

Submonolayer sensitivity of InSb on InP determined by friction-force microscopy

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(Received 11 February 1997; revised manuscript received 13 March 1997)

Using molecular-beam-epitaxy-grown InAs and InSb on InP(001) surfaces, we show that the friction-force microscope is sensitive to monolayer coverage. Those surfaces are characterized by three-dimensional islands separated by flat regions. For a constant load, the frictional forces measured on the InAs island and on the substrate are the same. This is due to the formation of a two-dimensional wetting layer (1.5 ML) of InAs covering the InP(001). The frictional force is controlled by the interaction of this layer and the tip. In contrast, the deposition of 2 ML of InSb on InP(001) produces a different behavior. The frictional force changes when the tip moves from the island to the flat region. Photoluminescence and atomic-force-microscopy experiments show the formation of an InSb submonolayer. The sensitivity of the friction-force microscope to monolayer coverage illustrates its usefulness for wetting-layer analysis. Based on these results we discuss the potential of the friction-force microscope to develop a spatially resolved friction spectroscopy. [S0163-1829(97)51920-5]

The understanding of friction at atomic and molecular levels is a subject of intensive research with relevant technological implications. Several experimental and computational techniques are being applied to obtain the fundamental basis of friction, wear, and lubrication.^{1,2} From those studies a picture is emerging where the friction between two surfaces implies hysteresis in the adhesion forces between them.³ It also shows the importance of phonons and electrons as mechanisms to dissipate energy during the sliding of two solid surfaces.⁴

The measurement of lateral forces with an atomic force microscope has introduced a proximal probe technique called friction-force microscopy (FFM).^{5,6} Its rapid development has allowed systematic studies of the friction between a single, nanometer-size asperity and several surfaces.^{7,8} FFM studies have underlined the anisotropy of the friction in crystalline surfaces.^{9,10} It has also been pointed out that lateral forces could be used to differentiate chemical species in heterogeneous samples.¹¹⁻¹⁵ Those findings could establish the basis for a spatially resolved spectroscopy based on force microscopy that could combine high spatial and compositional resolution. However, in many cases the forces contributing to the torsion of the cantilever come from topographic features, capillary or mechanical properties, i.e., not from what could be thought a friction property between the tip and the bare sample surface.

In a previous paper we demonstrated that variations of less than 10% of indium composition in $\text{In}_x\text{Ga}_{1-x}\text{As}$ structures produce measurable changes in the frictional force while the normal load remains constant.^{15,16} Here we report on the sensitivity of the FFM to detect the presence of adsorbed monolayers of semiconductor compounds. We also discuss the potential of FFM to develop a spatially resolved friction spectroscopy.

As model systems to perform FFM studies with stiff and heterogeneous surfaces, we deposited InSb and InAs on semi-insulating InP(001) substrates. Those are highly strained semiconducting materials. It is known that beyond a

certain thickness threshold, the strain can be relieved through free surfaces and substrate deformation. The resulting surface is characterized by the formation of nanostructures and quantum dots. The small size of the structures has raised interest of this process to fabricate devices such as arrays of quantum dots.¹⁷ In this paper, the presence in the same surface of three-dimensional islands (dots) and flat regions in between is used to evaluate, among other properties, the thickness of the overlayer to give a friction signal different from the substrate.

The structures were grown in ultrahigh vacuum using a solid-source molecular-beam epitaxy system (MBE) in a pulsed mode.¹⁸ The MBE was equipped with valved phosphorus, antimony, and arsenide cells. For the FFM examination, the samples have been transferred into a dry N_2 gas chamber. The transfer of the samples from UHV to ambient pressure will imply the formation of a very thin oxidized layer. Auger spectroscopy analysis of InP(001) samples exposed to ambient pressure revealed the presence of oxygen atoms up to a depth of 0.5 nm, i.e., about two atomic monolayers. Similar results should be expected for InSb and InAs samples.

The FFM was operated with commercially available software and electronics.¹⁹ The experiments have been performed with sharpened Si_3N_4 tips with nominal curvature radii below 20 nm. The tips are integrated in cantilevers with torsional constant values of 158 N/m (Olympus, Japan). Absolute values of frictional forces are determined following a method similar to the one used by Meyer *et al.*¹³ Instrumental details can be found elsewhere.²⁰

Figure 1 shows the formation of quantum dots after deposition of 3.5 ML of InAs and InP. The topographic images show the dots as truncated pyramids of lateral dimensions of $60 \times 35 \text{ nm}^2$ (mean values measured in the base), and a mean height of 4.8 nm.

