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Characterization of Poly(tetrafluoroethylene) Surfaces by Atomic Force Microscopy - Results and Artifacts

A. J. Howard and R. R. Rye
Sandia National Laboratories
MS 0603 - PO Box 5800
Albuquerque, NM 87185-0603

K. Kjoller
Digital Instruments, Inc.
520 E. Montecito St.
Santa Barbara, CA 93103

ABSTRACT

The surfaces of virgin and chemically etched poly(tetrafluoroethylene) (PTFE) have been studied using atomic force microscopy (AFM) in both contact and tapping modes. While attempting to perform AFM in contact mode on this relatively soft polymeric material, tip-induced imaging artifacts (presumably due to blunt tips and tip-to-surface interactions) were identified when the results were compared to scanning electron microscopy (SEM) surface images. When subsequent AFM imaging was performed in tapping mode it was apparent that these tip-induced artifacts were eliminated. Comparable tapping mode AFM and SEM images were obtained for even the highly porous, unstable surface that results from sodium naphthalenide etching of PTFE. AFM imaging in tapping mode of virgin and etched PTFE surfaces shows the three-dimensional character of the etched surface necessary for mechanical interlocking and resultant strong adhesion.

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INTRODUCTION

Due to its low dielectric constant (~2.0), PTFE is a substrate of interest in our laboratory for device applications which operate at very high frequencies or have capacitive coupling problems. Strong metal adhesion directly to PTFE is attainable by chemical etching the PTFE in a sodium napthalenide solution[1]. Chemical etching in this case refers to a specific reaction with the F atoms of PTFE which produces a very porous, unstable, carbon-rich surface. Understanding how it is possible to get strong, reliable, and controllable adhesion to this well known non-stick surface is a major concern for scientists and engineers who are fabricating devices or PC boards and manufacturing products from etched PTFE and PTFE-like materials.

In previous surface science studies of etched PTFE we have determined that the surface roughness (measured area to geometric area ratio) is extremely high ~200, based on BET adsorption isotherms, indicating that it is a porous, high energy surface[2]. Pull tests were also performed on Cu-coated, etched PTFE samples and the adhesive strength, ~27 kg load failure, was found to be comparable to commercial Cu coated PTFE (glass fiber filled) (Duroid, ~34 kg load failure, Rogers Corp.)[1]. XPS analysis of the fracture surfaces from the pull test yield spectra that are nearly identical to virgin PTFE which indicates that failure is not due to adhesive failure but near cohesive failure in the bulk PTFE[3]. Finally, RBS analysis of Cu coated etched PTFE shows Cu penetration and PTFE defluorination to a depth of ~3000 Å. Thus, the conclusion is that strong Cu adhesion is due to penetration deep into the etched PTFE surface, a process which results in strong mechanical interlocking[4]. The common denominator to all of the surface studies of etched and virgin PTFE is that obtaining surface morphological information is central to understanding and controlling adhesion to etched PTFE. Consequently, we have investigated the surface morphology of etched and virgin PTFE using contact mode atomic force microscopy, tapping mode AFM, and scanning electron microscopy. The results and implications of this study will be discussed in this paper.

EXPERIMENTAL

All PTFE samples were cut into approximately 2.5 cm X 2.5 cm squares from the same 1.3 mm-thick commercially available sheet. The virgin white PTFE samples were degreased in an ultrasonic bath in acetone and methanol prior to etching. The samples were then etched at room temperature for ~30 sec using a sodium napthalenide solution (Poly-Etch, Matheson Gas Products or Tetra-Etch, W.L. Gore & Assoc.). Etching time for this ~3000 Å deep etch is not critical since this step is self-limiting, apparently due to the build-up of etch products[5]. The etched samples were then quickly rinsed in running water and then thoroughly rinsed sequentially for ~5 min in ultrasonic baths of water, acetone, and methanol, and then air dried. Due to the highly reactive nature of the etched, now brown in color, PTFE surface, characterization steps were normally performed soon (< 24 hours) after etching. For SEM micrographs, the etched and virgin PTFE samples were coated with a ~100 Å conductive carbon coating.

The contact mode AFM images were taken using a Digital Instruments Nanoscope III, SA-AFMJ atomic force microscope operating in clean room controlled air (40% R.H., 21 ^{o}C). Standard Si_3N_4 pyramidal tips with ~500 Å end tip diameters were used for the contact mode imaging. For both modes of AFM operating, no additional sample preparation, other than etching and cleaning was performed. The tapping mode AFM images were also taken using a Digital Instruments Nanoscope III, multi-mode atomic force microscope operating in normal room air. Si tips with ~100 Å end tip diameters and ~ 300 kHz resonant oscillating frequency were used for the tapping mode imaging. To get representative images for both contact and tapping mode, several 5 X 5 μm and 10 X 10 μm square areas were imaged at a resolution of 512 data points per line. A discussion contrasting these two types of AFM imaging will be given in the next section.

