Resonant Raman scattering in GaAs-$Ga_{1-x}Al_xAs$ quantum wells in an electric field

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We apply resonant Raman scattering for studying the effect of an electric field on the electronic structure of GaAs-$Ga_{1-x}Al_xAs$ quantum wells. The evolution with the field of the intensities and frequencies of both "allowed" and "forbidden" transitions is measured. In order to show the advantages of this technique over the ones currently used, we compare it with photoluminescence excitation spectra of the same system. The analysis of the experimental results is performed by a tight-binding calculation which includes the effect of the electric field on the mixing between different electronic states.

The effect of an electric field on the optical properties of semiconductor quantum wells (QW's) and superlattices (SL's) has been the object of recent interest. Changes in both the electronic energy levels and the transition probabilities have been observed in the last years by photoluminescence[1-3] and optical absorption[4] in GaAs-$Ga_{1-x}Al_xAs$ SL's, and more recently also by electroreflectance[5] and by photocurrent spectroscopy.[6,7] The main results are shifts of the electronic transitions towards lower energies with increasing field together and a decrease of their intensities (probabilities). This holds for the "allowed" transitions, i.e., those involving electrons and holes of the same subband index ($\Delta n=0$). This behavior has been explained by several calculations[4,8-11] in which the intensity decrease (when nonradiative channels can be neglected) is due to the field-induces spatial separation of the carriers in the well. Transitions with $\Delta n\neq 0$ (sometimes called "forbidden") have been observed[2,3] and ascribed to mixing of valence-band state.[12] E_{12h} and E_{13h} transitions (which involve $n=1$ electron states and $n=2$ and 3 heavy holes, respectively) have also been observed by photocurrent spectroscopy;[6] their intensity was increased by the electric field. This was attributed to a field-induced change of the heavy- and light-hole mixing and also to the opposite electron hole polarizations which increases the probabilities of forbidden transitions.

The use of resonant Raman scattering (RRS) has in principle the following two main advantages when compared with more conventional techniques.

(i) It is sensitive to the spatial localization of the transitions under study, depending on which phonon resonates.[13,14] In this way problems like leakage of the wave functions from the wells into the barriers, as well as their coupling to the phonons, can be investigated.

(ii) RRS is expected to be more sensitive than photoluminescence excitation (PLE) because the former is a single-step process involving two simultaneously small energy denominators (three if one considers also forbidden Fröhlich effects)[15] whereas PLE is a "one-denominator" process. Thus much sharper singularities are expected for RRS than for PLE. Our results provide a good example of this.

To our knowledge only one other study has been made of the RRS dependence on an electric field for GaAs-$Ga_{1-x}Al_xAs$ SL's.[16] There, a decrease of the E_{33h} intensity with the applied voltage is reported, whereas no significant changes in the transition frequencies are observed. Besides, it is difficult to draw conclusions from the intensity data of these authors because no relation between the applied voltage and the resulting electric field in the QW is provided. Moreover, a striking feature of these experiments is that they do not show any forbidden transitions that should appear when the external electric field is present. Recent calculations[17] of the electric-field dependence of the resonant Raman profiles predict clear decreases of both the transition frequencies and intensities, the amount of these changes being quite sensitive to well thickness, effective masses, band offsets, and composition of the barriers.

We present here a RRS study of the electric-field effects on the frequencies and intensities of the electronic transitions in a QW structure of GaAs-$Ga_{1-x}Al_xAs$. PLE measurements have been performed in the same sample in order to have a direct comparison of both techniques. The results for both allowed and forbidden transitions are explained by a simple model calculation including mixing of heavy- and light-hole states. The energy transitions between the ith conduction state and the jth valence state will be labeled as E_{ij}. In some cases, e.g., for zero field, it will be possible to clarify the discussion by assigning a heavy- or light-hole label to the valence states attending to their main character. The sample was made of five GaAs QW's of thickness 230 Å