The friction-force image taken simultaneously with the topography does not show any contrast between the top of the dots and the regions between dots. This is better observed

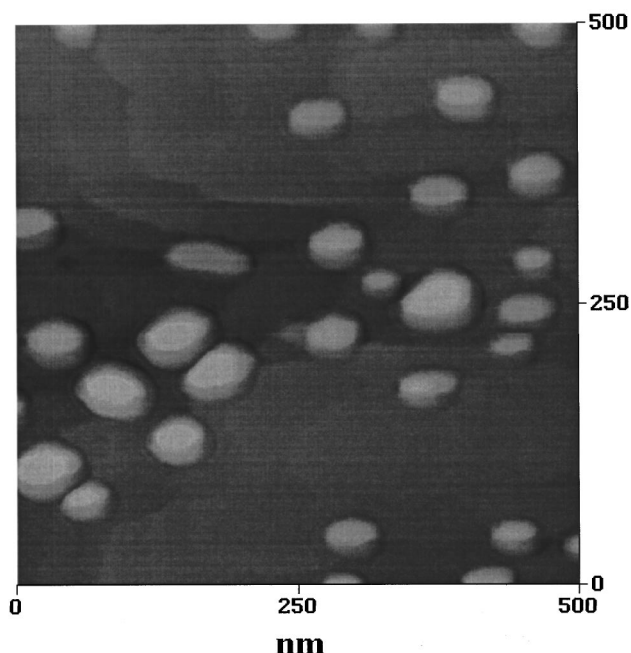


FIG. 1. Topographic force microscopy image (top view) of 3.5 ML of InAs deposited on InP(001). In addition to the dots, several terraces separated by monoatomic and multiatomic steps are observed.

in the friction-force profile along a single scan-line (Fig. 2). Back and forward scans are presented (friction loop). Topographic effects may contaminate the friction signal. For instance, edge effects produce a sudden change of the lateral force when the tip contacts or leaves the dot. However, in principle, topography can be separated from friction. The sign of the frictional force depends on the scanning directions, while the sign of topographic contributions to the torsion of the cantilever is independent of scanning direction.

The average width of the friction loop is 5.5 ± 0.5 nN on the terrace. This figure coincides with the value measured on the flat portion of the dot. The differences fall within the error. We interpret this lack of contrast as both surfaces having similar chemical compositions. This suggests the presence of a two-dimensional (2D) wetting layer covering the InP. In fact, transmission-electron-microscopy analysis²¹ revealed the formation of 2D wetting layer for coverages larger than 1.8 ML. The wetting layer was estimated at 1.4–1.5 ML, and was approximately independent of InAs deposited amount. In short, 1.5 ML of InAs on InP gave the same frictional force as 16 ML of InAs. Previously we verified that FFM can differentiate epitaxies of InAs on InP, so the absence of contrast should not be attributed to a lack of sensitivity.

We also examined a dot system formed when 2 ML of InSb are deposited on InP. Previous topographic atomic-force-microscopy (AFM) images²² showed the formation of three-dimensional islands of lateral dimensions of 72×51 nm², and a height of 18 nm (mean values). From the volume of the deconvoluted topographic images of the dots, we estimated that less than 1 ML of InSb should cover the InP surface.

