation is some 56.5 meV away from the well-resolved heavy-hole exciton peak. We believe the proposed origin of the PLE oscillations is the same as in the bulk[2] and should be referred to the subband edge since the exciton formation rate will be a maximum there, so the difference between this number (56.5 meV) and the oscillatory period of 48 meV gives us a value of ~8.5 meV for the heavy-hole exciton binding energy in this 25-Å–8-Å GaAs-AlAs superlattice.[14] We see no series of oscillations that originate from the light-hole exciton peak so are unable to estimate its binding energy in a similar way. We are confident that the oscillatory behavior should be referred to the band edge and *not* the exciton position since we see an enhancement in the period of the oscillations over the phonon frequency. No such enhancement would be expected if the resonances were related simply to the simultaneous creation of excitons and phonons.

Oscillations in the photoconductivity signal are also seen in this sample. The period of the oscillations is identical to those seen in the PLE spectrum. The appearance of the oscillations in the PC spectrum and their variation as a function of sample temperature are most conveniently discussed in the context of the observations on the following sample, as we shall see below.

Let us now turn attention to the 25-Å–5-Å sample. The PLE signal from this is dominated by a single exciton peak, once more the sample geometry being such that virtually no continuum absorption could be detected.[6] Oscillatory behavior in this sample is best discussed by looking at the PC spectrum. This is shown in Fig. 2 for both 4.2 and 77 K. In previous measurements[15] on uncoupled GaAs-(AlGa)As multiple quantum wells the PC spectrum consisted of a background due to interband photoconductivity in the sample's GaAs buffer layer with, superimposed upon it, the absorption spectrum of the quantum wells, through which the light passes first. In the present superlattice samples the barriers are relatively thin so carrier transfer out of the wells can take place quite quickly and efficiently, with the consequence that conductivity in the buffer layer can occur due to absorption in both the superlattice and buffer layers. Competition between the two processes can lead to some distortion of the spectrum in the vicinity of the lowest heavy-hole excitonic feature. However, clearly seen at higher energy are a series of oscillatory features which we conclude are a manifestation of the electron-phonon interaction.

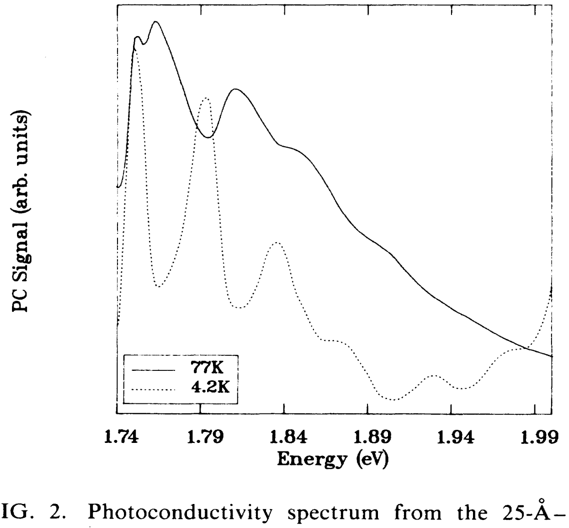

FIG. 2. Photoconductivity spectrum from the 25-Å–5-Å GaAs-AlAs sample at 4.2 K (dotted curve) and at 77 K (solid curve). Note that to illustrate the phase reversal of the oscillations the 77-K curve has been shifted to higher energy by 8 meV, reflecting the energy dependence of the GaAs band gap.

In the PLE spectrum of the previous sample we measured the peak of the oscillations relative to the subband edge; arguing that we were monitoring the excitonic radiative transition and that the maximum probability of reaching this emitting state was for electrons at the band edge or an integer number of steps of LO away from the edge. The situation for the 4.2-K PC process is somewhat different. Here we believe that the PC signal comes predominantly from the GaAs buffer layer—the signal from this is modulated therefore by the various relaxation and recombination processes that occur in the SL region of the sample. At 4.2 K electrons photoexcited high above the subband edge relax toward the subband edge. When they have relaxed to within LO of the subband edge then they proceed to lose energy via acoustic phonon emission, which is a relatively slow process and thus increases their probability of escape to the buffer layer, so they contribute positively to the PC signal. However, electrons at the subband edge or exact multiples of LO from the edge have the greatest probability of excitonic formation and subsequent recombination. Hence electrons which cascade directly down to the subband edge give the minimum contribution to the conductivity but give a peak in the PLE spectrum.

