

Compositional mapping of semiconductor structures by friction force microscopy

J. Tamayo, L. González, Y. González, and R. García^{a)}

Instituto de Microelectrónica de Madrid, CSIC, Serrano 144, 28006 Madrid, Spain

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Topographic and chemical mapping of materials at high resolution define the goals of a microscope. Force microscopy can provide methods for simultaneous topography and chemical characterization of materials. Here we describe the use of the atomic force microscope to map chemical variations of semiconductor samples. Chemical maps of semiconductor InP/InGaAs alloys have been determined with 3 nm spatial resolution while 10% changes in indium composition are resolved in $\text{In}_x\text{Ga}_{1-x}\text{As}$ structures. The present resolution is limited by the tip's curvature radius, cantilever lateral force constant, and the total applied force. Theoretical calculations predict lateral compositional resolutions of about 1 nm. © 1996 American Institute of Physics. [S0003-6951(96)00516-9]

Simultaneous mapping of topography and chemical composition has always been one of the goals of microscopic techniques. The atomic force microscope (AFM) is one of the youngest and provides arguably the most versatile scanning probe technique. The AFM probes the force between a sharp tip attached to a cantilever beam and the sample. Independent of their origin, forces are always present between two surfaces,¹ which gives the AFM an astonishing flexibility to image materials.² However, and not unlike the scanning tunneling microscope, the capability to achieve chemical contrast is inferior and not as straightforward as topographic imaging.³ The introduction of segmented quartered photodiodes has allowed simultaneous measurement of lateral as well as normal forces.^{4,5} Lateral force measurements are exploited to study lubrication, friction, and wear mechanisms at the molecular level.⁶⁻¹⁰ It was also suggested that lateral forces could be used to extract information about the chemical composition of the sample.¹¹ Pioneering applications have included studies on phase separated and mixed organic films and patterned self-assembled monolayers.¹²⁻¹⁴

Here we attempt to apply lateral force measurements as a tool to perform chemical maps of semiconductor surfaces. We demonstrate the ability of friction force microscopy (FFM) to reveal the spatial arrangement of semiconductor heterostructures and alloys with a lateral compositional resolution of 3 nm. The data also show the ability of FFM to resolve variations of 10% in indium composition. Additionally, semiconductor heterostructures could be used as standards for tip characterization and resolution in scanning force microscopy.

Semiconductor structures based on III-V compounds and their alloys can be fabricated with accurate control in thicknesses up to one monolayer (~ 0.3 nm). These structures can combine materials with different electronic and mechanical properties. Both features make them suitable to develop standards of resolution and sensitivity for FFM. The samples were grown under ultra high vacuum conditions by molecular beam epitaxy. The samples were cleaved exposing

the (110) face for examination. They were mounted in a special AFM cell that allows environmental control (relative humidity between 0 and 95%) as well as optical micropositioning of the tip on the epitaxial layer. Electronics and software came from Nanoscope III (Digital Instruments, Santa Barbara, CA). The experiments have been performed with sharpened Si_3N_4 cantilevers with nominal curvature radius of 10 nm (Olympus, Japan).

To determine the ability of FFM to map chemical variations, we have designed a test sample made of a stack of layers of 2, 3, 4, 5, and 10 nm thicknesses. First, the 2 nm structures are grown on the substrate. They consist of $20 \times [\text{InGaAs}(2 \text{ nm})/\text{InP}(2 \text{ nm})]$ structures. On top of these, a similar heterostructure of 3 nm thickness (width in FFM images) for each individual layer is deposited. This is followed by the 4, 5, and 10 nm heterostructures. This sample will also provide a direct determination of the spatial resolution to map chemical variations by FFM. The discussion is centered on InP/ $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ structures grown on InP (100) substrates. InGaAs alloy composition was chosen to be lattice matched to InP (0.587 nm).

Figure 1 shows topography and friction images of a region of the sample with 3, 4, and 5 nm structures. The ability of friction to reveal chemical variations is illustrated by comparison of topography and friction cross-sections [Figs. 1(c) and 1(d)]. The analysis of single scan lines (not shown here) reveals that the contrast is independent of topographic features.¹⁵ We determine a ratio of friction coefficients of 1.6 ± 0.2 , InP regions giving higher friction forces. However, in these experiments dissipation of energy is not accompanied by wear. Repeated imaging of the same area shows no structural changes. Damage is avoided by applying loads per atom smaller than the force that holds these covalent bonded atoms (~ 2 nN).