and $Ga_{0.57}Al_{0.43}As$ barriers of 250 Å, grown by molecular-beam epitaxy MBE on an GaAs: Si substrate. Before evaporating the QW a 0.5-μm thick layer of n^+ GaAs followed by a layer (900 Å) of n^+ $Ga_xAl_{1-x}As$ and 540 Å of intrinsic $Ga_xAl_{1-x}As$ were deposited. On the top of the wells a 1200-Å thick layer of $Ga_xAl_{1-x}As$ and a Ni electrode (60 Å) were evaporated. The intrinsic carrier concentration was estimated to be 2×10^{14} cm^{-3}. RRS spectra were obtained at 4 K with an LD-700 dye laser and a double-grating spectrometer with photon-counting electronics. The spectrometer response has been previously calibrated with a CaF_2 crystal in the energy range fro 1.55 to 1.70 eV. The Raman signal below 1.57 eV was hidden by the sample luminescence. PLE measurements were made at 4 K using the lowest heavy-hole exciton emission as detecting signal. For this reason no information was obtained on the intensities of this peak (E_{11} in our notation). Some unsuccessful attempts were made to distinguish between heavy- and light-hole transitions by measuring the circularly polarized photoluminescence of the sample. The flat-band potential of the sample is $\approx+1.1$ V (+ mean forward polarization, i.e., front electrode positive). The voltage-field relationship was established using the intrinsic carrier concentration in a depletion-layer model due to the metal-semiconductor Schottky contact[18] (the dielectric constants of GaAs and $Ga_xAl_{1-x}As$ have been taken to be equal).

RRS profiles corresponding to the LO phonon of GaAs (that is the Raman integrated intensity of that phonon versus incident light energy) are shown in Fig. 1 for different applied voltages. The main peaks below 1.62 eV correspond (see data for +0.2 V) to the outgoing resonances associated with the E_{14} and E_{2i} ($i=1-4$) transitions, as will be discussed below. PLE spectra for two applied voltages are included for comparison. Besides the different behavior of the various peaks, both in energy and intensity as a function of the applied field, it is worth drawing attention to the fact that RRS sensitivity is higher than that of PLE (note the logarithmic and linear scales, respectively). This is an example of the advantage (ii) mentioned above. As for the background increasing towards lower energies in RRS, it could be ascribed to the tail of the E_0 resonance of bulk GaAs (1.554 eV for the outgoing resonance) since roughly 90% of the incoming light reaches the substrate at these photon energies. However, this would imply an E_0 resonance much broader than usually observed.[15] No traces of AlAs-like phonon resonances were found in our measurements, indicating that there is negligible coupling in this case between the electronic levels of the well and the barrier phonons takes place. This information on the spatial localization of electronic transitions illustrates the advantage (i) mentioned above.

Let us now concentrate on discussing the usefulness of the technique. It must be stressed that the E_{22}-E_{23} doublet is clearly resolved in the RRS curves for -0.4 and -0.8 V. This is not the case for the PLE spectra, as seen in Fig. 1(b). In this case PLE has the advantage of covering a broader spectral range that RRS, where background problems appear at the low-energy side of Fig. 1.

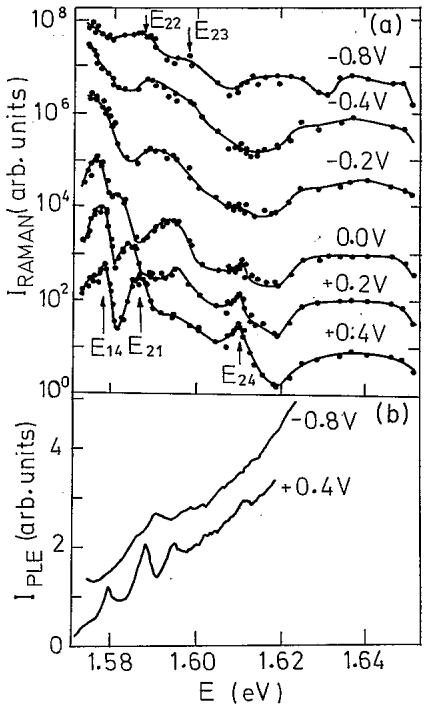

FIG. 1. (a) RRS spectra (in logarithmic scale) of the GaAs-LO phonon for different applied voltages (+ means forward and − reverse polarization). (b) PLE spectra (in linear scale) for two different applied voltages. I_{RAMAN} and I_{PLE} are the Raman and PLE intensities, respectively. The PLE curves are shifted 36 meV (the GaAs LO frequency) to higher frequencies in order to be compared with the outgoing Raman resonances of part (a) (see text). The arrows indicate the assigned transitions. The ordinate scale is shifted from each curve to the next one by one decade in (a) and by one unit in (b).

