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Acoustic-phonon Raman scattering in InAs/InP self-assembled quantum dots

J. R. Huntzinger,* J. Groenen, M. Cazayous, and A. Mlayah
Laboratoire de Physique des Solides, UMR5477 Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cédex 4, France

N. Bertru, C. Paranthoen, and O. Dehaese
Institut National des Sciences Appliquées, 20 Avenue des buttes de coesmes, 35043 Rennes Cédex, France

H. Carrère and E. Bedel
Laboratoire d'Analyse et d'Architecture des Systèmes, UPR8001, 7 Avenue du colonel Roche, 31077 Toulouse Cédex, France

G. Armelles
Instituto de Microelectronica de Madrid, CSIC, Isaac Newton 8, 28760 Tres Cantos, Madrid, Spain

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Single layers of self-assembled InAs/InP quantum dots (QD) are studied by Raman scattering excited in resonance with the confined E_1 transition of InAs. Intense periodic oscillations are observed in the low-frequency Stokes and anti-Stokes spectra of both capped and uncapped QD. By using a controlled chemical etching, we progressively reduced the thickness of the InP cap layer. We found that the oscillations period is determined by the sample surface-QD layer separation and by the sound velocity of the longitudinal acoustic phonons. A model based on the interaction between confined electronic states and standing sound waves due to the sample surface showed a reasonable agreement with the measurements. The dependence of the low-frequency scattering on QD size is discussed.

Recent progress in controlling the growth of highly strained semiconductor layers has allowed the appearance of a new class of quantum systems referred to as self-assembled QD. The interest lies in the potential applications in optoelectronic devices, especially in infrared laser emitters, and in the fundamental physics related to quantum confinement. In particular, quantum confinement strongly affects the electron-phonon interaction and subsequent effects such as energy relaxation dynamics and homogeneous broadening of interband transitions.[1,2] Investigations of the optical and acoustical phonons and their coupling to electrons have been carried out in zero-dimensional systems using Raman spectroscopy. However, up to now the published Raman studies devoted to self-assembled QD concern only optical phonons in connection with strain, alloying and vibrational confinement effects.[3–7] In contrast, Raman scattering by both optical[8–11] and acoustical phonons[12–14] has been investigated in nanocrystals embedded in solid matrices (semiconductor doped glasses) and in colloidal nanoparticles mainly of II-VI compounds. There, confined acoustic phonons were observed and their frequency dependence on QD size well established.[12]

In this paper we report on Raman scattering by acoustic phonons in InAs/InP self-assembled QD. Intense periodic oscillations of the scattered intensity are observed for resonant excitation with the confined E_1 transition of InAs. To the best of our knowledge, such features were not reported before for QD structures. Evolution of the oscillations period and intensity with separation between the free surface of the sample and the QD layer is pointed out. Calculations based on the interaction of confined electronic states with acoustic phonons are compared to the experimental data. We found that the oscillatory behavior of the low-frequency Raman scattering is possibly due to the proximity of the sample surface acting as a sound wave mirror.

Two samples (labeled *A* and *B*) of buried nm-sized InAs QD were grown on InP (001) by gas source molecular beam epitaxy. The QD are formed with a 2.1 monolayer (ML) InAs deposition. The average QD dimensions are as follows: height $h=5$ nm and width $w=70$ nm. The QD are capped by a InP layer: 15 nm for sample *A* and 20 nm for sample *B*. Details of the growth conditions are described elsewhere.[15] Notice that the QD are on the top of a 1.5 ML wetting layer (WL). Results obtained on a sample (sample *C*) with uncapped QD (corresponding to a 5 ML InAs initial deposit) are also presented; $h=5$ nm and $w=40$ nm.

Chemical etching was performed to reduce the InP cap layer thickness for sample *A*. $AH_3PO_4(85\%){:}H_2O_2(30\%){:}H_2O(1{:}1{:}10)$ solution was used; it allows a very slow InP etch rate, around 3 nm/min at room temperature.

Raman measurements were performed at room temperature using a T800 Coderg triple monochromator setup coupled with a conventional monochannel detector. Samples were kept in vacuum, in order to avoid air related Raman peaks in the low frequency range. Resonance enhancement of the scattering has been achieved using several Ar^+ laser lines.