RESULTS AND DISCUSSION

As was stated previously, one of the main potential uses for PTFE is as a substrate for high frequency (~10 GHz) device applications; this is the driving force for PTFE-related research in our laboratory. We have previously developed three new fabrication processes for patterning microwave circuits directly on etched PTFE[6]. During the development of these processes, we experimentally observed intermittent problems with fine-line metal feature resolution and metal line edge roughness. These problems were later attributed to improper photolithographic patterning steps, but since surface roughness, which is necessary for strong adhesion, can be a potential problem in high resolution lithography, three-dimensional characterization of the etched surfaces is necessary. We first investigated the surfaces of virgin and etched PTFE by SEM. Representative plan-view SEM images of these two surfaces are shown in Figure 1. The virgin samples have a moderately open surface structure with considerable filament-like features present (see Figure 1A) and several long, unidirectional scratches. The etched PTFE surface (see Figures 1B, 1C) however, has a high density of small cracks, all running ~perpendicular to the long scratches. At high magnification, Figure 1C, a fibrillar network is seen connecting the two sides of the cracks in the etched PTFE surface. For more details on these SEM characterization results of PTFE and other PTFE-like materials, like FEP, see Rye[7]. The SEM results are invaluable due to their great depth of field but unfortunately plan view SEM images are not calibrated for height.

To obtain more detailed morphological information, AFM imaging in contact mode (tapping mode AFM wasn't available yet at Sandia) was performed. Several attempts in contact mode yielded the same basic results, see Figure 2 for examples, in complete disagreement with the previous plan view SEM images. In all of the AFM images, changes in brightness indicate height differences such that the brightest regions have the maximum height and the darkest regions are low. It should be noted that during contact mode AFM imaging of PTFE it was extremely difficult to get stable, reproducible images; often the image appeared to shift from scan to scan. The contrast between contact mode AFM and SEM of etched PTFE is particularly informative; SEM shows a high density of small cracks while AFM shows a surface dominated by square plates. These results suggest that since the PTFE surface is extremely soft, and the etched PTFE surface even worse, tip-to-surface interactions were causing our images to be dominated by artifacts. An SEM image of our blunt tip is shown in Figure 3. The only clear correlation that can be made from these images is between the square plate structure observed for etched PTFE in contact mode AFM and the square, blunt nature of the pyramidal tip. (Apparently, etched PTFE is so soft that attempts at imaging reflect the shape of the AFM tip and not the surface.) Our results are in agreement with the observations made by Grutter et al.[8] when imaging even hard diamond thin films; they noted that AFM imaging with blunt tips of can cause severe misrepresentation of the true surface morphology. Subsequent attempts at contact mode AFM of PTFE with oxidatively sharpened Si tips, end tip radius ~100 Å, also yielded images which contained artifacts (streaks) and also did not agree with our SEM results. Our conclusions at this point were: (1) due to the soft nature of PTFE, imaging it is a severe test for an AFM, and (2) since contact mode AFM operates with continuous surface contact at typical force loads of 100 nN, it is highly unlikely that any contact mode AFM images of PTFE would be meaningful. Consequently, after discussing our dilemma with Digital Instruments, they agreed to attempt tapping mode AFM on our virgin and etched PTFE samples.

In tapping mode, see Zhong et al.[9] for more details, the cantilever/tip oscillates at its resonant frequency (~300 kHz) with an oscillation amplitude of 20 to 100 nm. Hence, the tip has only brief intermittent contact with the surface at a force load estimated to be roughly 0.2 to 5 nN[9]. This combination of intermittent contact at lower force loads and large oscillation amplitudes is, as we have discovered, ideal for imaging soft materials such as PTFE in a non-destructive, artifact free fashion. Typical tapping mode (plan view) AFM images of virgin and etched PTFE, which were taken at Digital Instruments in a blind test fashion, are shown in Figure 4. Note the striking resemblance of the tapping mode images, even down to the detail of the fibrillar network, shown in Figure 4 to the SEM images shown in Figure 1. It is clear that with tapping mode, it is possible to obtain meaningful 3-D surface morphological information on PTFE.

