Excitons, Phonons, and Interfaces in GaAs/AlAs Quantum-Well Structures

D. Gammon, B. V. Shanabrook, and D. S. Katzer
Naval Research Laboratory, Washington, D.C. 20375
(Received 19 June 1991)

We report photoluminescence and resonant-Raman-scattering studies of single GaAs/AlAs quantum-well structures. Splittings in the exciton peaks show that there is a large-scale island structure at the interfaces. Shifts in the absolute exciton energies of quantum wells grown at different substrate temperatures and also the form of the optical-phonon energies as a function of both mode index and quantum-well width indicate that there also exists a small-scale structure on the interfaces.

PACS numbers: 63.20.−e, 61.16.−d, 78.30.−j, 78.55.−m

Detailed microscopic descriptions of the structure of the semiconductor-semiconductor heterointerface are required if technology is to take full advantage of the opportunities provided by modern growth techniques. The best understood interface is that of the prototypical GaAs/AlAs system grown along a [100] direction. The perfect or "truly smooth" interface occurs when the cation layers change from pure Ga to pure Al. Deviations of the interface from perfection require a map of the Ga and Al atoms in the interface layers. The most important probe of the interface has been the exciton confined within a GaAs quantum well (QW) and measured by photoluminescence (PL) [1]. From the results of this spectroscopy it has become accepted that the interfaces in the highest-quality samples are approximately one monolayer thick and that the Ga and Al atoms in this monolayer are concentrated in islands with diameters much larger than that of the exciton Bohr orbit (200 Å). This is inferred from the observation that exciton peaks in PL spectra split into doublets or triplets with energy splittings which correspond to QW widths which differ by approximately one monolayer.

The above description of the character of the interface was recently suggested to be incomplete by an experiment using the chemical-lattice-imaging (CLI) technique [2]. This experiment, which was done on samples that earlier PL measurements claimed to be truly smooth, found a significant amount of disorder at the interface. These results have led to the surprising suggestion that the island size distribution is bimodal [3]. In other words, not only is there a peak in the size distribution for islands much larger than the exciton, corresponding to a large-scale structure, but there must also be a significant amount of microroughness, or small-scale structure, on top of the islands. This suggestion has remained controversial, partly because of questions concerning the possibility of damage during the CLI measurement due to the high-energy electron beam, but also because of the limited range of the island size distribution over which previous experiments were sensitive [4,5]. The CLI measurements have a field of view less than 200 Å, and therefore, are not sensitive to long-range structure. On the other hand, the exciton averages over structure with dimensions less than the Bohr diameter. In spite of the large number of investigators that have examined the PL properties of QW's, the results from the most recent studies of the problem remain in conflict. Specifically, it has been argued that the interfaces of the QW can be made truly smooth [5] or exhibit microroughness [3]. In this paper, we take advantage of the recent advances in the growth of high-quality single QW's of GaAs/AlAs [6] and we show by PL and vibrational Raman scattering that it is possible to probe simultaneously the large- *and* small-scale structure of the interface.

We describe results from samples grown by molecular-beam epitaxy. During growth the cation flux was interrupted for 30–120 s at each interface. The best samples have exciton linewidths such that the ratio of linewidth in the PL spectra to doublet splitting is about 0.15. This is as low as any reported in the literature with [7] or without [3,5] pure AlAs barriers. Typical sample structures consist of three independent GaAs QW's with pure AlAs barriers with 600 Å of GaAs between each QW structure. The substrate temperature either was kept the same during the entire growth or else was changed during the 600 Å of GaAs grown before the last QW. The samples were not rotated during growth, to maximize the change in layer thicknesses across the 1.5-in. wafer due to inhomogeneous Ga and Al fluxes. Thus, by moving the laser spot across the sample, the exciton and phonon spectra from each QW could be measured as a function of QW width. At any given point on the sample the widths of the first and second QW's were 2 and 1.5 times the width of the third. This insured that the exciton energies from the different QW's were well separated in energy at any given location on the sample, and also that there was sufficient overlap in the range of QW widths across the wafer so that the sets of exciton energies from the three different QW's could be compared. The barrier layers were kept wide enough (10–40 monolayers) so that tunneling out of the QW's would not change the exciton energies. The GaAs QW width at any given point on the sample was estimated from the exciton energy which was calibrated by reflection-high-energy-electron-diffraction oscillation data and x-ray-diffraction experiments. The PL and Raman measurements were

made at temperatures $T=10$ K and power densities of 1–1000 W/cm^2. The spectra were excited with either an argon laser, a dye laser, or a Ti:sapphire laser which was focused to a spot size on the sample of about 200 μm.