Figure 1 presents Raman spectra of sample *A* excited in the vicinity of the E_1 transition of InAs and detected in both optical and acoustical phonon frequency regions. Before focusing on the low-frequency range, we briefly comment on the scattering due to longitudinal optical (LO) phonons which gives valuable information on the E_1 transition in the QD and in the wetting layer. Following Ref. 16, one can identify both transitions by tuning the excitation energy in order to selectively enhance the signal of either the QD or the wetting layer.

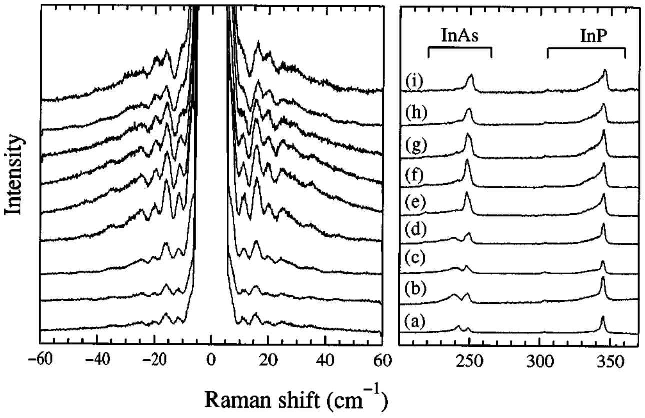

FIG. 1. Raman spectra of sample *A* recorded in the acoustical and optical phonon frequency regions (left and right panel, respectively). Spectra (*a*) to (*i*) were excited at 2.41, 2.47, 2.50, 2.54, 2.60, 2.62, 2.66, 2.71, and 2.73 eV, respectively.

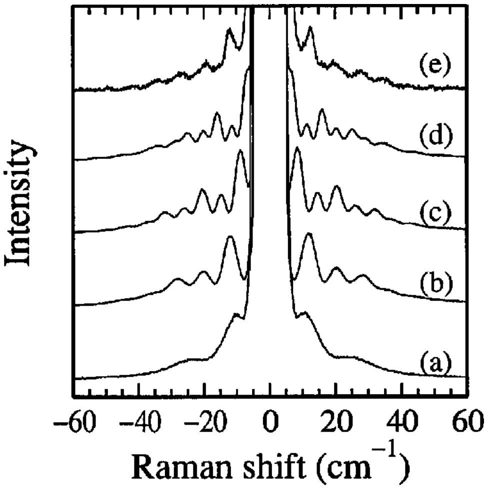

FIG. 2. Low frequency Raman spectra: (*a*) sample *C* (uncapped QD), (*b*) sample *A* etched 2 min (9 nm cap), (*c*) sample *A* etched 1 min (12 nm cap), (*d*) sample *A* (15 nm cap), (*e*) sample *B* (20 nm cap). Spectra were excited at 2.54 eV.

The spectra in Fig. 1 display InAs and InP LO peaks. Because of small deviations from the backscattering configuration, weak structures due to transverse optical phonons are also observed. Two resonances can be identified from Fig. 1. The first one occurs around 2.47 eV and is assigned to the wetting layer.[16] Different contributions typical of ultrathin two-dimensional quantum wells can be pointed out in the signal of the wetting layer: first and second confined LO modes [spectrum (*a*)], and also InAs-like interface phonons [spectra (*b*) to (*d*)]. The latter have their counterpart in the InP frequency range. As matter of fact, the InP LO peak is asymmetric on its low-frequency side due to scattering by InP-like interface phonons. The second resonance is around 2.7 eV. As reported in Ref. 16, this resonance is assigned to the QD. According to the QD dimensions, only one InAs LO peak is observed in spectra (*e*) to (*i*). It is noteworthy that only the samples with capped QD exhibit the two resonances discussed above. For the sample with uncapped QD, no InAs-like E_1 transition related to the wetting layer could be detected, certainly because of oxidation. The fact that the E_1 transition energy of the wetting layer is lower than that of the QD, and even than that of the bulk InAs, has been already reported in modulation reflectivity and Raman measurements but is still not understood.[16]

