Resonant Raman scattering in GaAs induced by an embedded InAs monolayer

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We studied the resonant Raman intensity of GaAs optical phonons when the laser energy is tuned to the optical transition of an InAs monolayer embedded in the bulklike GaAs. The GaAs longitudinal-optical modes interact with heavy and light holes of the InAs via elastic scattering followed by Fröhlich interaction. The redshift of the Raman profile compared to photoluminescence excitation measurements and the vanishing of the GaAs resonance around 30 K are explained by the homogeneous exciton linewidth in the InAs monolayer.

Resonant Raman spectroscopy is a widely used tool for the investigation of both vibrational and electronic properties of semiconductors, as the scattering intensity is enhanced for energies of incoming or scattered light close to an allowed optical transition.[1] In polarization-dependent Raman experiments, the symmetries of the involved electronic states can also be studied. Consider a quantum well of only a few monolayers thickness embedded in a larger band-gap zinc-blende-type material. Electrons and holes are tightly bound to this monolayer, but their wave functions extend deeply into the surrounding material. While thicker quantum wells are often linked to the textbook example of a simple square potential, the monolayer corresponds to a δ-like potential. The broken symmetry perpendicular to the layer plane—the growth direction—reduces the point group of the structure to $D_{2d}^{\star}$ including spin.[2,3] The symmetry of the electronic state ($E1$) at the Γ point is the same as for bulk, Γ_6, whereas the bulk Γ_8 valence-band state splits into two states with Γ_6 (heavy hole, HH1) and Γ_7 (light hole, LH1) symmetry. In-plane polarized light can couple the Γ_6 and Γ_7 valence bands to the Γ_6 conduction band. In contrast, optical transitions for z-polarized light are only allowed between the Γ_7 light hole and the Γ_6 electronic state.[2,4]

Alexandrou *et al.*[5] studied the symmetries of the valence-band states and the selection rules for optical absorption by circularly polarized Raman experiments. They performed resonant measurements on a GaAs/AlAs superlattice with the light propagating along the growth direction. The maximum of the Raman enhancement was found to differ by ≈ 20 meV in the corotating and contrarotating spectra, in agreement with doubly and triply resonant conditions. The intensity under corotating polarization they explained by an impurity-induced second-order Raman process and the mixing of the valence-band for $k \neq 0$ similar to the two-phonon case.[6,7] Recently, our group studied heavy- and light-hole splitting in an InAs/GaAs monolayer by polarization-dependent photoluminescence measurements.[4] The splitting was found to be a few meV at low temperatures, increasing strongly with temperature. The increase is due to the different temperature renormalization for the heavy- and light-hole states. Also, we found that the in-plane component of the light-hole wave function is small compared to the z-polarized one.

In this paper we present Raman measurements on an InAs/GaAs monolayer structure with in-plane scattering ge-ometries. We investigate the scattering intensity of the GaAs LO modes when the laser is tuned in resonance with the optical transitions of the InAs monolayer. The resonance maximum of the GaAs modes depends on the polarization of the incoming photon, in good agreement with the heavy- and light-hole splitting of the InAs valence states. We also investigate the dependence of the Raman profile on the exciton coherence lifetime, as previously described by Shields *et al.*[8]

The sample consisted of a single InAs layer with an effective thickness of 1.5 ML, embedded in 600-nm bulklike GaAs with two $Al_{0.5}Ga_{0.5}As$ cladding layers forming a waveguide. It was grown on top of a buffer superlattice by metalorganic vapor phase deposition on a semiinsulating (001) GaAs substrate. The InAs monolayer fundamental transition is about 100 meV below the GaAs band gap. Raman experiments were performed at low temperatures (2–40 K) in backscattering geometry from the cleaved edge of the sample, with the light propagating along the monolayer plane in the $(\bar{1}10)$ direction and polarized parallel (x') or perpendicular (z) to the monolayer. The inset of Fig. 1 shows a sketch of the setup and the coordinate system used. Raman spectra were excited with a Ti-sapphire laser, tuned from
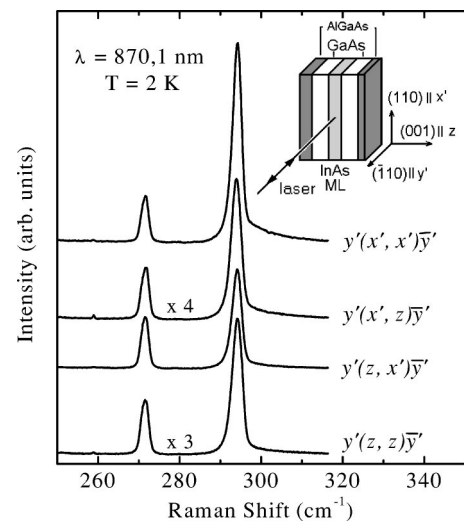

