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Reflectance difference spectroscopy of an ultrathin indium arsenide layer on indium phosphide (001)

C. H. Li, Y. Sun, S. B. Visbeck, D. C. Law, and R. F. Hicks[a)]
Department of Chemical Engineering, University of California, Los Angeles, Los Angeles, California 90095

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A model system has been created which allows the surface and bulk contributions to the reflectance difference spectrum to be distinguished. In particular, an indium arsenide film, less than 10 Å thick, has been grown on indium phosphide (001). Reflectance difference spectra of the InAs/InP surfaces were collected and compared to those of InP and InAs. It was found that the InAs/InP heterostructures exhibited electronic transitions between surface states characteristic of InAs (001), while retaining the surface-perturbed bulk transitions characteristic of InP (001). Furthermore, the optical anisotropy arising from the arsenic dimer bonds was shifted 0.2 eV higher for InAs/InP compared to that for InAs. This shift is proportional to $1/a^2$, where a is the bulk lattice constant. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1523650]

Metalorganic vapor phase epitaxy (MOVPE) is a widely used process to manufacture heterostructures of III–V compound semiconductors.[1] In this process, growth proceeds through a series of surface reactions such as adsorption, diffusion, and desorption of volatile products. Thus, the surface plays an important role in the properties of the structures grown. As device dimensions continue to shrink, it becomes increasingly important to monitor and control the heterogeneous reactions at the atomic scale and in real time. Since the MOVPE process is carried out at pressures ranging from 20 to 760 Torr, only techniques based on photons can be employed to monitor the semiconductor surface during growth.[2,3] Reflectance difference spectroscopy (RDS) has shown potential for this application because it can operate at a wide range of pressures and is sensitive to the structure and chemical composition of the surface.

The physical origin of the reflectance anisotropy has been attributed to contributions from transitions between surface and bulk electronic states.[4–7] Theoretical studies by Aspnes and Studna,[6] and Schmidt *et al.*[7] suggest that the RD signal originates either directly from surface states, or from transitions involving surface-perturbed bulk states. In this study, we have created a model system where these two types of components to the optical spectrum are distinguished. In particular, an ultrathin InAs film less than 1-nm-thick was grown on InP (001) through an arsenic–phosphorus exchange reaction.[8] Reflectance difference spectra were obtained for the (2×1), (2×4), and (4×2) reconstructions of the InAs/InP heterostructure. By comparing these spectra to those of InP and InAs (001), we have identified the bulk and surface contributions to the reflectance anisotropy.

Indium phosphide films were grown in a horizontal MOVPE reactor at 530 °C with 6.5×10^{-4} Torr of trimethylindium, 1.3×10^{-2} Torr of tertiarybutylphosphine, and 20 Torr of hydrogen.[9–11] The H_2 carrier gas was passed through a SAES gas hydrogen purifier (PS4-MT3-H) to remove any remaining oxygen, nitrogen and carbon containing impurities. Indium arsenide samples were grown under similar conditions except with 1.3×10^{-2} Torr of tertiarybutylarsine and a temperature of 560 °C. Following growth, the samples were transferred directly into a UHV cluster tool with a base pressure of 2.0×10^{-10} Torr.[12]

Inside the UHV system, the InP (001) crystals were annealed at 400 °C for 15 min to obtain a clean and well-ordered indium-rich (2×4) reconstruction, as verified by low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM).[11] Arsine was then introduced into the chamber at 1×10^{-5} Torr through a leak valve for 5–200 min (3.0–1200×10^3 L, $1\ \mathrm{L}=10^{-6}$ Torr s) at 250–450 °C. Each InAs/InP (001) reconstruction was characterized by LEED, XPS, and STM.[8] In particular, x-ray photoelectron spectra were collected with a PHI 3057 spectrometer equipped with a hemispherical analyzer, multichannel detector, and Al K_α x-ray source. All XPS spectra were taken in small area mode with a 7°-acceptance angle and 23.5 eV pass energy. A 65° take-off angle with respect to the surface normal was used. Reflectance difference spectra were obtained with an Instruments SA J-Y Nisel reflectance difference spectrometer.[13,14] The signal, $\mathrm{Re}(\Delta R/R)$, corresponds to the real part of $[(R_{[\bar{1}10]}-R_{[110]})/\langle R\rangle]$. Base line correction was achieved by taking the average of two spectra collected with the polarizing axis oriented +45° and −45° relative to the $[\bar{1}10]$ azimuth.

Shown in Fig. 1 are reflectance difference spectra of the InP, InAs/InP, and InAs (001) surfaces recorded at 30 °C. The spectrum of the InP (2×1) contains a sharp negative peak at 1.9 eV, an intense positive peak at 3.1 eV, two positive overlapping bands at 4.1 and 4.6 eV, and a negative feature at 4.7 eV. The 3.1 eV peak arises from the phosphorous dimers on the InP surface.[7] The RD spectrum of the InP (2×4) contains an intense negative band ranging from 1.8 to 2.0 eV, three small positive bands at 2.8, 3.7, and 4.6 eV, and two negative peaks at 3.2 and 4.7 eV. The first negative anisotropy in the (2×4) spectrum is due to transitions between states involving In-dimers on the surface.[7] The 3.2 and

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[a)] Author to whom correspondence should be addressed; electronic mail: rhicks@ucla.edu