Figure 3(a) shows a topographic cross section of a repre-

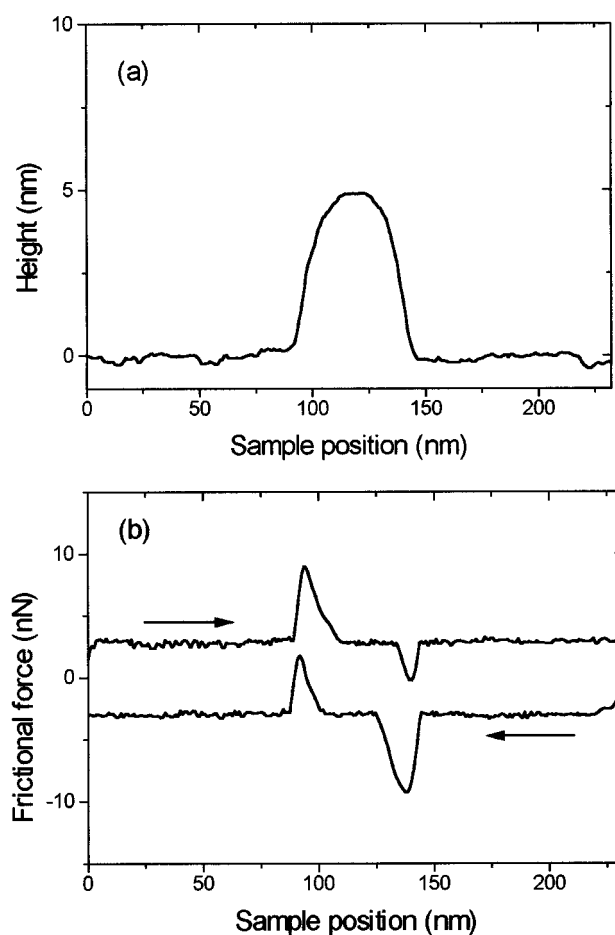


FIG. 2. Cross section of an InAs dot. (a) Topography and (b) forward and backward friction-force scan lines (friction loop). Edge effects produce the presence of peaks in the lateral force signal. Those topographic effects can be separated from friction contrast because they are independent of scanning direction. Effective normal force 6.6 nN.

sentative dot in InSb. In Fig. 3(b) we plot the simultaneous friction-force cross section. In addition to the peaks associated with topographic effects, the friction loop shows two different levels. A large frictional force of 14.0 nN is measured in the regions between dots. This force is roughly three times the value found when the probe is on top of the dot (5.0 nN). We identify this change in contrast to a variation of chemical composition. The friction-force cross section suggests that less than 1 ML of InSb is adsorbed on the InP(001) surface.

To obtain an alternative estimation of the InSb coverage in the region between dots, we applied a method based on photoluminescence (PL) experiments. First, the PL signal is recorded in a system that shows the formation of quantum dots. This reveals two major peaks centered around 1.00 and 1.38 eV, respectively. The latter corresponds to InP [Fig. 4(a)]. Both peaks are independent of dot's size. This shows that the emission centered at 1.00 eV is not associated with the dots. This is indicative of the presence of a wetting layer formed on InP during InSb deposition.

Next, we studied the evolution of the spectrum for several InSb coverages up to a monolayer [Fig. 4(b)]. The spectrum shows a broad peak and an emission corresponding to the

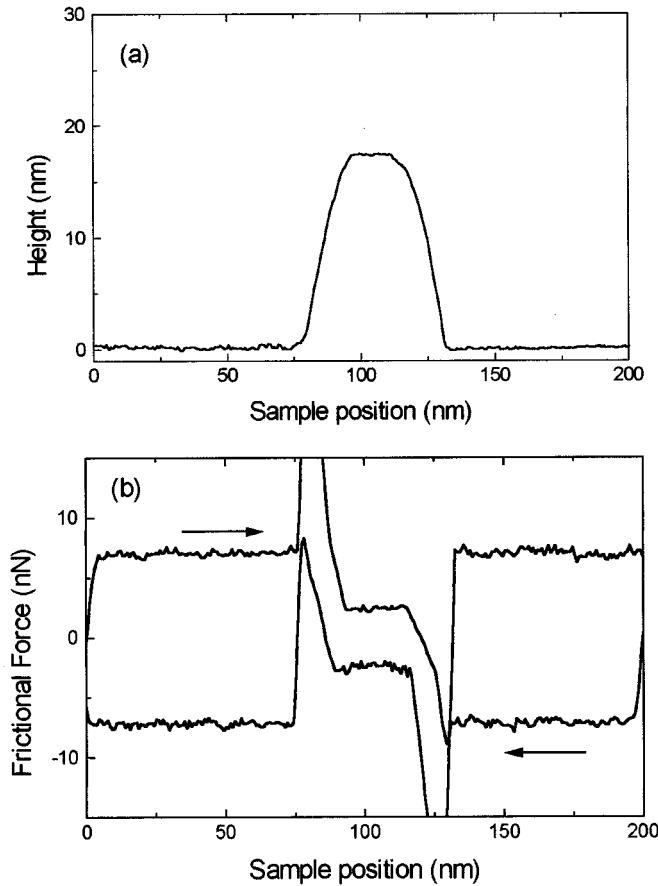


FIG. 3. Topography (a) and lateral force cross sections of an InSb dot formed after 2-ML deposition on InP(001). The width of the friction loop on the top of the dot is approximately three times smaller than in the regions between dots. The effective normal force is 7.2 nN.

substrate (1.38 eV). The position of the latter remains unaltered, though its relative intensity depends on coverage. However, the broad emission is shifted toward lower energies as the coverage increases. Its evolution is presented in the inset. The redshift is in agreement with numerical calculations based on the solid model theory. From it, we deduced that the position of the peak observed in the quantum-dot system matches the emission at 0.7 ML. This result confirms that FFM contrast is due to the presence of a submonolayer.

