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Piezoresponse Force Microscopy for Piezoelectric Measurements of III-Nitride Materials

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Abstract

Piezoelectric constants and polarity distributions of epitaxial AlN and GaN thin films are investigated by piezoresponse force microscopy (PFM). The magnitude of the effective longitudinal piezoelectric constant d_{33} is determined to be 3 ± 1 pm/V and 2 ± 1 pm/V for wurtzite AlN and GaN/AlN layers grown by organo-metallic vapor phase epitaxy (OMVPE) on SiC substrates, respectively. Simultaneous imaging of surface morphology as well as the phase and magnitude of the piezoelectric response is performed by PFM on a GaN film with patterned polarities on a $c\text{-Al}_2\text{O}_3$ substrate. We demonstrate that the polarity distribution of GaN based lateral polarity heterostructures can be deduced from the phase image of the piezoresponse with nanometer scale spatial resolution. We also present images of AlN/Si samples with regions of opposite piezoresponse phase, which indicate the presence of antiphase domains. We discuss the potential application of this technique for determination of the orientation of bulk crystals.

I. Introduction

The measurement of the piezoelectric properties of III-nitrides with high spatial resolution is of importance for the design and performance of GaN based electronic and optoelectronic devices.^{1,2} Additionally, nanoscale level investigation of the piezoelectric behavior of nitride thin films, bulk crystals and heterostructures is of considerable interest for determining how interfaces, defects and inversion domain boundaries affect device performance.

III-nitrides are piezoelectric as well as pyroelectric materials in their wurtzite phase and have piezoelectric constants d_{ij} which are about one order of magnitude higher than in other III-V compound semiconductors.² The spontaneous polarizations calculated for GaN and AlN are $P_{SP} = -0.034$, and -0.090 C/m^2 , respectively.² In GaN the [0001]-axis points from the N-face to the Ga-face. The orientation of spontaneous polarization is defined by convention to be parallel to the crystallographic [0001] axis. Since the sign of the spontaneous polarization is predicted to be negative, the spontaneous polarization is oriented pointing from the Ga-face towards the N-face side of the crystal (i.e. in the $[000\bar{1}]$ direction).¹⁻³ At the surfaces of relaxed GaN and AlN crystals, a divergence in the spontaneous polarization induces a polarization bound surface charge with a density of 2.12×10^{13} and $5.62 \times 10^{13} \text{ cm}^{-2}$, respectively. The sign of the polarization induced charge at each surface is related to the orientation of the polarization and therefore to the polarity of the crystal. For epitaxial layers of GaN with Ga-face polarity, the bound surface charge is negative, whereas for N-face GaN the bound surface charge is positive.

While spontaneous polarization is independent of strain, piezoelectric polarization is strain-induced.³ The total polarization of a nitride layer is the sum of the spontaneous and of the piezoelectric polarizations. As shown by Ambacher, *et al.*^{1,3} the piezoelectric and the

spontaneous polarizations are parallel for tensile strain and are antiparallel for compressive strain.

Scanning probe microscopy based techniques have been employed to perform high-resolution characterization of the local electronic properties of III-nitrides.⁴⁻⁶ We have applied a scanning probe technique termed piezoresponse force microscopy (PFM) to investigate the local electromechanical properties of III-nitrides. PFM offers a significant advantage compared to macroscopic techniques⁷⁻⁹ in studying the properties of piezoelectric films in that PFM can resolve nanometer variations in the piezoelectric properties of a sample and is ideally suited for a nanoscale level investigation of the piezoelectric properties.

II. Experimental

The PFM imaging method was developed to visualize the domain structure in ferroelectric thin films and has been described in detail elsewhere.¹⁰⁻¹⁶ With PFM, when a modulation voltage is applied to a piezoelectric material, the vertical displacement of the probing tip, which is in mechanical contact with the sample, accurately follows the piezoelectric motion of the sample surface. The voltage V applied across a film of thickness t , generates an electric field E_3 along the c -axis, which strains the film by a thickness Δt . The d_{33} piezoelectric coefficient is then proportional to the applied voltage: $d_{33} = \Delta S_3/E_3 = \Delta t/V$, where $E_3 = V/t$ and $\Delta S_3 = \Delta t/t$ is the change of strain along the c -axis. Thus, the amplitude of the tip vibration measured by the lock-in technique, provides information on the piezoelectric strain, and the piezoelectric coefficient, d_{33} , can be determined. The polarity of III-nitride domains, films or crystals can be determined based on the dependence of the sign of the piezoelectric coefficient on the crystallographic axis; the oscillation of the film is either in-phase or out-of-phase with the modulation voltage, corresponding to either a Ga- or N-face film, respectively. This effect is

shown schematically in Figs. 1a and 1b. Therefore, in a PFM phase image, Ga- and N-face polarities will exhibit opposite contrast.