Figure 2 shows PLE spectra for different applied voltages. Here, the transitions associated with the first conduction-band state are well resolved, allowing a detailed analysis. For instance, besides the expected shift to lower energies of the peaks with increasing field, one observes an intensity decrease of the peak at 1.531 eV at zero field (Fig. 2(a)]. As will be discussed below this peak corresponds to the transition from the third (E_{13}) valence-band state to the first conduction level. At the same time the peak 1.533 eV shifts and grows with the applied field and a new peak splits off from E_{13}, disappearing at higher fields. This split peak will be interpreted in our model as the E_{12} transition which is forbidden in the flat-band limit because the second valence state is mainly the second heavy-hole state. The peak at 1.533 eV [Fig. 2(a)] which becomes dominant for +0.2 V [Fig. 2(d)] and the one at 1.523 eV [Fig. 2(e)] are tentatively assigned to higher-order exciton transitions associated with E_{12} (see below). In contrast, this rich structure is not present for transitions involving the second conduction band state. In fact only weak features [Fig. 1(b)] are observed in PLE corresponding to E_{14}, E_{21}, E_{22}, and E_{23} (badly resolved in PLE) and E_{24} transitions. It is in this energy region that RRS gives much better information about the electronic transitions.

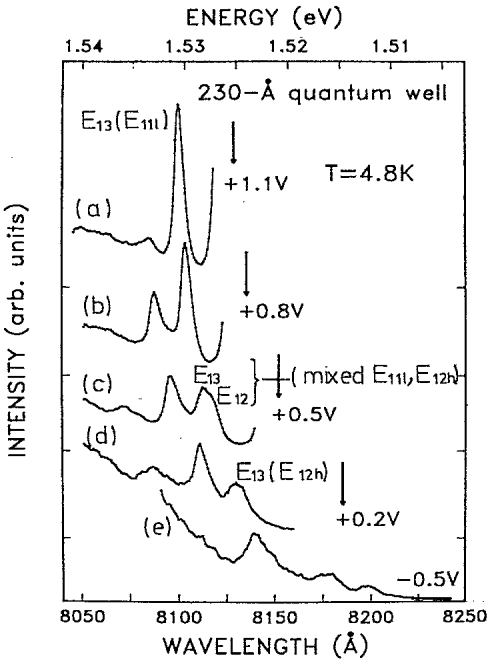

FIG. 2. PLE spectra for different voltages. The arrows show the detection energy.

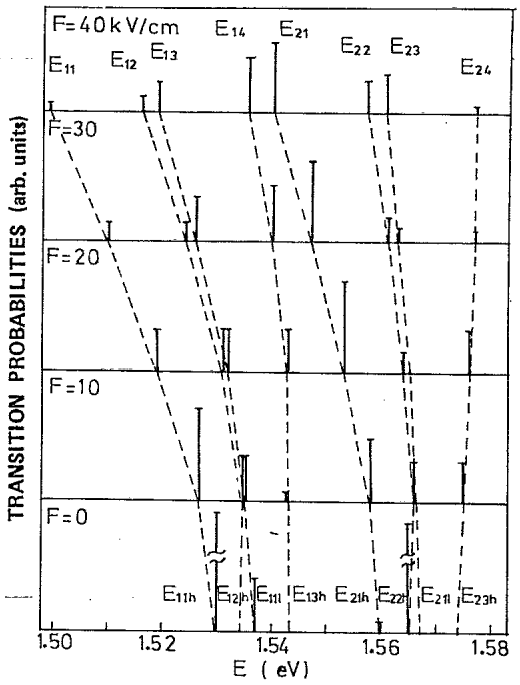

FIG. 3. Calculated energy positions of the electronic transitions for different applied electric fields. The vertical bars indicate the corresponding transition probabilities. The lines linking the values for different fields are drawn to better show the energy shifts of the transitions. For zero field the heavy- and light-hole character is indicated.