FIG. 1. Raman spectra recorded at $T=2$ K with an excitation energy of 1.424 eV. The scattering geometry is given in Porto's notation. The inset shows a sketch of the sample and the scattering geometry.
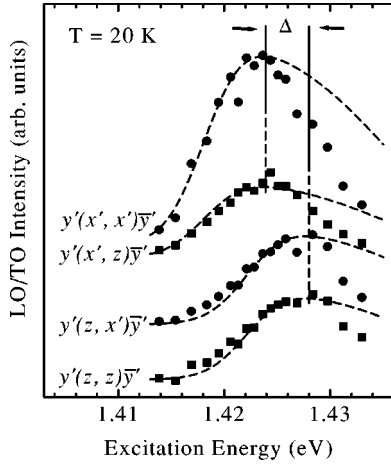
FIG. 2. Raman profiles of the 1.5-ML InAs/GaAs heterostructure. The Raman profiles show the scattering intensity of the GaAs LO-phonon mode normalized to the TO scattering intensity as a function of incoming photon energy. The lines were calculated with Eq. 2 and the parameters given in the text. The center E_i of the distribution is at 1.444 eV for x'-polarized incoming light, and at 1.448 eV for z-polarized *incoming* light.

1.41 to 1.435 eV, which covers the energy range of the InAs monolayer optical transitions. The scattered light was analyzed by a triple-grating spectrometer and detected with a charge-coupled-device camera.

In Fig. 1 we show Raman spectra excited with an energy of 1.424 eV close to the energy of the InAs monolayer fundamental transition; the spectra were recorded at 2 K with four different polarizations (compare the inset). The GaAs LO (296 cm^{-1}) and TO (273 cm^{-1}) frequencies are the same as in the bulk material. The much weaker InAs phonons are not visible on the scale of Fig. 1; they were discussed elsewhere.[9] The GaAs LO scattering is up to four times stronger than the TO scattering intensity, although LO scattering by deformation-potential interaction is forbidden in this geometry. In resonance, Fröhlich interaction can induce normally forbidden LO scattering. As the Raman tensor for Fröhlich interaction has A_1 symmetry, Fröhlich-induced one-phonon scattering is allowed only for parallel polarization of the incoming and outgoing light. However, we, as others,[5,10] observe LO scattering in crossed polarizations as well. Note that the spectra in the two crossed polarizations are not symmetric, which points to an incoming resonance with two different electronic transitions. The two resonances become more obvious in Fig. 2, where we show the LO scattering intensity as function of the incoming laser energy. Since we found the TO intensity to be independent of the excitation energy, we normalized the LO intensity to the TO intensity in Fig. 2. The GaAs LO phonon is resonant with the InAs transitions in all polarizations, but the Raman profile depends on the polarization of the incoming light: In (x',x') and (x',z) configurations the maximum is at 1.424 eV, whereas the strongest enhancement is at an excitation energy of 1.428 eV for (z,z)- and (z,x')-polarized light.

According to the selection rules for optical absorption, x'-polarized incoming light mainly couples the heavy-hole Γ_6 state with the conduction band; for z-polarized light only
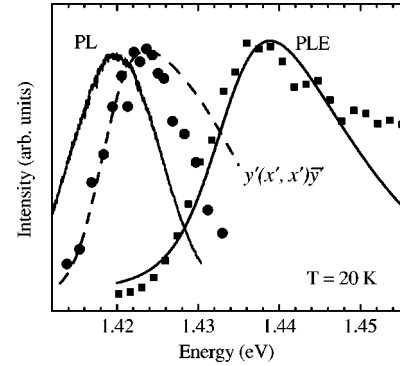

FIG. 3. Photoluminescence (PL), photoluminescence excitation (PLE) spectra, and the $y'(x',x')\bar{y}'$ Raman profile of the 1.5-ML InAs/GaAs heterostructure at 20 K. The PL and PLE spectra were recorded with the light polarized parallel to the monolayer plane (x'). The solid and dashed lines were calculated with Eqs. (1) and (2), respectively.

transitions starting from the Γ_7 light-hole valence-band are allowed. The observed energy difference $\Delta = 4$ meV between the two resonances agrees well with the valence-band splitting as determined by photoluminescence measurements.[4] Nevertheless, a simple one-phonon Fröhlich process cannot explain the spectra in crossed polarization; a higher-order impurity induced process has to be invoked.[5,7] If the wave-vector component parallel to the layer plane is different from zero, $k_\parallel \neq 0$, the valence bands are of mixed heavy- and light-hole character. This gives rise to a fourth-order process where the hole first is scattered by an impurity to a mixed state away from the Γ point; the phonon scatters the hole back to a virtual state, thereby fulfilling k conservation. For a transition starting from the light-hole state (z-polarized incoming light) doubly resonant conditions may arise, in contrast to a heavy-hole absorption as the first step. Therefore, the Raman profiles in (x',z) should be weaker than in the (z,x') configuration. This is not clearly seen in our measurements, which is probably due to the very small valence-band splitting of only 4 meV, in particular, when compared to the phonon energy of ≈ 36 meV. On the other hand, the light-hole resonances, i.e., the (z,x') configuration, are in general weaker in quantum wells than the heavy-hole ones.[8]