With PFM, there are two main approaches: measurements can be performed by applying a voltage between a conducting tip and a bottom electrode, or between deposited top and bottom electrodes. For example, Gruverman *et al.*¹¹ performed measurements of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) thin films by applying a voltage between a bottom electrode and a conducting tip which is used as a moveable electrode. With this configuration, the polarization distribution in PZT thin films were imaged with a lateral resolution of about 10 nm.¹¹ However, the electric field generated by the PFM tip is highly inhomogeneous which makes quantitative measurements of the field dependent parameters difficult. Alternatively, Christman *et al.*¹⁵ made measurements by applying a voltage between deposited top and bottom electrodes and demonstrated a sub-micron variation of piezoelectric properties in PZT capacitors. With this configuration, a homogeneous electric field is generated throughout the piezoelectric layer and the electrostatic tip-sample interaction is suppressed, although at the expense of lower lateral resolution.

Both approaches were utilized in this study to perform PFM with a TM Microscopes AutoProbe M5, conducting tips and a dual-phase lock-in amplifier (SR830).¹⁶ The commercially available conducting cantilevers (force constant 2.1 N/m) had a 1000 Å layer of 0.1 Ω-cm *p*-type diamond over the Si tips and were mounted on alumina squares. A schematic of the PFM setup is shown in Fig. 2.

III. Results and Discussion

For measurements of d_{33} using epitaxial GaN/AlN and AlN layers prepared by OMVPE on SiC, a frequency of 1 kHz was used and the driving voltage (0.5 – 5.0 V) was applied to a 800

Å Pt top electrode. In order to determine the effective piezoelectric coefficient, once a piezoresponse magnitude image was obtained, a histogram was generated, and the peak value noted. For GaN/AlN/SiC films we observe $d_{33} = 2.0 \pm 1$ pm/V, and for AlN/SiC, we observe 3.0 ± 1 pm/V. The reported uncertainty represents the standard deviation and is indicative of variation in piezoelectric properties across a film's surface. For $d_{33} = 2.0$ pm/V, the application of 5V would result in a tip deflection of 10pm. We attribute this tip deflection to a change in sample thickness, and while such small displacements are difficult to measure accurately, we have previously reported that the measurement limit of our experimental setup is less than 0.5 pm/V.¹⁶

The results of our microscopic measurements can be compared to data of macroscopic methods such as interferometric techniques. Using an interferometric method, C. M. Lueng *et al.* reported $d_{33} = 3.9 \pm 0.1$ pm/V for AlN/Si(111) and 2.65 ± 0.1 pm/V for both GaN/AlN/Si(100) and GaN/AlN/Si(111) heterostructures (all films were prepared by MBE).¹⁷ I. L. Guy *et al.* reported 2.0 ± 0.1 pm/V for polycrystalline GaN/Si(100) grown by laser assisted chemical vapor deposition (CVD); 2.8 ± 0.1 pm/V for single crystal GaN/SiC grown by hydride vapor phase epitaxy; and 3.2 ± 0.3 pm/V and 4.0 ± 0.1 pm/V for polycrystalline AlN/Si(100) heterostructures grown by plasma assisted and laser assisted CVD respectively.¹⁸

To explore the imaging capability of PFM and the influence of polarity on the amplitude and the phase of the measured piezoresponse, a plasma induced molecular beam epitaxy (PIMBE) grown GaN film with patterned Ga- and N-face polarities was examined at a modulation frequency of 10 kHz with a driving voltage of 5 V applied to the tip, as reported previously.^{19,20} The Ga-face GaN (1 μm thick) was grown on an AlN nucleation layer (10 nm thick), while the N-face GaN (1 μm thick) was grown directly on the sapphire substrate.²¹