A set of PL spectra from one QW are shown in Fig. 1. The different spectra are taken by moving the laser spot across the sample in steps of 300 μm. At any given point on the sample a doublet is observed which has an energy splitting corresponding to a change in confinement energy due to a difference of one monolayer in GaAs QW width. The exciton peaks are labeled by the number of monolayers in the QW. Note that it is a primary result of this paper that there exists a microroughness at the interface which makes the definition of the QW width ambiguous. As the laser spot is moved, one peak gains intensity at the expense of the other without changing energy until almost all the intensity is in one peak, and then another peak starts to grow approximately one monolayer higher in energy. This quantized movement of the exciton peaks when the laser spot is moved in any direction indicates that *both* interfaces have large island structures [6]. In addition, by moving across the sample it is possible to find places where, because of cation flux nonuniformities, the three different QW's have the same QW width and the same exciton energies to within the exciton linewidth. The quantization of the exciton energies, the equality of the exciton energies from different QW's with the same well width grown at the same substrate temperature, and the lack of any noticeable Stokes shift between the peak energies measured with PL and photoluminescence excitation spectroscopy are entirely consistent with the assertion that the interfaces can be made truly smooth [3,5]. However, as discussed below, we show that this is *not* the proper description for interfaces in the GaAs/AlAs system.

Spectra from two samples in which the growth temperature differed by 30 °C are shown in Fig. 2. Both samples show the same behavior depicted in Fig. 1. However, the two sets of quantized exciton energies are not the same; there is a shift between samples of each quantized energy which is about 40% of the doublet splitting. This occurs over the entire well-width range covered by the nonuniform sample. Moreover, in these samples which contain three QW's, all grown at the same temperature, we find that all QW's on the same sample have sets of exciton energies which are equal to within the linewidth. However, in other samples, in which the temperature was changed after the first two QW's were grown, the corresponding exciton energies of the first two QW's are equal but are shifted from those of the third in a way similar to that shown in Fig. 2. If the interfaces were perfect within an island, the set of exciton energies from a given QW should be independent of sample, depending only on the fundamental properties of GaAs and AlAs. Since this is not the case, and because small changes in the microroughness will cause small shifts in the exciton confinement energies, we conclude that the interfaces, in addition to the large-scale structure, must have a small-scale structure with a length scale much smaller than the exciton diameter. We note that this fine structure, though sensitive to temperature, is remarkably independent of other growth parameters such as the As flux, and also to some extent, the thickness of the AlAs barriers. This must be so because both the As and the Al fluxes are changing across these samples, and yet the set of exciton energies from, for example, the first QW on one side of a given sample matches very closely those of the second QW (grown at the same temperature) on the other side of the same sample.

The resonant Raman measurements (Fig. 3) were made on the third QW of the $T_G=580$ °C sample. In this experiment the PL spectra were excited with high-energy laser light. Then at the same position on the sample, the laser was tuned to create an outgoing resonance with one of the excitons of the multiplet, creating a very large enhancement of the scattered GaAs optical-phonon spectrum. Therefore, the phonon spectrum probes the interface structure within the large island on which the ex-

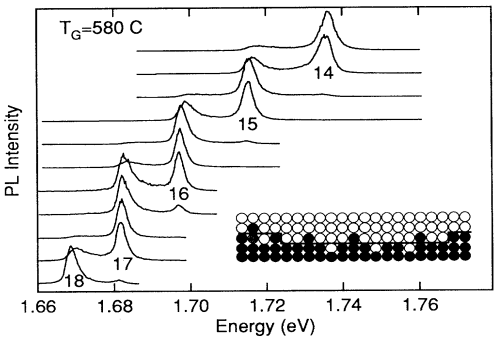

FIG. 1. PL spectra of one QW taken at different spots across a sample. The numbers are the QW widths in monolayers. Inset: A possible schematic representation of the interface. The black and white circles are the two types of cations. The anions have been omitted. The diagram is not to scale since the islands must actually be much larger than the exciton (70 cations in diameter).

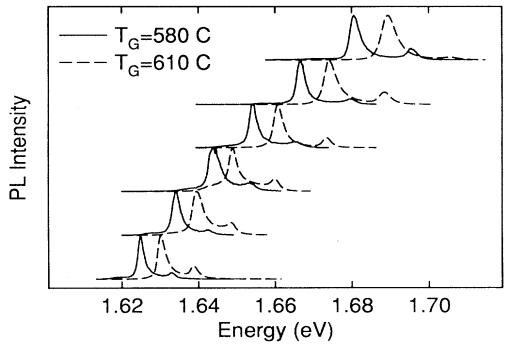

FIG. 2. A comparison of PL spectra from two QW's grown at different temperatures (T_G).