Up to now we did not discuss the absolute position of the measured Raman profiles. In Fig. 3 we again show the Raman intensity in $y'(x',x')\bar{y}'$ as a function of the laser energy together with x' polarized photoluminescence and photoluminescence excitation (PLE) spectra. The PLE peak at 1.439 eV corresponds to the HH1 exciton of the InAs monolayer. The photoluminescence peak is shifted by about 20 meV to lower energy, partly due to exciton localization effects caused by fluctuations in the monolayer width. In addition, we find that the Raman profile is shifted to the *red* with respect to the PLE spectrum. The energy shift between the Raman profiles and the PLE peak can be attributed to an inhomogeneously broadened exciton linewidth, as shown by Shields *et al.* for a GaAs/AlAs multiple quantum well.[8]

Consider a quantum well with a small fluctuation in the

width and hence confinement energy. In wider-well regions the exciton states are energetically lower, and vice versa. If an exciton at energy E_h can scatter with equal probability to all energetically lower states, the homogeneous linewidth $\Gamma_h(E_h)$ of the exciton is determined by the number of exciton states below E_h. Therefore, $\Gamma_h(E_h)$ increases with E_h depending on the distribution of homogeneously broadened exciton states.[11] The smaller linewidth, i.e., longer lifetime, makes the resonances for the excitons with lower energy stronger, thereby shifting the maximum of the Raman profile to the red.

In order to describe our results quantitatively we assume a Gaussian distribution $G(E_h)$ of exciton states, centered at E_i with a half-width Γ_i. $\Gamma_h(E_h)$ is obtained by integrating the Gaussian distribution from $-\infty$ to E_h; a second integration over all homogeneously broadened states yields the absorption of the monolayer. In the approximation that the PLE spectrum resembles the absorption, Shields et al.[8] obtained the PLE intensity as

$$I_{\text{PLE}}(E) \propto \int_{-\infty}^{\infty} \frac{\Gamma_h(E_h)G(E_h,E_i,\Gamma_i)}{(E_h-E)^2+\Gamma_h^2} dE_h. \qquad (1)$$

The resonant Raman scattering (RRS) intensity for an incoming resonance with the Gaussian-like distributed exciton states of energy E_h may be written as

$$I_{\text{RRS}}(E) \propto \int_{-\infty}^{\infty} \frac{G(E_h,E_i,\Gamma_i)}{(E_h-E)^2+\Gamma_h^2} dE_h. \qquad (2)$$

Note that Eq. (2) considers only the strongest resonant term in the Raman matrix element, and does not fully account for the higher order process. The additional factor of $\Gamma_h(E_h)$ in Eq. (1) compared to Eq. (2) leads to a shift of the Raman profile.

The PLE spectrum and the resonant Raman profile calculated with Eqs. (1) and (2) are shown in Fig. 3 by full and dashed lines, respectively. The parameters were $E_i = 1.444$ eV for the $y(x',x')\bar{y}$ Raman profile, $\Gamma_i = 14.5$ meV, $\Gamma_0 = 2\times10^{-6}$ eV, and $\Gamma_1 = 1\times10^{-2}$ eV, where Γ_0 and $(\Gamma_0+\Gamma_1)$ are the low- and high-energy limits of Γ_h. It is seen that the energy shift between the PLE peak

and the Raman profile is reproduced well by this calculation. We find, however, that the measured Raman profile is less asymmetric than the calculated one. A possible reason for this is that the measured PLE spectrum resembles the exciton continuum state more closely than the ground state. The energetic difference between the Raman profiles and the PLE peak should actually be lowered by the exciton binding energy. A smaller energy difference in our calculations results in a less asymmetric Raman profile, as we find experimentally. The calculated Raman enhancement for the other configurations are shown in Fig. 2. We used the same parameters as given above, except that the center of the exciton distribution E_i was shifted to 1.448 eV for z-polarized incoming light. The overall agreement is similar to that in Fig. 3, the Raman profiles being less asymmetric than predicted by Eq. (2).

As first pointed out by Zucker et al., the temperature dependence of the homogenous linewidth leads to a strong decrease of the resonant Raman intensity with rising temperature.[12] The excitonic nature of the InAs electronic states involved in the scattering process is confirmed by the temperature dependence of the GaAs LO scattering: We find a sharp decrease of the maximum Raman intensity from 2 to 40 K. Around 30 K the resonance of the GaAs modes vanishes. This is precisely the behavior expected for the resonant Raman intensity for localized excitonic states.[12,11]

In conclusion, we studied the polarization and temperature dependence of the GaAs Raman scattering in an InAs/GaAs monolayer if the laser is in resonance with the InAs optical transitions. We found that the Raman profiles of the LO GaAs modes depend on the polarization of the incoming photons, in agreement with the optical selection rules and the heavy-hole–light-hole splitting (4 meV) of the InAs monolayer. The redshift of the Raman resonance enhancement compared to the PLE spectrum is due to fluctuations in the monolayer width and the dependence of the excitonic lifetime on its energy.

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