Let us now discuss our experimental findings. As can be seen in Fig. 1, intense and equally spaced oscillations of the low-frequency Raman scattering are clearly observed in both Stokes and anti-Stokes regions. The oscillations period is about 4.5 cm^{-1}. The frequencies of the intensity maxima showed no appreciable change with excitation energy, whereas a resonant enhancement of the Raman scattering is observed around the E_1 transitions of both the wetting layer and the QD. The overall scattered intensity smoothly varies with excitation energy certainly because of inhomogeneous broadening due to thickness fluctuations of the wetting layer and size distribution of the QD. The spectral shape of the low-frequency scattering does not change when varying the incident power density from 0.2 to 4 kW cm^{-2}.

The observed oscillations cannot be interpreted in terms of acoustic vibrational modes confined inside the QD as reported for nanoparticles embedded in a glass matrix. The first reason is the acoustic impedance of InP (barrier) and of InAs (wells) which are very similar and should lead to rather weak confinement effects in contrast with the strong oscillatory behavior of the scattering in Fig. 1. The second reason concerns the QD size. According to the average height and width of the QD, we found that confinement models do not account for the frequencies of the intensity maxima. A strong indication for the origin of the observed scattering can be found in the oscillations period $\Delta\omega$. Indeed, assuming InP longitudinal acoustic phonons with sound velocity[17] v_p and $\Delta\omega = (v_p \pi/d) = 4.5$ cm^{-1}, we deduce $d \approx 18$ nm which is roughly the thickness of the InP cap layer for sample *A*. To establish whether the oscillation period $\Delta\omega$ depends on the cap layer thickness, we chemically etched sample *A*. This method has the advantage of changing only the cap layer thickness, and thus changes in QD size and shape, from a growth run to another, are avoided.

Figure 2 shows Raman spectra of sample *A* before and after one and two min etching. The oscillation period of the low-frequency scattering has increased from 4.5 to 8.3 cm^{-1} when decreasing the cap layer thickness. According to the spectrum of sample *C* (Fig. 2), oscillations are also present for uncapped QD; their period is rather large (13.3 cm^{-1}). Moreover, Fig. 2 also shows that the relative intensities of the oscillations depend on the cap layer thickness. Indeed, whereas in spectrum (*b*) the oscillation intensity decay is monotonic, a modulation of the intensity at twice the period is observed in spectrum (*c*) and even more clearly in spectrum (*d*). Indeed, each intense oscillation (first and third) is followed by a weaker one (second and fourth). This modulation becomes thus more pronounced when the cap layer thickness increases. At first sight, the spectrum of sample *B* is rather odd (Fig. 2): unlike what is expected, the oscillation period (8.3 cm^{-1}) is larger than the one reported for sample *A* (4.5 cm^{-1}). However, owing to its thicker cap layer, we expect the intensity modulation discussed above to be stronger for sample *B*. Therefore, we suggest that only one oscillation of two is observed in spectrum (*e*) (i.e., only the intense peaks remain). The measured frequency separation should then be twice a period and not a period.

We shall now attempt to account for these data. Let us

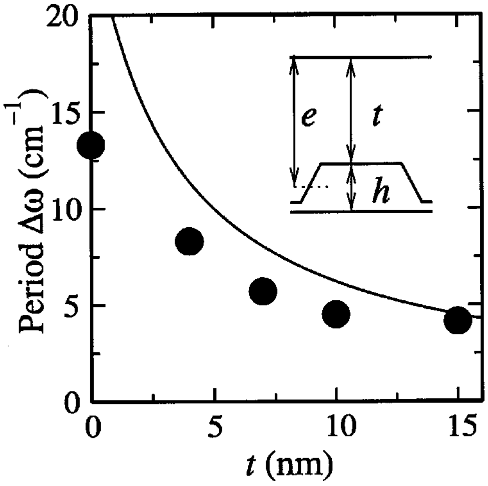

FIG. 3. Plot of the measured (dots) and calculated (full line) periods of the low-frequency oscillations $\Delta\omega$ as a function of the top layer thickness t. $e = t + h/2$ is the distance between the surface and the QD center as shown in the inset.

consider Raman scattering by *bulklike* acoustical phonons in a single QD. We assume deformation potential interaction between electrons and phonons. Because of the lack of translational invariance, due to spatial confinement of the electronic wave functions, vibrational modes with wave vectors belonging to the whole Brillouin zone do participate in the scattering of light. Therefore, a continuous spectrum of acoustical phonons' emission and absorption should come out in the low-frequency range. Its shape reflects the phonons' density of states, the electronic confinement and the wave vector dependence of the electron-phonon interaction. This has been already reported for single[18] and multiple two-dimensional quantum wells,[19–21] and is relevant to our case where confinement along the growth axis is much more important than in the plane.