On the other hand, friction-force images do not show any noticeable variation of friction properties in the regions between dots. This indicates a homogeneous composition in those regions which could be associated with the formation of an $\text{In}_x\text{Sb}_{1-x}\text{P}$ alloy.

FFM images of heterogeneous semiconducting surfaces show changes in contrast associated with compositional variation. However, to develop a useful spatially resolved friction spectroscopy, a more quantitative description of the interface should be given. This requires a theoretical model that relates the measured frictional force with the real contact area, and interatomic potential, and probably with the phonon spectra of the interface. To our best knowledge, this model is still not available for nanometer-size contacts. However, classical theories may provide insight into how a friction-force spectroscopy could be developed.

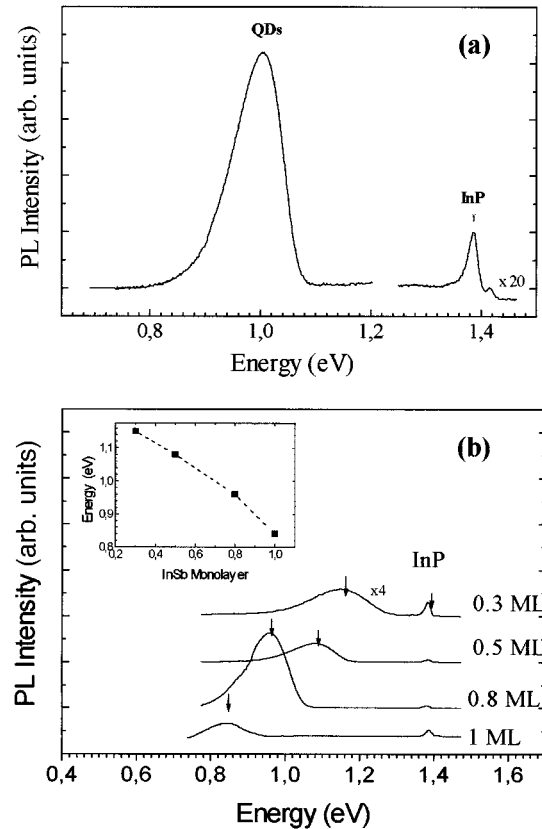


FIG. 4. (a) PL spectrum of 2 ML of InSb on InP. The emission peak at 1.00 eV is associated with the InSb wetting layer. (b) PL spectra taken at 10 K of several InSb submonolayers. The inset shows the wetting layer's emission dependence on InSb coverage.

The adhesion model of Bowden and Tabor²³ provides a relationship between the frictional force and the real contact area,

$$F_f = \tau \times A_R. \quad (1)$$

The shear stress τ is a parameter that depends on the mean pressure p . Briscoe and Evans proposed a thermal activated model of friction that establishes a relationship between τ and parameters of the interface,²⁴

$$\tau = \tau_0 + \alpha p. \quad (2)$$

This equation is consistent with recent molecular-dynamics calculations.^{25,26} Here τ_0 could be related to the barrier that a sliding atom must overcome, while α could reflect the increase of this barrier due to the external load.

Those parameters are accessible to FFM. Preliminary experiments with InP(001) surfaces give values of $\tau_0 = 0.1$ GPa and $\alpha = 0.6$, respectively. Those values are different, but comparable to the ones obtained with GeS and C_{60} samples⁸ (1.2 GPa, 1.08) and (3.3 GPa, 0), respectively.

However, several issues should be addressed before a practical spatially resolved friction spectroscopy could be achieved. Shear stress values obtained by FFM are several orders of magnitude larger than those measured by other techniques.²⁷ Another crucial problem, common to all scanning probe techniques, is to determine the influence of the

tip—more precisely, how the tip's geometry, mechanical properties and composition could affect the measurements.

In studies of boundary lubrication, it has been shown that the friction properties may be substantially altered by the presence of an organic monolayer; however, we would like to emphasize that there are significant differences between those and these observations. Molecular-dynamics simulations^{25,28} show that organic chains may have various pathways for energy dissipation due to the activation of different excitation modes such as chain oscillations, intramolecular vibrations, and torsional modes. Here the interface is composed of one or two layers in a solid-state form, where

above modes are not present. Nevertheless, changes in frictional forces are still measurable in the nanonewton regime.

In addition to the relevance of these results to study the relationship between friction and coverage, we would like to stress the potential of the friction-force microscope to reveal wetting layer formation, and more generally to develop a spatially resolved spectroscopy based on friction. Further experiments should be directed to obtain a quantitative relationship between FFM measurements and intrinsic properties of the interface.