Chemical contrast between InP and InGaAs regions is observed in the friction image [Fig. 1(d)] with 3 nm lateral resolution. The highest resolution has been achieved by using beam-shaped cantilevers with torsion force constant (156 N/m) and applying total forces smaller than 5 nN.

The frictional force is assumed to be proportional to the contact area⁶ ($F_f = sA$). Then, the lateral compositional reso-

^{a)} Author to whom correspondence should be addressed. Electronic mail: rgarcia@imm.cnm.csic.es

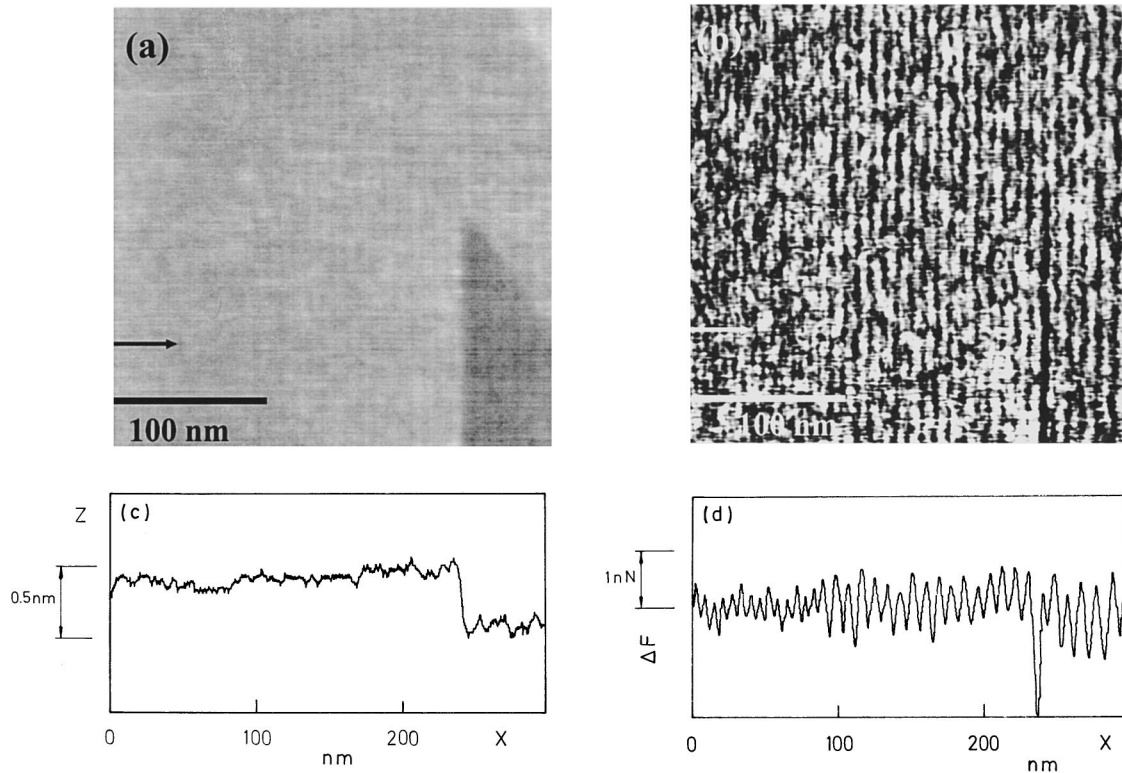


FIG. 1. (a) AFM topographic image of a region with 3, 4, and 5 nm structures. Ideally the interface should be atomically flat. However, either the cleavage or the formation of a thin oxide could raise one region with respect to the other. Scan size 300 nm. (b) Friction image of the same region. Notice that (i) the position of the structures is clearly resolved and (ii) topographic features (terraces) are removed from the image. This indicates that there is little crosstalk between normal and lateral forces. (c) Topographic cross section along the arrow marked in (a). (d) In the friction cross-section [along the arrow in (b)], InP and InGaAs 3, 4, and 5 nm regions are resolved. Total force 4.6 nN.