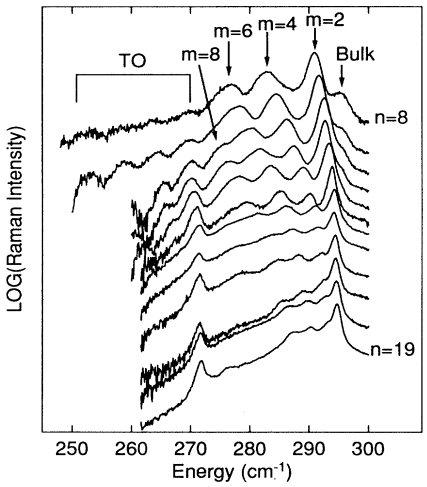

FIG. 3. A logarithmic plot of the resonant Raman spectra of the GaAs optical phonons for each QW width (n). Each of the spectra was recorded in resonance with excitons with energy differences that corresponded to monolayer changes in well width. The confined LO phonons with $m=2$–8 are discussed in the text.

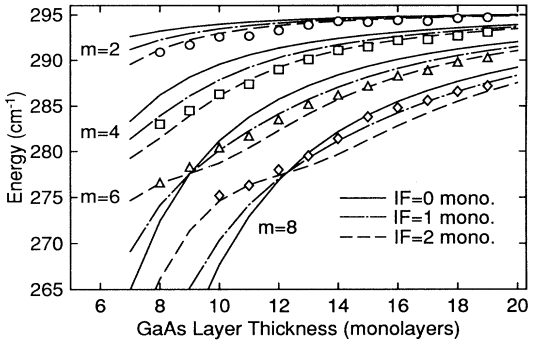

FIG. 4. The measured and calculated confined LO-phonon energies as a function of QW width. The symbols represent the data taken from Fig. 3.

citon that is involved in the resonance process exists. The phonon spectra were taken in resonance with the entire set of quantized excitons by moving the laser spot across the sample. This allows the vibrational properties to be probed as the QW width is changed, monolayer by monolayer. We see only even-order confined phonons, consistent with the resonant Raman selection rules [8]. We see no evidence of forbidden interface phonon scattering. Some forbidden TO phonons are also observed, but we consider only the confined LO phonons here. The energies of these modes are plotted in Fig. 4 as a function of QW width.

The optical phonons, for which there is a large vibrational mismatch between GaAs and AlAs, are confined to the GaAs layer and decay within a monolayer in the AlAs. As a result it is very common for the phonons to be modeled as a particle in an infinite square QW with a width equal to $n+1$ monolayers, where n is the number of GaAs monolayers and the extra one increases the well width to account for the common As atom at each interface [8]. Alternatively, one can use a linear-chain superlattice model with force constants which reproduce the bulk energy bands for GaAs and AlAs [8]. In the case of perfect interfaces both of these simple models yield results that are in good agreement with more sophisticated theoretical calculations [9]. In Fig. 4 the results of a linear-chain-model calculation for perfect interfaces is shown as the solid lines. As apparent in the figure the agreement with the data is poor. In particular, for modes close to the bulk phonon zone center (which we measure as 295.5 cm^{-1}) the phonon energies are shifted down from the calculated energies. However, for energies below approximately 280 cm^{-1} the measured phonon energies cross the calculated curves for perfect interfaces and lie at higher energies. This is evidence of short-range interface disorder and can be understood qualitatively as follows. If the short-range structure at the interface is fine enough the interface layer may be modeled as one or two monolayers of an $Al_xGa_{1-x}As$ alloy [10–12]. The vibrational properties of bulk $Al_xGa_{1-x}As$ have two-mode character, meaning that, in addition to an AlAs-like mode, there is a GaAs-like LO mode with a dispersion curve which is shifted down in energy from that of pure GaAs and flattened out so that it is entirely resonant with the dispersion curve of bulk GaAs at all values of x. We model the interface layer by the two-mode isoamplitude model [13] with force constants which reproduce the bulk alloy dispersion curves for $x=0.5$. The calculated mode energies of the QW are shown in Fig. 4 for one and two alloy monolayers at each interface. Although simplistic, this model reproduces the qualitative behavior of the more sophisticated model of Ref. [9]. It also shows the same behavior as the data; there is a crossover of the curves with those of the perfect structure. This occurs approximately at the beginning of the alloy dispersion curve (278 cm^{-1} in our model). Physically, this crossover occurs because the alloy layer acts like a barrier for modes with energies which do not overlap with the alloy dispersion (i.e., for energies larger than 278 cm^{-1}). For phonon modes with lower energies the interface layer can participate in the vibration and the effective well width becomes wider, thereby reducing the confinement shift and increasing the absolute energies above those calculated with perfect interfaces. The data are fitted qualitatively by the model, indicating that there is a short-range structure at the interfaces. However, we note that the above theory is fairly crude. In particular, we would not expect one or two simple $x=0.5$ monolayers at each interface. Perhaps a more realistic expectation would be as shown schematically in Fig. 1 with two monolayers at each interface—one having large x and the other having small x. We also note that the two interfaces of the QW are unlikely to be totally symmetric.

