

# Phonons in self-assembled (In,Ga,Al)Sb quantum dots

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Quantum dots of InSb, GaSb, and AlSb were grown on GaAs substrates by molecular beam epitaxy and characterized by atomic force microscopy and Raman spectroscopy. There is a clear correlation between the observation of quantum dots by atomic force microscopy and a phonon mode at an energy a few wavenumbers below the longitudinal optic phonon energy for thick (In,Ga,Al)Sb layers. In the case of nominally AlSb quantum dots, a two-mode behavior is observed and attributed to the segregation of Ga into the AlSb during growth. © 1996 American Institute of Physics. [S0003-6951(96)02007-X]

Strain-induced islands form during heteroepitaxy in many material systems. Under appropriate growth conditions, these islands are isolated, coherent, and sufficiently small to be considered quantum dots (QDs). Because no lithographic patterning is required, the QDs are said to be self-assembled. Recently, QDs have been reported in III-V heterostructures including InAs/GaAs, InGaAs/GaAs, InAlAs/GaAs, InP/InGaP, InSb/GaAs, GaSb/GaAs, and AlSb/GaAs.<sup>1-3</sup> Structural properties have been investigated with atomic force microscopy (AFM), transmission electron microscopy (TEM), and scanning tunneling microscopy (STM). Transport and photoluminescence results have also been reported. These techniques have not, however, provided any direct information regarding the chemical composition of the QDs. In this letter, we observe phonons in quantum dots of InSb, GaSb, and AlSb with Raman spectroscopy (RS). The phonon spectra provide information about the chemical composition of the QDs, and we use the spectra to identify the segregation of atoms from the substrate into the QDs.

We grew samples by molecular beam epitaxy (MBE) on semi-insulating and  $n^+$  GaAs substrates, oriented within  $0.1^\circ$  of (001). Details of the growth are given in Ref. 3. Growth was monitored by reflection high-energy electron diffraction (RHEED). All samples were characterized by RS and ambient AFM measurements. RS data were collected at 4 K in the  $Z(X,X)\bar{Z}$  and  $Z(X,Y)\bar{Z}$  configurations where  $Z$  and  $\bar{Z}$  are the directions of the incident and scattered light,  $(*,*)$  denote the directions of polarization of the incident and scattered radiation, and  $X$ ,  $Y$ , and  $Z$  denote the [100], [010], and [001] crystallographic directions, respectively. Radiation from an Ar ion laser operating at 514.5 nm was employed in the measurements.

AFM measurements of GaAs homoepitaxial layers prior to antimonide deposition reveal 3 Å monolayer steps and large terraces with a lateral spacing of a few tenths of a micron. The growth of all three antimonides appears to follow the Stranski-Krastanov model under certain conditions. After an initial two-dimensional wetting layer is deposited, QDs are formed.<sup>3</sup> We found the onset of dot formation to occur after approximately 1.5 ML InSb, 2.5 ML GaSb, or 3.5 ML AlSb, although these values may be a function of several variables including substrate temperature, surface reconstruc-

tion, growth rate, and anion flux. In Fig. 1, we show AFM images of AlSb on GaAs, grown at 510 °C. For sample A, the nominal AlSb thickness is 2 ML. Monolayer (3 Å) terraces are visible, indicating two-dimensional growth. The AlSb thickness for sample B is 4 ML and three dimensional growth is apparent. QDs with a density of about  $6 \times 10^9/\text{cm}^2$ , height =  $87 \pm 23$  Å, and diameter =  $560 \pm 130$  Å are present. Appropriate growth conditions yield similar QDs of InSb and GaSb on GaAs.<sup>3</sup>

Raman spectra for two GaSb/GaAs samples in the  $Z(X,Y)\bar{Z}$  scattering geometry are shown in Fig. 2. The estimated GaSb coverage, based upon RHEED oscillations for GaSb on GaSb, was 1.8 ML for sample C. AFM measurements indicate a relatively flat surface, with no indication of QDs. Sample D consists of 3 ML GaSb, and AFM reveals about  $10^{10}/\text{cm}^2$  dots with height =  $32 \pm 9$  Å, and diameter =  $280 \pm 40$  Å. As expected, the GaAs longitudinal-optic (LO)