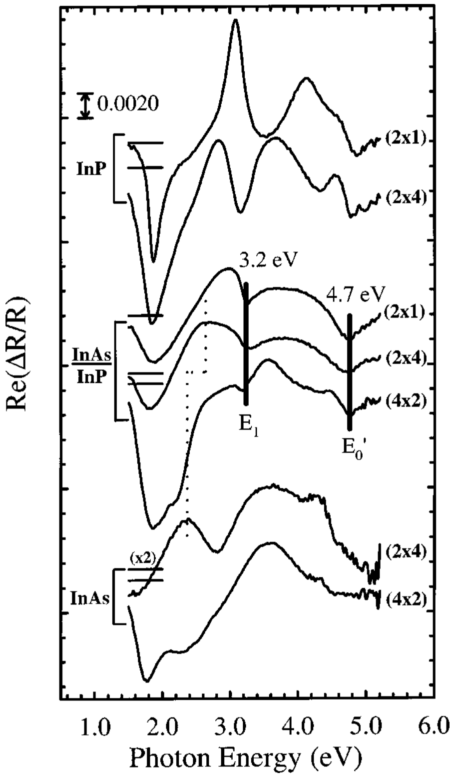

FIG. 1. Reflectance difference spectra of InP, InAs/InP, and InAs (001) surfaces at 30 °C. The locations of the zeros are consecutively indicated for each spectrum by short horizontal lines on the left side of the figure.

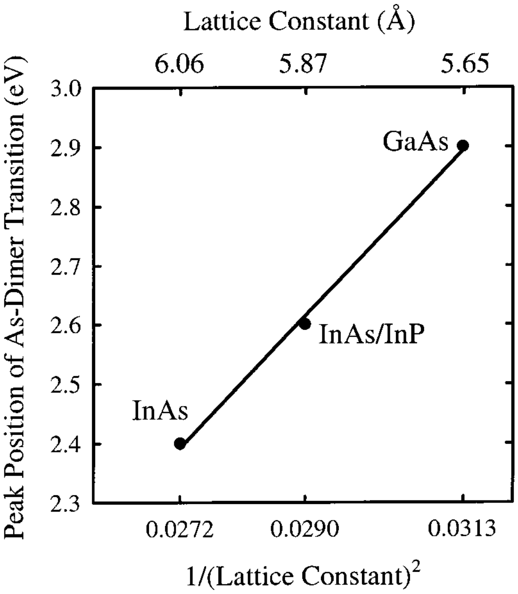

FIG. 2. The position of the RDS peak due to arsenic dimer states as a function of the inverse of the lattice constant squared.

4.7 eV signals are due to transitions involving bulk states, since their energies match the E_1 and E_0' interband critical points of indium phosphide.[15]

The InAs (2×4) RD spectrum contains a positive peak at 2.4 eV, a broadband centered around 3.6 eV, and a peak at 4.3 eV. The feature at 2.4 eV is thought to be due to transitions involving arsenic dimer bonds, while the signal at 4.3 eV coincides with the InAs E_1' bulk critical point.[16–20] When the InAs (001) reconstruction changes from (2×4) to (4×2), a large negative band is observed with minima at 1.8 and 2.3 eV. This feature has been assigned to transitions between states associated with In dimers.[16,17]

The middle three spectra in Fig. 1 are for the indium arsenide films deposited on InP (001) with (2×1), (2×4), and (4×2) reconstructions. The line shapes for the (2×1) and (2×4) are similar: both exhibit a negative band at $\sim$1.8 eV, a positive peak in the region of 2.6–3.0 eV, a broadband centered at approximately 3.6 eV, and two local minima at 3.2 and 4.7 eV. Sobiesierski *et al.*[21] has reported RD spectra of InP (001) surfaces exposed to an As_2 flux in a molecular beam epitaxy chamber at 420–530 °C, which are nearly the same as those reported here for the (2×1) and (2×4) structures. Finally, the RD spectrum of the InAs/InP (4×2) phase exhibits an intense negative band at 1.9 eV with a shoulder at 2.3 eV, a positive peak at 3.5 eV, and two negative depressions at 3.2 and 4.7 eV.

The two minima at 3.2 and 4.7 eV, observed in all the RD spectra of the indium arsenide thin films on indium phosphide, coincide with the E_1 and E_0' bulk critical points of InP. Furthermore, the small 4.3 eV peak observed in the InAs (2×4) and (4×2) spectra, associated with a surface-perturbed bulk transition for InAs,[16,17] does not appear in the data from the InAs/InP heterostructures. This clearly demonstrates that the bulk crystal contributes specific features to the reflectance difference spectra.

On the other hand, the thin film of indium arsenide on indium phosphide exhibits electronic transitions between surface states characteristic of InAs (001). The bands at 1.9, 2.3, and 3.5 eV in the spectrum of the (4×2) reconstruction are seen on both the InAs/InP heterostructure and on the InAs crystal. In addition, for the As-rich (2×4), both the heterostructure and the crystal produce RD spectra with positive bands centered around 2.5 and 3.5 eV. The former, lower energy feature is due to transitions between states associated with the arsenic dimers.[16,17,22]

Further examination of Fig. 1 reveals that the RD band arising from the arsenic dimers shifts from 2.4 eV for InAs (001) to 2.6 eV for the ultrathin film of indium arsenide on indium phosphide. According to an analysis of the energy band structure of tetrahedral solids, transitions associated with the dimer states should scale by $1/d^2$, where d is the dimer bond length.[16,23] Since InP has a smaller lattice constant (5.87 Å) than that of InAs (6.06 Å), the ultrathin indium arsenide layer is under compressive stress, and may produce arsenic dimers with shorter bond lengths. Assuming the dimer bond length, d, is proportional to the lattice constant, a, one can plot the peak position as a function of $1/a^2$ for the As dimers on GaAs, InAs, and InAs/InP. This has been done in Fig. 2, where one obtains a straight line passing through the three points, consistent with the $1/d^2$ relationship. While this is an interesting observation, it is possible that changes to the arsenic dimers other than lengthening their bonds may be responsible for this trend.

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