To account for these results we have performed tight-binding calculations of the electronic band structures. The parameters are fitted to give the value 1.518 eV (Ref. 19) for the GaAs gap. Excitonic effects are not explicitly included in the Hamiltonian so that our fitting implies that exciton binding energy is that of bulk GaAs. This is not a bad approximation for wells as wide as the ones we are concerned with. In order to work with manageable matrices, we use a perturbative procedure where the energy range of interest is selected.[20] Since in our case the barriers are very wide, we consider independent wells. This is done by embedding the wells within infinite barriers far away from them. The valence-band offset is taken to be $0.37\Delta E_g$, where ΔE_g is the gap difference of the two semiconductors. The electric field is described by means of a linear potential shifting each atomic level as a function of its energy. In this way the valence and conduction states are computed as a function of the electric field, including mixing between light and heavy holes. For zero field we obtain that the first, second, and fourth valence states are essentially the first, second, and third heavy holes, respectively, while the third valence state is essentially the first light hole. The frequencies and probabilities for the allowed and forbidden optical transitions have been computed[20] as a function of the electric field and are shown in Fig. 3. It must be stressed that the calculation of transition probabilities is very helpful for identifying the experimentally observed transitions.

In order to compare theory and experiments, the RRS and PLE frequencies are shown together in Fig. 4 as a function of the electric field. The Raman data have been shifted 36 meV (the LO-phonon frequency of GaAs) to lower energies to take care of the fact that the reso-

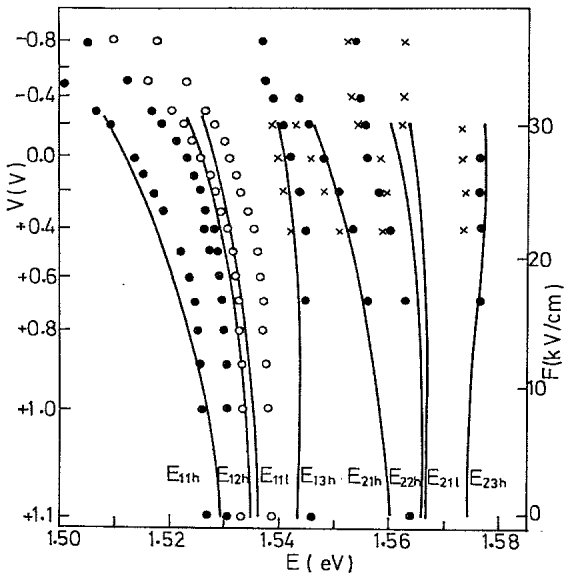

FIG. 4. Experimental energies of the electronic transitions as a function of the applied voltage and electric field. The Raman data (X) has been shifted by 1 LO phonon to lower energies in order to convert then to incoming resonances (see text). PLE data are also shown for the assigned transitions (solid circles) and for tentatively ascribed higher-order exciton states (open circles). The curves depict the calculated results (from Fig. 3). For zero field the heavy- and light-hole character is indicated.

nances are mainly "outgoing".[21] Besides the good agreement found between RRS and PLE data in the common region (1.54–1.58 eV) one observes that all the experimental results are well accounted for by the theory. Thus the transitions involving the first valence-band state E_{11} ($E_{11h}=1.527$ at zero field) and E_{21} ($E_{21h}=1.56$ at zero field is forbidden) show the highest rate of frequency change with the field. This rate decreases with increasing band index. The E_{12} (E_{12h}) and E_{14} (E_{13h}) transitions, initially forbidden, appear slightly below 20 kV/cm. For this field the second and third valence-band states have a strongly mixed heavy and light character and their oscillator strengths become comparable. At higher fields E_{12} loses intensity again (Figs. 2 and 3) whereas E_{14} is still growing above 30 kV/cm (Figs. 1 and 3). The E_{22} and E_{23} transitions, (only E_{22} is allowed at zero field) increase their energy difference around 30 kV/cm (Figs. 1 and 3, this splitting is not observed in PLE). The theory predicts that the E_{24} transition, forbidden at zero field, reaches its maximum intensity around 20 kV/cm, decreasing again for higher fields without changing appreciably its frequency (Fig. 3). This behavior is borne out in the experimental results (Fig. 1). The peaks running parallel to E_{12} (E_{12h} at zero field) and shifted 3 and 10 meV towards higher energies, respectively (open symbols in Fig. 4), are tentatively assigned to higher-order excitonic counterparts of E_{12} interacting with other states.[22]

In conclusion, we present a RRS study of the effect of an electric field on the energies and intensities of electronic transition in QW. In a given energy range this technique has advantages over PLE, which has been used here for comparison purposes. Allowed and forbidden transitions are observed in both techniques, and their complex dependence on the field is well accounted for by a theory including mixing of valence band states.

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