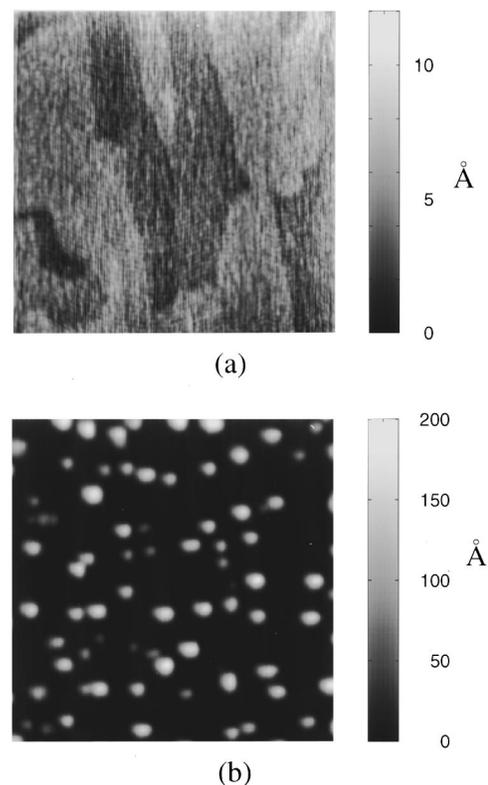


FIG. 1. AFM images ( $1 \mu\text{m}$  by  $1 \mu\text{m}$ ) of 2 ML (a) and 4 ML (b) AlSb on GaAs. Note the large difference in vertical scales. Monolayer steps are visible for A; quantum dots are present on B.

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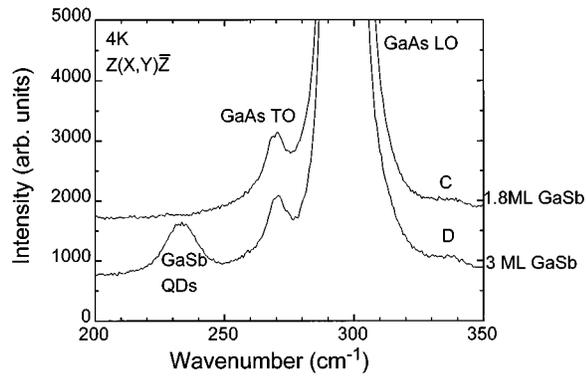


FIG. 2. Low-temperature RS spectra for 1.8 ML (C) and 3.0 ML (D) GaSb on GaAs. AFM measurements reveal QDs for D but not for C. A mode attributed to GaSb QDs is observed at  $234\text{ cm}^{-1}$  for sample D.

mode is present at  $295\text{ cm}^{-1}$  for both samples. In addition, a second weak peak due to the GaAs transverse-optic (TO) mode is present at  $271\text{ cm}^{-1}$ . A third peak at  $234\text{ cm}^{-1}$  is observed only for sample D. Because its energy lies between the energies of the LO ( $238\text{ cm}^{-1}$ ) and TO ( $228\text{ cm}^{-1}$ ) phonons in bulk GaSb, we attribute it to vibrational excitations in the GaSb QDs. The vibrational phonons in bulk GaSbAs alloys exhibit two-mode behavior, with a GaAs-like mode at an energy about  $243\text{ cm}^{-1}$  for small As concentrations.<sup>4</sup> The fact that no such mode is observed for sample D suggests that the dots are composed of relatively pure GaSb.

In contrast, the Raman spectra shown in Fig. 3 for nominally pure AlSb dots indicate that the QDs are composed of an alloy of AlGaSb. The Raman data for sample A, with 2 ML of AlSb and no QDs, is essentially identical to that of a GaAs substrate, sample J. Sample B with 4 ML of AlSb exhibited QDs in the AFM measurements and has a much different spectrum with additional scattering at  $226$  and  $331\text{ cm}^{-1}$ . While the high-energy peak in B, which lies between the LO ( $344\text{ cm}^{-1}$ ) and TO ( $323\text{ cm}^{-1}$ ) modes for bulk AlSb, is expected for AlSb QDs, the peak at  $226\text{ cm}^{-1}$  is not. This low-energy peak is  $8\text{ cm}^{-1}$  below the mode attributed to phonons in GaSb QDs in sample D of Fig. 2. Because of the similarity of this two-peak structure to the two-mode

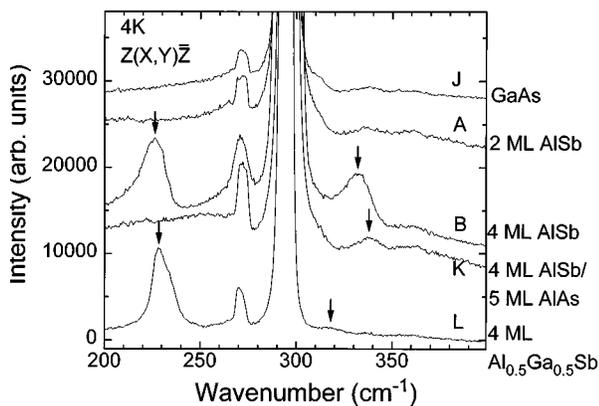


FIG. 3. RS spectra for Al(Ga)Sb layers and a virgin GaAs substrate. QDs are present for samples B, K, and L based upon AFM measurements. Evidence for both AlSb-like ( $315\text{--}331\text{ cm}^{-1}$ ) and GaSb-like ( $226\text{--}228\text{ cm}^{-1}$ ) modes is observed.