AT 77 K the situation is somewhat different. The phase of the oscillations in the PC is reversed with respect to those at 4.2 K and there is a decrease in the modulation depth, although the period remains unchanged. At this temperature the heavy-hole exciton creation peak is at lower energy than the peak in the PL, suggesting that at this temperature the radiative recombination process is predominantly due to free-electron-hole recombination. Excitons, therefore, tend to dissociate before recombining radiatively. In addition, no oscillatory structure is observed at an intermediate temperature (~46 K). Putting all these observations together suggests that at 77 K the modulation has a different ori-

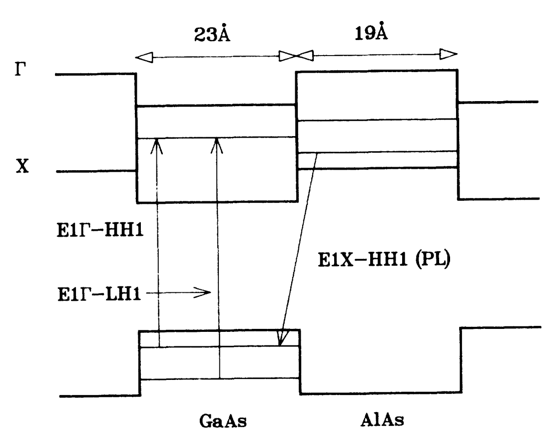

FIG. 3. Schematic diagram of the band-edge configuration of the 23-Å–19-Å GaAs-AlAs sample.

gin, possibly either due to an energy dependence in the ease with which carriers transfer out of the superlattice region or due to the role of some energy dependent nonradiative process.

We estimate the period Δ for this sample to be ~ 45 meV from the PC measurements. The lowest electron subband is ~ 170 meV above the GaAs band edge in this sample so the electron effective mass is $\sim 0.081 m_0$. The confined phonon frequency $\hbar\omega_{\mathrm{LO}_2}$ is identical to the previous sample so following the same procedure as before we calculate the hole mass to be $0.33 m_0$ in this instance. The heavier-hole mass derived in this case reflects the increased coupling between the light and heavy holes as their energy splitting is reduced by virtue of the increased well-to-well coupling through thinner AlAs "barriers."

The remaining sample a 23-Å–19-Å GaAs-AlAs superlattice differs from the others in that its band alignment is staggered or type-II.[6] A schematic of the band-edge configuration for this sample is shown in Fig. 3. It is possible to record PLE spectra in both the type-II energy range and also in the region of the lowest GaAs Γ states.[6] The PLE from this latter region of the spectrum is shown in Fig. 4, PL being detected at the position of the X_z-Γ excitonic transition. The feature at 1.896 eV corresponds to the lowest, direct heavy-hole exciton while the one at 1.947 eV we identify with the lowest, direct light-hole excitonic transition. The feature at 2.243 eV corresponds to the creation of excitons involving an electron at Γ and hole in the split-off valence band.[16] Between the light hole and split-off features are three evenly spaced transitions with a period of ~ 51 meV. The shape and strength of the light-hole transition is most likely influenced by the proximity of another of the oscillatory features at about 1.971 eV. The period of the oscillations once more indicates that the dominant mechanism in the excited electron decay is via the emission of GaAs confined LO phonons, at least down to some energy after which transfer to the folded AlAs X_z minimum becomes favorable. As far as we are aware this is the only report of the observation of such oscillatory behavior in a pseudodirect system. In the resonance Raman spectrum of this sample the GaAs confined phonons are almost identical with those seen from the previous sample, as expected for almost the same GaAs thickness. Using the same procedure as above we estimate the in-plane hole mass to be $0.22 m_0$, the decreased value again being consistent with the increased light- to heavy-hole splitting. Unlike the 25-Å–8-Å sample it is not possible to trace the origin of the oscillations back to the GaAs conduction-subband edge unless one assumes an unreasonably large value of the exciton binding energy of ~ 25 meV. Any interpretation will be complicated by the fact that we are monitoring the pseudodirect PL so that thermalization in the GaAs is followed by transfer to the AlAs followed by yet further thermalization in the AlAs prior to the actual emission process. Therefore we can only speculate on the energy position from which the oscillations originate. For the particular dimensions of this sample there are two confined X_z, electron states. The first is ~ 245 meV above the bulk GaAs conduction-band edge, the second is at ~ 374 meV. The lowest electron subband edge sits between these levels at ~ 307 meV. If we assume that the last oscillation is at 1.971 eV this is extremely close to the calculated position of the $n=2$, X_z electron subband in the AlAs at 1.978 eV. This may just be coincidental and further work on samples of somewhat different dimensions would be necessary to see if the oscillations need to be referred, in general, to the position of the highest X_z subband in the AlAs.