This work was supported by Dirección General de Investigación Científica Técnica of Spain (PB94-0016).

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¹I. L. Singer, *J. Vac. Sci. Technol. A* **12**, 2605 (1994).

²B. Bhushan, J. Israelachvili, and U. Landman, *Nature (London)* **374**, 607 (1995).

³H. Yoshizawa, Y.-L. Chen, and J. Israelachvili, *J. Chem. Phys.* **97**, 4128 (1993).

⁴See chapters by B. N. J. Persson; M. O. Robbins, and J. B. Sokoloff, in *Physics of Sliding Friction*, edited by B. N. J. Persson and E. Tosatti (Kluwer, Dordrecht, 1996).

⁵C. M. Mate, G. M. McClelland, R. Erlandsson, and S. Chiang, *Phys. Rev. Lett.* **59**, 1942 (1987).

⁶G. Meyer and N. M. Amer, *Appl. Phys. Lett.* **57**, 2089 (1990).

⁷R. Lüthi, E. Meyer, H. Haefke, L. Howald, W. Gutmannsbauer, and H.-J. Güntherodt, *Science* **266**, 1979 (1995).

⁸U. D. Schwarz, W. Allers, G. Gensterblum, and R. Wiesendanger, *Phys. Rev. B* **52**, 14 976 (1995).

⁹R. M. Overney, H. Takano, M. Fujihira, W. Paulus, and H. Ringsdorf, *Phys. Rev. Lett.* **72**, 3546 (1994).

¹⁰P. Sheenan and C. Lieber, *Science* **272**, 1158 (1996).

¹¹C. D. Frisbie, L. F. Rozsnyai, A. Noy, M. S. Wrighton, and C. M. Lieber, *Science* **265**, 2071 (1994).

¹²J. L. Wilbur, H. A. Biebuyck, J. C. MacDonald, and G. M. Whitesides, *Langmuir* **11**, 825 (1995).

¹³E. Meyer, R. Lüthi, L. Howald, M. Bammerlin, M. Guggisberg, H.-J. Güntherodt, L. Scandella, J. Gobrecht, A. Schumaker, and R. Prins in *Physics of Sliding Friction*, edited by B. N. J. Persson and E. Tosatti (Kluwer, Dordrecht, 1996), p. 349.

¹⁴M. Fujihira, D. Aoki, Y. Okabe, H. Takano, H. Hokari, J. Frommer, Y. Nagatani, and F. Sakai, *Chem. Lett.* **7**, 499 (1996).

¹⁵J. Tamayo, L. González, Y. González, and R. García, *Appl. Phys. Lett.* **68**, 2297 (1996).

¹⁶R. García, J. Tamayo, L. González, and Y. González, in *Micro/Nanotribology*, edited by B. Bhushan (Kluwer, Dordrecht, 1997), pp. 275–282.

¹⁷D. Leonard, M. Krishnamurthy, C. M. Reaves, S. P. Deubars, and P. M. Petroff, *Appl. Phys. Lett.* **63**, 3203 (1993).

¹⁸F. Briones, L. González, and A. Ruiz, *Appl. Phys. A* **49**, 729 (1989).

¹⁹Nanoscope III, Digital Instruments, Santa Barbara, CA.

²⁰J. Tamayo and R. García, *Mater. Sci. Eng.* **42**, 122 (1996).

²¹J. Groenen, A. Mlayah, R. Carles, A. Ponchet, A. Le Corre, and S. Salaün, *Appl. Phys. Lett.* **69**, 943 (1996).

²²T. Utzmeier, P. A. Postigo, J. Tamayo, R. García, and F. Briones, *Appl. Phys. Lett.* **69**, 2674 (1996).

²³F. P. Bowden and D. Tabor, *The Friction and Lubrication of Solids* (Clarendon, Oxford, 1964).

²⁴B. J. Briscoe and D. C. B. Evans, *Proc. R. Soc. London, Ser. A* **380**, 389 (1982).

²⁵J. N. Glosli and G. M. McClelland, *Phys. Rev. Lett.* **70**, 1960 (1993).

²⁶M. R. Sorensen, K. W. Jacobsen, and P. Stoltze, *Phys. Rev. B* **53**, 2101 (1996).

²⁷J. Krim, *Langmuir* **12**, 4564 (1996).

²⁸J. A. Harrison, C. T. White, R. J. Colton, and D. W. Brenner, *J. Chem. Phys.* **97**, 6573 (1993).