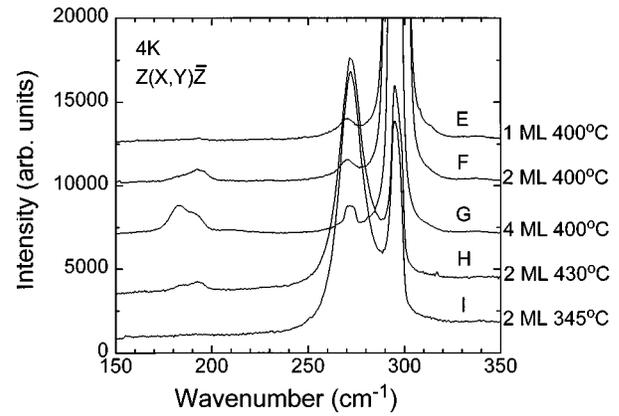


FIG. 4. RS spectra for InSb on GaAs; coverages and growth temperatures are noted. AFM measurements reveal QDs for samples F, G, and H only. These three samples exhibit scattering in the  $182\text{--}192\text{ cm}^{-1}$  range which we attribute to the InSb QDs.

behavior observed in the vibrational properties of bulk AlGaSb alloys, we propose that the two peaks represent the two-mode behavior of phonons in  $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$  QDs. [In bulk  $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$ , the energy of the AlSb-like mode increases from  $319\text{ cm}^{-1}$  ( $x=0$ ) to  $334\text{ cm}^{-1}$  ( $x=1$ ), while the energy of the GaSb-like mode decreases from  $235$  ( $x=0$ ) to  $212$  ( $x=1$ ).<sup>5</sup>] Presumably the alloyed QDs result from Ga segregation from the buffer layer into the AlSb quantum dots during growth. To confirm this hypothesis, we grew two additional samples. Sample K is identical to sample B except that 5 ML AlAs is inserted between the AlSb and the GaAs buffer. For sample L, 4 ML of  $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$  with a nominal  $x$  of 0.5 were grown directly on GaAs. AFM reveals QDs for both K and L. The RS spectra for sample K does not contain a GaSb-like peak near  $226\text{ cm}^{-1}$ , indicating the absence of GaSb in the QDs. The 5 ML AlAs apparently acts as a barrier, preventing Ga segregation into the AlSb layer. The AlSb-like peak moved to a higher energy ( $338\text{ cm}^{-1}$ ), but its intensity decreased. The direction of the peak shift is consistent with bulk AlGaSb alloys. Sample L exhibits a strong GaSb-like mode at  $228\text{ cm}^{-1}$ . The fact that this energy lies between those of samples B and D is qualitatively consistent with the behavior of the GaSb-like mode in bulk AlGaSb alloys. Scattering near  $317\text{ cm}^{-1}$  for sample L could be a weak AlSb-like mode. The lower energy and weaker intensity compared to sample B is consistent with a lower AlSb mole fraction.

The vibrational modes associated with InSb dots are shown in Fig. 4 for five samples of InSb on GaAs with the indicated growth temperatures and coverages. GaAs LO and TO modes are present for all samples. The strong mode near the GaAs TO energy for samples I and H arises from the  $L^-$  plasmon mode of the  $n^+$  GaAs buffer layer. (The other samples are on undoped buffer layers.) The additional scattering near  $182\text{--}192\text{ cm}^{-1}$  for samples F, G, and H is identified with the InSb QDs as the bulk InSb energies are 193 and 182 for LO and TO modes, respectively. There is a clear correlation between the additional scattering and the observation of QDs in AFM. Specifically, sample H, 2 ML of InSb grown at  $430^\circ\text{C}$ , had a QD density of  $3 \times 10^9/\text{cm}^2$  with diameters of  $600 \pm 50\text{ \AA}$  and heights of  $58 \pm 5\text{ \AA}$ . The QD dis-