Figure 3(a) shows a topographic image of the GaN film with alternating concentric squares of Ga- and N-faces (the innermost square is Ga-face). In Figs. 3(b) and 3(c), PFM magnitude and PFM phase images, respectively, are displayed. It is interesting to note that the piezoresponse magnitude, which should be independent of polarity, is higher (as denoted by a lighter contrast in Fig. 3(b)) for the N-face GaN. Several effects could contribute to this effect, including differences in material quality, differences in total polarization and differences in surface charge. We suggest the difference in piezoresponse magnitude results from the slightly different biaxial compressive strain, which was measured using x-ray diffraction to be 6.35×10^{-3} and 5.47×10^{-3} for the Ga- and N-face regions, respectively. This strain causes a piezoelectric polarization of $+0.0055 \text{ C/m}^2$ for the Ga-face and of -0.0047 C/m^2 for the N-face. Accounting for spontaneous polarization (-0.034 C/m^2 and $+0.034 \text{ C/m}^2$ for Ga- and N-face, respectively), the magnitude of the total polarization and the corresponding bound surface charge is larger for the N-face ($P = 0.0293 \text{ C/m}^2$, $\sigma/e = 1.83 \times 10^{13} \text{ cm}^{-2}$) in comparison to the Ga-face GaN ($P = -0.0285 \text{ C/m}^2$, $\sigma/e = -1.78 \times 10^{13} \text{ cm}^{-2}$), which could lead to a higher magnitude of the piezoresponse of the N-face. From Fig. 3(b) we also observe a higher piezoresponse close to the inversion domain boundaries (IDBs) between Ga- and N-face regions. This could result from differences in band bending at the IDB and is the subject of ongoing work. A schematic of the spontaneous and piezoelectric polarizations in the N- and Ga-face regions is shown in Fig. 4.

In the PFM phase image (Fig. 3 (c)), the N-face regions have a lighter contrast than the Ga-face regions. A histogram representation of the relative areas of the Ga- and N-polarity phases is shown in Fig. 3 (d). From Fig. 3 (d) it can be seen that while the Ga-face vibrates almost in-phase with the modulation voltage (~ 20 degrees), the oscillation of the N-face is out-of-phase with respect to the applied voltage (~ 160 degrees). In-phase vibration is an indication

that the crystallographic [0001] axis points toward the surface while the total polarization points toward the substrate, which is consistent with Ga-face polarity. Accordingly, a region with out-of-phase vibration should have the crystallographic [0001] axis directed toward the substrate, as in the N-face region. The fact that the phase difference between the Ga- and N-polarity regions is not exactly 180 degrees may be attributed to parasitic capacitance of the tip-sample structure.

A line scan cross-sectional analysis of the PFM phase image of the GaN heterostructure (Fig. 5) reveals that the lateral resolution achieved in imaging of the Ga- and N-face regions is about 100 nm. The lateral resolution is limited by the width of the IDB. We expect that in the case of a sharp IDB, the Ga- and N-face regions can be imaged with higher resolution.¹¹

Since we have demonstrated the ability of PFM to image polarity in a sample purposely prepared to have patterned polarities, an additional test would be to image the polarity of a film with mixed or random polarity. Lebedev et. al. grew a 200nm AlN thin film on a silicon substrate by plasma-assisted molecular beam epitaxy (PAMBE) and observed mixed polarity by x-ray photoelectron diffraction (XPD).²² We investigated a similar film with PFM and observed contrast inversion on specific 300-400nm domains of hexagonal shape as illustrated in Fig. 6. The lateral resolution in these measurements is less than 30nm.

In the PFM experimental setup, both electrostatic forces and the electromechanical response of the surface could contribute to the measured signal. However, diamond coated tips have been shown to be long lasting and ideally suited for PFM since the tip-field electrostatic interaction is minimized when they are used in contact mode due to the high force constant.¹⁶ In addition, the observed PFM contrast was stable and did not change after subsequent measurements. On the other hand, images obtained using electrostatic force microscopy (EFM) were found to be sensitive to preceding PFM measurements, apparently due to changes in the

surface charge distribution which takes place during the PFM imaging scans. Therefore, we attribute the observed PFM contrast mainly to the piezoelectric effect.