The phonon data as well as the absolute energies of the excitons clearly demonstrate the existence of a small-scale structure in addition to the large-scale structure required to explain the splitting of the excitons. Although we cannot comment on the objections raised in Ref. [4] concerning the earlier CLI measurements [2,3], the results of our work substantiate the conclusion reached in Refs. [2] and [3] that there can exist interfaces with both large- and small-scale structures. Moreover, we establish that this small-scale structure is sensitive to the growth temperature. In view of the present results on interfaces, which are representative of the best currently available, it must be assumed that the interfaces in other samples, especially those of less well studied systems, are no better and are probably worse. This has important ramifications for many fields of research which involve interfaces. Specifically, it is common for researchers to observe the splitting of the excitons in QW's in a variety of semiconductor systems and ascribe this observation to a *proof* of the existence of truly smooth interfaces. Our study shows that such conclusions must be reexamined. In addition, in vibrational studies it is quite common for the dispersion curves of bulk materials to be deduced from the phonon energies obtained from thin layers. As was pointed out from theoretical considerations in Ref. [9], if a monolayer or two of an alloy exists at the interface, such a conclusion is quite wrong. The phonon data presented above illustrate this quite clearly in that if such a procedure is carried out we find that the dispersion does not follow the parabolic form of bulk GaAs, but in fact becomes closer to linear away from the zone center. Finally we note that in addition to clarifying the nature of the interface, the present data sets of both the exciton energies and the optical-phonon energies, continuously covering a fairly wide range of well widths, monolayer by monolayer, should be valuable to theorists attempting to test detailed models. The application of the techniques described in this manuscript provides an "all optical" method for exploring the parameter space involved in growth to determine whether or not it is possible to grow a truly smooth interface.

This work was supported in part by the Office of Naval Research.

[1] C. Weisbuch, R. C. Miller, R. Dingle, A. C. Gossard, and W. Wiegmann, Solid State Commun. **37**, 219 (1981).

[2] A. Ourmazd, D. W. Taylor, J. Cunningham, and C. W. Tu, Phys. Rev. Lett. **62**, 933 (1989).

[3] C. A. Warwick, W. Y. Jan, A. Ourmazd, and T. D. Harris, Appl. Phys. Lett. **56**, 2666 (1990).

[4] B. Deveaud, B. Guenais, A. Poudoulec, A. Regreny, and C. d'Anterroches, Phys. Rev. Lett. **65**, 2317 (1990); A. Ourmazd and J. Cunningham, Phys. Rev. Lett. **65**, 2318 (1990).

[5] R. K. Kopf, E. F. Schubert, T. D. Harris, and R. S. Becker, Appl. Phys. Lett. **58**, 631 (1991).

[6] D. Gammon, B. V. Shanabrook, D. S. Katzer, Appl. Phys. Lett. **57**, 2710 (1990).

[7] K. Fujiwara, K. Kanamoto, N. Tsukada, H. Miyatake, and H. Koyama, J. Appl. Phys. **66**, 1488 (1989).

[8] For a recent review, see B. Jusserand and M. Cardona, in *Light Scattering in Solids V,* edited by M. Cardona and G. Guntherodt (Springer-Verlag, Heidelberg, 1989), p. 49.

[9] E. Molinari, S. Baroni, P. Giannozzi, and S. de Gironcoli, in *The Physics of Semiconductors,* edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 1429.

[10] B. Jusserand, F. Alexandre, D. Paquet, and G. Le Roux, Appl. Phys. Lett. **47**, 301 (1985).

[11] D. Levi, Shu-Lin Zhang, M. V. Klein, J. Klem, and H. Morkoc, Phys. Rev. B **36**, 8032 (1987).

[12] G. Fasol, M. Tanaka, H. Sakaki, and Y. Horikoshi, Phys. Rev. B **38**, 6056 (1988).

[13] J. Leng, Y. Qian, P. Chen, and A. Madhukar, Solid State Commun. **69**, 311 (1989).