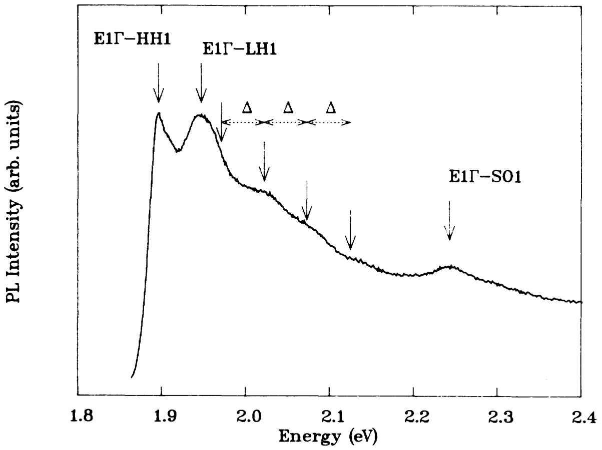

FIG. 4. Low-temperature PLE spectrum from the 23-Å–19-Å GaAs-AlAs superlattice in the region of the direct Γ-Γ transitions. The PL was detected at the position of the lowest X_z-Γ transition.

SUMMARY

We have seen oscillatory behavior in either the PC or PLE spectrum from a series of GaAs-AlAs superlattices. Oscillations in the PLE of a type-II system have been observed for the first time. The period of the oscillations has allowed us to estimate the in-plane heavy-hole mass in the GaAs as the coupling between adjacent layers is varied; the in-plane mass becoming lighter as the light- to heavy-hole coupling is reduced. In addition we estimate the heavy-hole exciton binding energy in a 25-Å–8-Å, GaAs-AlAs superlattice to be about 8.5 meV.

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[1] C. Weisbuch, Solid State Electron. **21**, 179 (1978).
[2] R. E. Nahory, Phys. Rev. **178**, 1293 (1969).
[3] R. W. Shaw, Phys. Rev. B **3**, 3283 (1971).
[4] H. J. Stocker and H. Kaplan, Phys. Rev. **150**, 619 (1966).
[5] A. Chomette, B. Lambert, B. Clerjaud, F. Clerot, H. W. Liu, and A. Regreny, Semicond. Sci. Technol. **3**, 351 (1988).

[6] K. J. Moore, P. Dawson, and C. T. Foxon, Phys. Rev. B **38**, 3368 (1988).

[7] See, for example, A. Fasolino and M. Altarelli, in *Two Dimensional Systems; Heterojunctions and Superlattices,* edited by G. Bauer, F. Kuchar, and H. Heinrich (Springer, Berlin, 1984).

[8] M. V. Klein, IEEE J. Quantum Electron. **QE-22**, 1760 (1986), and references therein.

[9] K. J. Moore (unpublished); for *experimental detail* see K. J. Moore, P. Dawson, and C. T. Foxon, Phys. Rev. B **34**, 6022 (1986).

[10] J. Singleton, R. J. Nicholas, D. C. Rogers, and C. T. B. Foxon, Surf. Sci. **196**, 429 (1986).

[11] K. J. Moore, G. Duggan, P. Dawson, and C. T. Foxon, Superlatt. and Microstruct. (to be published).

[12] A. S. Plaut, J. Singleton, R. J. Nicholas, R. T. Harley, S. R. Andrews, and C. T. B. Foxon, Phys. Rev. B **38**, 1323 (1988).

[13] R. Eppenga, M. F. H. Schuurmans, and S. Colak, Phys. Rev. B **36**, 1554 (1987).

[14] Complementary magnetoreflectivity measurements on this sample indicate a value for the binding energy consistent with this estimate—N. J. Pulsford and R. J. Nicholas (unpublished).

[15] D. C. Rogers, J. Singleton, R. J. Nicholas, C. T. Foxon, and K. Woodbridge, Phys. Rev. B **34**, 4002 (1986).

[16] G. Duggan, H. I. Ralph, P. Dawson, K. J. Moore, C. T. B. Foxon, R. J. Nicholas, J. Singleton, and D. C. Rogers, Phys. Rev. B **35**, 7784 (1987).