Since III-nitrides are both piezo- and pyroelectric they have unique advantages for device design. Devices made with III-nitrides can utilize the bound surface charges that result from the spontaneous polarizations, and the difference in spontaneous polarizations between film layers, to trap electrons or holes (depending on the heterostructure polarity) in two-dimensional gases. Therefore, it is important to be able to measure the polarity of a thin film. Moreover, a film with mixed polarity would deplete the total charge density on a two-dimensional gas, and being able to identify such defects is advantageous. We can also utilize PFM to determine the polarity of III-nitride bulk crystals. Measurements of bulk samples would have the advantage of an ideal capacitor structure where there is no substrate to influence the piezoresponse. Special care must be taken when using PFM to determine absolute polarity of bulk crystals and thin films. As stated above, surface charges could affect PFM and it becomes imperative to know the state of the surface; in particular whether there are bound or adsorbate charges on the surface. The state of the surface can be determined by employing EFM. With EFM, an oscillating voltage is applied to the tip, which interacts with charge on the sample surface and produces a force on the tip. With EFM it is possible to determine polarity, but only if the surface charge is known. For this reason, it is essential to develop a consistent cleaning method so that the state of the surface can be controlled.

The extent of the role of electrostatic effects on PFM contrast can be determined quantitatively using a combination of EFM and scanning kelvin probe microscopy (SKPM). EFM gives information regarding the charge on the surface, while SKPM measures the surface contact potential. With these tools we can explore the local band structure and measure the

bound surface charge of III-nitride thin films and bulk crystals. The combination of PFM, EFM and SKPM will be used in future work to give a complete picture of the piezoresponse, surface charge, and surface Fermi level, and a more complete understanding of the electrostatic and piezoelectric effects, and hence the relationship between such factors as strain and surface charge density.

IV. Conclusions

In summary, we have demonstrated the applicability of piezoresponse force microscopy for nanometer scale imaging and piezoelectric measurements of III-nitride thin films. The magnitude of the effective longitudinal piezoelectric constant d_{33} is determined to be 3 ± 1 pm/V and 2 ± 1 pm/V for wurtzite AlN and GaN/AlN layers grown by OMVPE on SiC substrates, respectively, and these values are in agreement with other values reported in the literature. The N- and Ga-face polarities of a patterned GaN film were verified using PFM, and regions of opposite polarity were observed in an AlN/Si thin film. The PFM method enables us to identify the location of inversion domain boundaries as well as the polarity of the adjacent crystals and to perform evaluation of the piezoelectric parameters at the nanoscale level. The applicability of PFM for determining the polarity of bulk crystals was also discussed.

Acknowledgements

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Figure Captions

Figure 1. Schematic showing that the piezoelectric response of a film is (a) in-phase for a Ga face film and (b) out-of-phase for a N-face film.

Figure 2. Schematic of the PFM experimental setup. A modulation voltage is applied to the conducting tip, which causes the piezoelectric film to oscillate at the same frequency as the applied voltage. The tip displacement at that frequency is used to calculate the piezoelectric coefficient d_{33} .

Figure 3. Topographic (a), PFM magnitude (b) and PFM phase (c) images of a GaN-based lateral polarity heterostructure. The innermost $5 \times 5 \mu\text{m}^2$ square is the Ga-face region. The N-face region has a higher piezoresponse magnitude as indicated by contrast, and there is a sharp contrast difference in the piezoresponse phase image, demonstrating inversions in film polarity. (d) Histogram of the PFM phase image (Fig. 3(c)). The magnitudes of the Ga- and N-face peaks correspond to the relative areas of each region.

Figure 4. A schematic of the spontaneous and piezoelectric polarizations in the N- and Ga-face regions.

Figure 5. PFM phase image of Ga- and N-face regions with corresponding cross-sectional profile.

Figure 6. Topography, PFM magnitude, and PFM phase images of AlN/Si antiphase domains.