lution derived from friction images will be equal to the contact diameter. The dependence of contact area on tip curvature radius, adhesion, and loading forces has been calculated following Johnson-Kendall-Roberts (JKR) theory.¹⁶ The results shown that the contact area decreases by decreasing the total applied force (adhesion+loading) and tip radius (Ref. 17). The best lateral compositional resolution obtained (3 nm) can be explained by the interplay between the finite tip radius and total normal force. From adhesion force measurements (3 nN) and the JKR model the diameter of the contact area is estimated to be 2.8 nm. This matches the lateral resolution when the effect of the load is considered. Compositional variations at higher resolution cannot be observed because the tip partially contacts different structures. The calculations also show that under reasonable experimental conditions, either tips with radius of 4 nm and adhesion forces of 1 nN or in absence of adhesion forces, lateral compositional resolutions of about 1 nm can be expected. Recent experiments performed on fullerenes grown on NaCl have separated the C_{60} islands from the substrate with 2 nm lateral resolution.¹⁸

To determine the compositional sensitivity a step graded $In_xGa_{1-x}As$ structure was grown on GaAs(100). In this sample, indium composition (with respect to gallium) was changed from 0 to 60% in 10% steps. FFM cross sections show five steps followed by terraces where the frictional force remains roughly constant (Fig. 2). The positions of the steps coincide with those of the interfaces that separate re-

gions of different composition while the lateral dimensions of the terraces match the thickness of the regions with constant composition. It is also observed that step sizes increase with the amount of indium. This could explain why the step associated to the 0–10% transition is missing. Instead a peak in the force, that could be attributed to topographic effects, marks the transition. On the other hand, the ratio of frictional forces (between 0.98 and 0.96) shows a slight drop with the total amount of indium. Further experiments are needed to establish the precise relationship between frictional forces and indium (or gallium) composition.

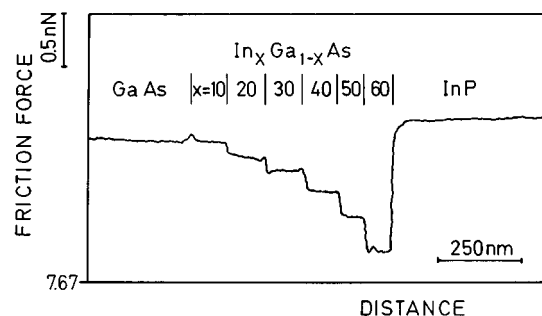


FIG. 2. Frictional force cross-section across a step graded $In_xGa_{1-x}As$ sample. Indium composition (x) has been changed in 10% steps from GaAs to $In_{0.6}Ga_{0.4}As$. The structure is terminated with an InP capping layer. The steps mark the position where the composition has changed while the terraces are indicative of regions where the composition is uniform. The cross section is an average over 300 FFM scan lines.

From Fig. 2, it can be concluded that FFM ability to separate these structures improves with increasing (decreasing) indium (gallium) composition. The size of the step for interfaces with indium concentrations higher than 30% suggests that compositional changes of 5% or less could be detected. The uniformity of the signal in the InP region provides the signal-to-noise reference level.

FFM experiments have resolved the atomic structure of mica,¹¹ graphite⁶ and several ionic crystals,¹⁸ however, those results do not imply atomic compositional resolution. The periodicity shown corresponds to identical atoms or molecules. The chemical contrast reported here is reproducible and general. It has been observed in all heterostructures examined so far (GaAs/GaSb, GaAs/InSb, Si/GaAs, GaInSb/AlInSb, InP/InSb, InP/InGaAs).

InP and In_{0.53}Ga_{0.47}As have the same crystalline structure and lattice parameter, and very similar cohesive energies and mechanical properties. Nevertheless variations of chemical composition with 3 nm lateral resolution are observed. Furthermore, 10% changes in indium composition have been observed in In_xGa_{1-x}As samples. These results demonstrate the sensitivity of FFM to perform chemical contrast studies with nanometer resolution.

Experiments with semiconductor samples and previous experiments with soft organic films and ionic crystals suggest a widespread applicability of friction force measurements to obtain compositional contrast with nanometer-scale lateral resolution. The advantages of this technique are its sensitivity, its high lateral compositional resolution, general applicability and nondestructive character. Additionally, semiconductor structures could be used as practical standards for tip characterization.

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