tribution was similar for sample F, 2 ML InSb at 400 °C. The QD sizes are larger (height= $210\pm 30$  Å, diameter= $1700\pm 300$  Å) and the density is lower ( $3\times 10^8/\text{cm}^2$ ) for sample G, 4 ML at 400 °C, suggesting dot coalescence. Sample E, 1 ML InSb at 400 °C, was relatively flat, with no evidence of dots from AFM. Sample I, 2 ML InSb at 345 °C exhibited a low density of irregular islands.<sup>3</sup> We note that the data is suggestive of two InSb dot related modes, at approximately  $182\text{ cm}^{-1}$  and  $192\text{ cm}^{-1}$ . The higher energy mode is dominant for low coverages (2 ML), and the lower energy mode is stronger for thicker layers (4 ML). This trend was supported by a 3.5 ML InSb sample (not shown) whose vibrational properties were almost identical to sample G. One possible explanation for the occurrence of two phonons is that we are observing two-mode behavior due to the presence of an  $\text{InAs}_x\text{Sb}_{1-x}$  or  $\text{In}_{1-y}\text{Ga}_y\text{Sb}$  alloy. However, InAs-like (small  $x$ ) and GaSb-like (small  $y$ ) modes in bulk layers are found at energies<sup>6,7</sup> near  $200\text{ cm}^{-1}$ , somewhat higher than observed here. The similarity between the energies of the two InSb QD features and the TO and LO modes of bulk InSb suggest another possible explanation: these features may arise from QD vibrations that have quasi-LO and quasi-TO character.

We have observed a strong correlation between the observation of QDs by AFM and phonon modes by RS. One may expect to observe scattering from, for example, the 1.8 ML wetting layer of GaSb that has grown two-dimensionally in sample C. However, we note that the samples are exposed to air before measurement and oxidation of the first few monolayers, including all the wetting layer, is expected. In the case of sample D, 3 ML GaSb, a uniform oxidation of 10 Å would leave a central core of unoxidized GaSb in each QD. The same argument could explain the absence of vibrational excitations from the InSb and AlSb wetting layers. One possible reason for the relatively weak intensity of the AlSb peak in sample K is that rapid oxidation is known to occur for pure AlSb. This tendency is weaker for the AlGaSb alloys, and may explain the larger intensity of the AlSb-like vibrational mode of sample B relative to K.

Phonon modes in QDs or microcrystallite structures have been theoretically investigated by several groups. In some cases, confinement effects were shown to result in a shift of the QD phonon to lower energies. This occurs because of the dispersion of the bulk phonons to lower energies at higher wavevectors.<sup>8-10</sup> In these cases, however, the effect of the polar lattice was neglected. In contrast, other workers ignored the dispersion of the LO and TO phonons and only considered the vibrational excitations that result from dielectric mismatch between the QDs and the surrounding medium. These studies showed that the energies of the surface (interface) phonon modes of the QDs are between the energies of the bulk LO and TO phonons.<sup>11-14</sup> Recently, Roca *et al.*<sup>15</sup> and Chamberlain *et al.*<sup>16</sup> included both the dispersion of the phonons and the mechanical and electrostatic boundary conditions in their calculations. These later works indicate that the phonon modes become of mixed TO, LO, and surface character. Our experimental results are qualitatively consistent with these studies, in that the vibrational excitations occur a few wavenumbers below the bulk LO energy. However, all of the above-mentioned calculations are performed for spherical or spheroid geometries. The QDs stud-

ied here are of lower symmetry. Specifically, the media surrounding our QDs is either oxide or buffer layer and the geometry of the QDs is not spheroidal. Because of this lack of symmetry, we do not expect to observe strong polarization selection rules that would allow a differentiation between the different vibrational excitations probed with Raman scattering. In particular, the Raman scattering observed from the quantum dots in the  $Z(Y,Y)\bar{Z}$  and  $Z(X,Y)\bar{Z}$  geometries are similar in energy and intensity. We note for the GaSb dots that the peak of the vibrational band shifts by  $3\text{ cm}^{-1}$  to lower energy in the  $Z(Y,Y)\bar{Z}$  orientation. This observation is reminiscent of the shift observed between the even and odd confined phonon modes in two-dimensional systems.<sup>17</sup>

In conclusion, we have shown a clear correlation between the observation of quantum dots of GaSb, AlSb, and InSb by AFM and the appearance of a phonon mode a few wavenumbers below the LO phonon of bulk antimonides. This strong correlation suggests that Raman scattering can provide a simple method to explore growth parameter space in search of the conditions required to produce self-assembled QDs. One still requires proximal probe measurements to determine the size and uniformity of the QDs. The proximal probes, however, provide little information about the chemical composition of the quantum dots. In contrast, Raman spectroscopy provides a method to identify the composition of the quantum dots. In particular, the phonon spectra can identify whether atoms are segregating from the substrate into the quantum dots.

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