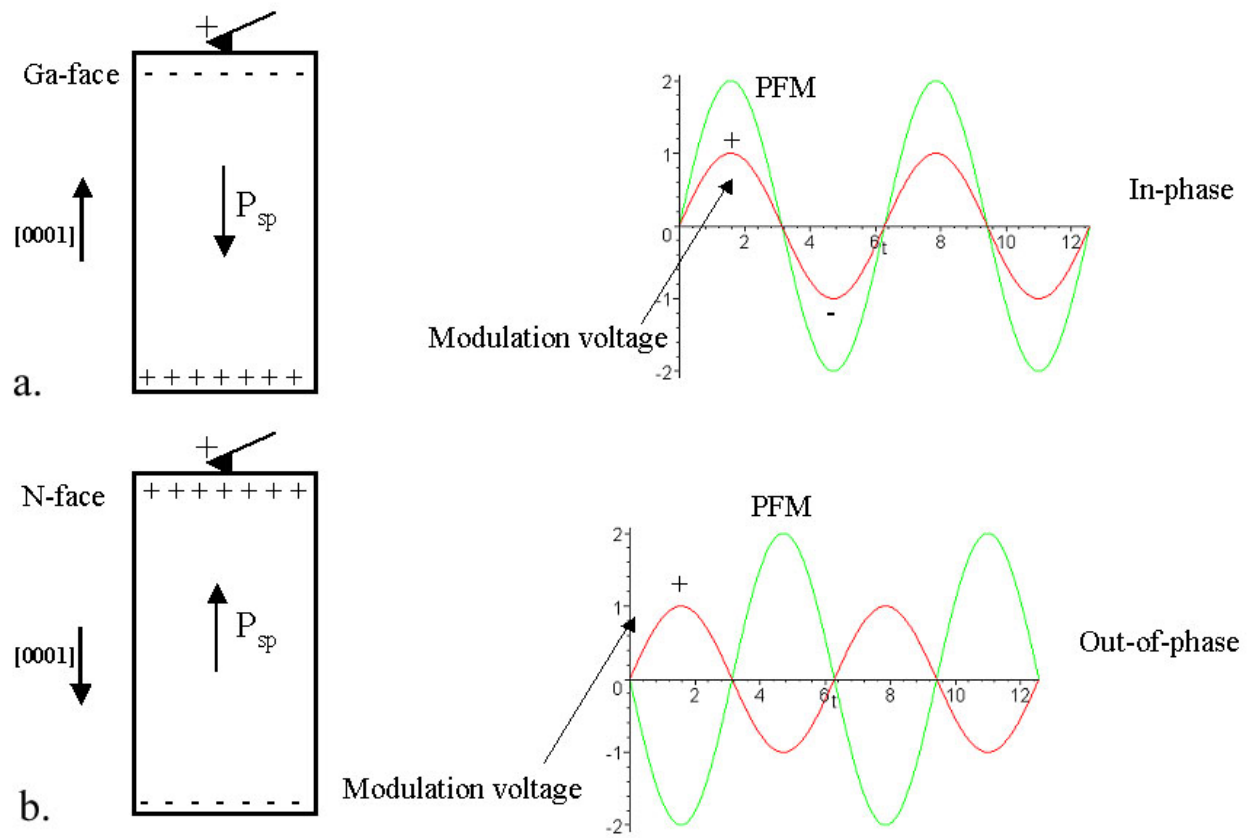


Fig. 1.

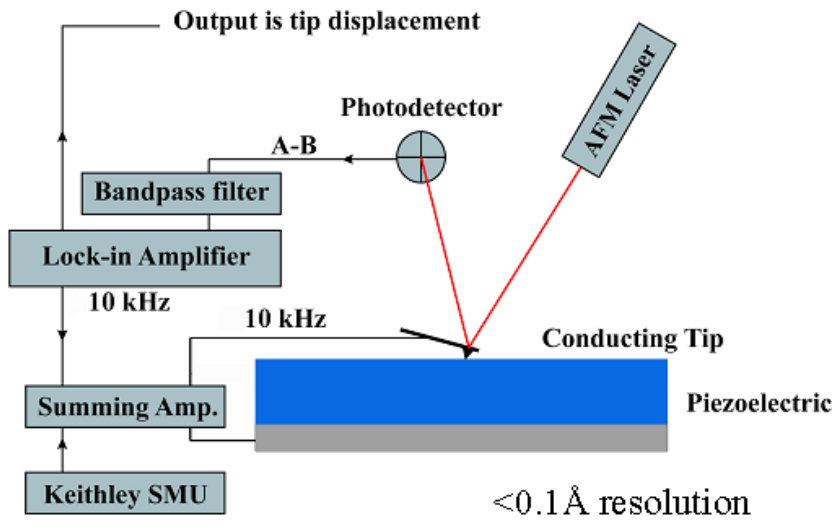


Fig. 2.