Figures 1 and 2 clearly show oscillations instead of a monotonic scattering. The dependence of these oscillations on the cap layer thickness indicates that the spatial separation between the QD layer and the sample surface plays an important role. At least two possible ways of generating a periodic modulation of the QD spectrum can be mentioned.

First, due to the proximity of a free surface, acoustic modes are standing waves with an antinode at the surface. Deformation potential electron-phonon interaction is proportional to the strain, which is maximum at the nodes of the standing wave.[22,23] We consider scattering by electrons in the fundamental state of the QD. As the wavelength of the acoustic phonon is varied, the electron centered on the QD experiences alternatively nodes and antinodes of the standing wave. As a result the Raman efficiency oscillates. The period of these oscillations is $\Delta\omega = (v_a \pi / e)/(1 - (1 - v_a / v_p) t/e)$, where v_p and v_a are the longitudinal sound velocities of InP,[17] and InAs,[24] respectively. t is the top layer thickness and $e = t + h/2$ is the distance between the surface and the QD center (see inset of Fig. 3). Figure 3 shows $\Delta\omega$ calculated as a function of the top layer thickness t ($h = 5$ nm was assumed for all samples). The period has been divided by a factor of 2 for sample B (see comments of Fig. 2). A qualitative agreement with the measured periods is obtained. The calculated curve presents an overall shift with respect to the experimental data. These discrepancies may have different origins. The cap layer thickness may not be nominal. In addition, actual electronic states are probably not centered in the QD. Fluctuations of QD size and, more important, the mechanical properties of the surface oxide layer have not been taken into account. Moreover, the envelope of the oscillations is related to spatial localization of the resonant electronic state. In Fig. 1, the low-frequency signal related to the wetting layer has a wider extension than the one related to the QD, indicating that the wetting layer electronic state is more localized than the QD state.

Second, electronic states localized in the vicinity of the surface may also induce modulation. These states could originate in the oxide layer, for example. Interferences between the scattering amplitudes associated to the QD layer and to the surface states would also lead to oscillations of the Raman efficiency. For scattering by *bulklike* acoustic modes, one can easily show that the oscillations period is $2\Delta\omega$. So, surface states cannot fully explain the results. However, it could account for the modulation of the oscillations' intensity which occurs at twice the measured periods (Fig. 2). Detailed calculations of the Raman intensities have to be undertaken in order to fully explain our experimental results and to make it possible to extract quantitative information on the confined electronic states and electron-phonon interaction.

In summary, resonant Raman measurements in self-assembled InAs QD were reported. A strong oscillatory behavior of the scattering efficiency was observed in the acoustic phonons' frequency range. We found that the oscillations' period is determined by the distance between the QD layer and the sample surface. We proposed that standing acoustic waves due to the sample surface could be responsible for the observed oscillations. Influence on the Raman scattering of possible surface electronic states was also discussed. In principle, one should obtain similar results with a single 2D layer located in the vicinity of the sample surface. Nevertheless, the spectral envelope of the oscillations strongly depends on dimensionality. Indeed, for a 2D layer, the confinement along one direction leads to the activation of a one-dimensional phonon density of states only. In this case, the Raman spectral shape is flat near $\omega = 0$; whereas for QD it increases linearly with ω because of full three-dimensional relaxation of the wave vector selection rule. In our samples, the QD width is much larger than the height so the spectral shape should not be modified much with respect to the 2D case except close to $\omega = 0$. Obviously, the Rayleigh signal hinders the investigation at very small wave numbers. In order to address this point, real QD having comparable height and width are required.

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*Electronic address: hunt@ramansco.ups-tlse.fr

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