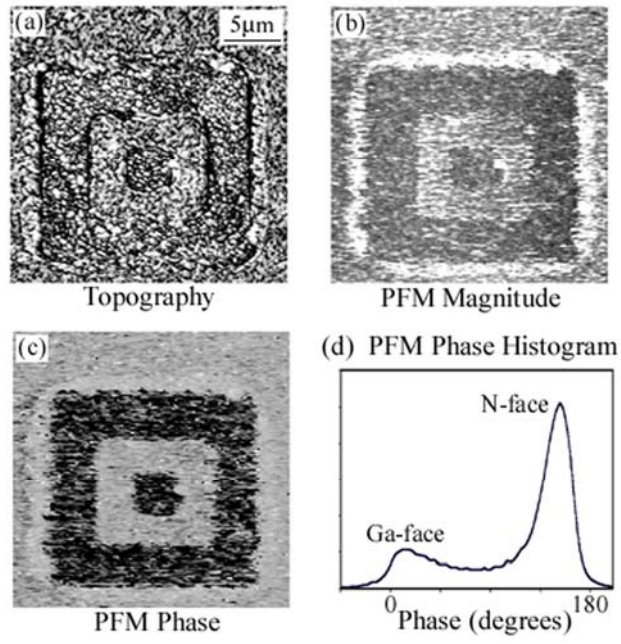


Fig. 3.

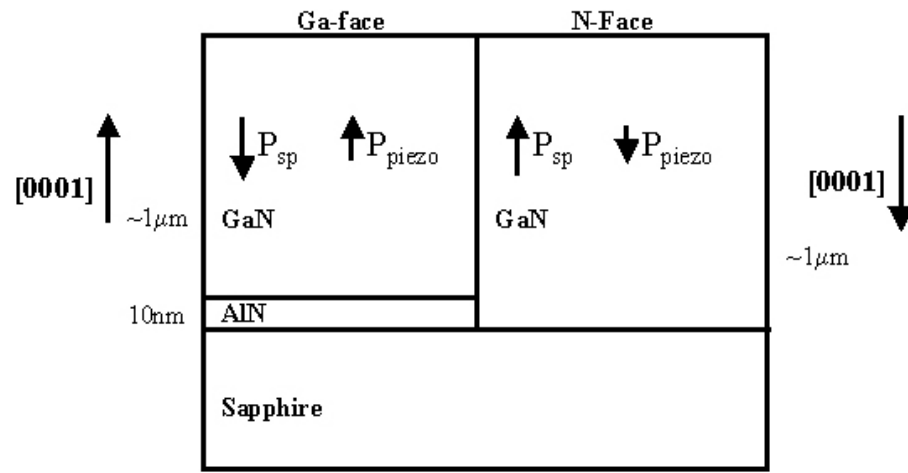


Fig. 4.

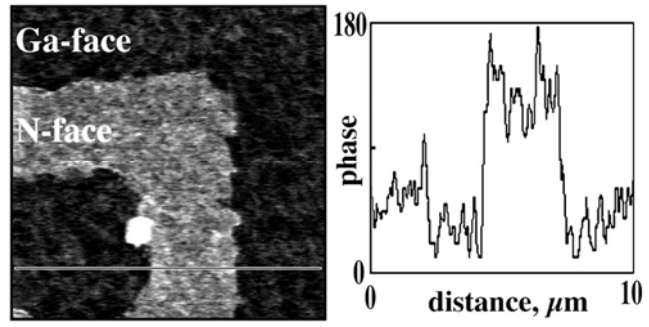


Fig. 5.

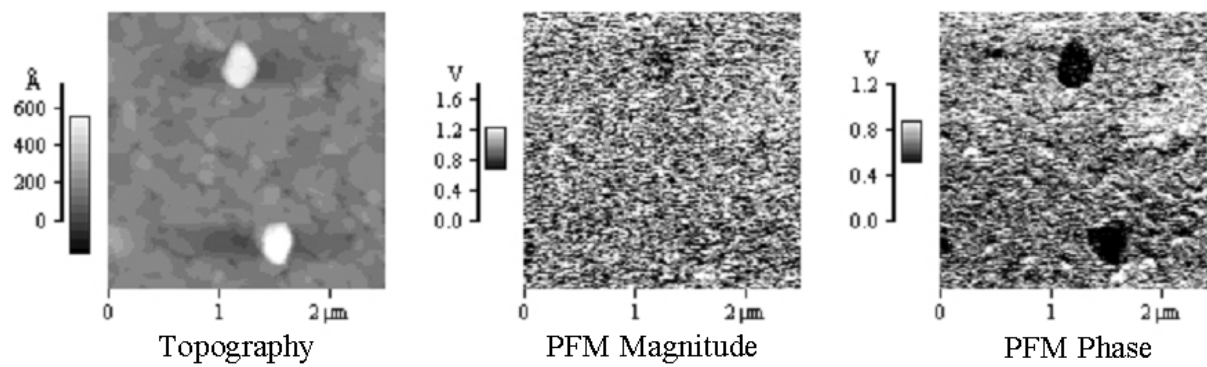


Fig. 6.