Now that we have confidence that the tapping mode AFM is giving us believable morphological information, 3-D views of the surfaces of virgin and etched PTFE were analyzed; representative 3-D surface plots are shown in Figure 5. It is interesting to note when comparing the two surfaces that the "hills" in the virgin PTFE surface, which are undoubtedly associated with skiving-induced stress, appear to open up and result in the fiber-connected cracks which are prevalent in the images of the etched surface. Further line-by-line cross-sectional analysis of these images shows that the heights of the "hills" and the depths of the cracks are comparable (~2000 to 8000 Å). So, finally by combining this AFM 3-D information with previous results, a complete explanation seems to be falling into place. Stress causes the "hills" in virgin PTFE which subsequently turn into cracks after chemical etching, and these cracks make it possible to get strong adhesion to etched PTFE through mechanical interlocking.

These tapping mode AFM results are in agreement with a previously published model which explains how it is possible to get strong metal adhesion to etched PTFE (see Reference [7] for more details). Basically, PTFE can not be melted without decomposition and no solvent exists which is capable of dissolving PTFE. As a result, thick sheets of commercial PTFE are produced by hot pressing from the powder, then direct pressing into thick sheets. Thin sheets, required for proper microwave device performance, that are less than 0.64 cm are skived from hot pressed cylinders[10]. Skiving is a process (similar to the one used for making plywood from logs) by which thin sheets are sliced from a rotating, hot-pressed, PTFE cylinder. Knowing that thin PTFE is produced from the skiving process explains why the long macroscopic scratches exist; inevitable nicks and imperfections in the knife edge are transferred to the skived PTFE. Also, the skiving process is expected to produce stress in the thin sheets which would be concentrated in an orientation parallel to the knife edge (or perpendicular to any macroscopic scratches). The chemical etching process apparently relieves this stress leading to fiber-connected cracks. These cracks allow for deep penetration of the electrolessly deposited Cu thin film which results in strong mechanical metal-to-PTFE interlocking and consequently strong metal adhesion[7].

This model is in agreement with previous failed attempts at metallizing other smoother forms of PTFE and FEP, which are produced directly from the melt and do not have the built in stress which is necessary to form etchant-induced mechanical interlocking[7]. This information has had a major impact on our microwave device fabrication on PTFE program as it clearly points out: (1) our limitations in substrate selection; (2) the need to perform in-line, non-destructive substrate roughness inspection prior to fabrication; and (3) that resolution and reliability improvements will depend on generation of a virgin PTFE substrate with a higher degree of stress uniformity.

CONCLUSIONS

Virgin and sodium napthalenide etched surfaces of PTFE have been studied using atomic force microscopy (AFM) in both contact and tapping modes. Contact mode AFM imaging on this relatively soft polymeric material is essentially impossible as images were in gross disagreement with SEM images. Tip-induced imaging artifacts, initially due to blunt Si_3N_4 tips and subsequently due to sharp Si tip-to-surface lateral force interactions showing up as streaks due to a lack of frictional force control, were identified as the problem. When AFM imaging was performed in tapping mode these tip-induced artifacts and deformation due to lateral and normal forces were eliminated as images were in perfect agreement with SEM results. Metal patterning with strong adhesion directly to PTFE, for high frequency microwave device applications is attainable by etching the PTFE in a sodium napthalenide solution. AFM imaging in tapping mode of virgin and etched PTFE surfaces has provided three-dimensional surface information which is in agreement with a previously published model[7]. This model states that strong metal adhesion to this non-stick surface stems from mechanical interlocking; deposited metal penetrates into deep stress-relieved cracks which are associated with the thin (<0.64 cm) PTFE sheet fabrication process. This information which complements previous surface science investigations of PTFE-like materials, has had a major impact on our microwave device on PTFE program. It has pointed out PTFE substrate selection rules, demonstrated the need to perform pre-fabrication substrate roughness acceptance inspections, and indicated a path for potential resolution and reliability improvements. Experiments are in progress along this way and also to further understand exactly why tapping mode is successful in imaging this soft, high energy, polymeric material.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1 - SEM images of virgin (A) and etched (B & C) surfaces of PTFE.

Figure 2 - Contact Mode AFM images (Top View) of Virgin, (A), and Etched, (B), PTFE.

Figure 3- SEM micrographs of a "Blunt" Contact Mode AFM tip.

Figure 4- Tapping Mode AFM images (Top View) of Virgin, (A), and Etched, (B), PTFE. Note the fine fiber structure across the cracks in the etched surface.

Figure 5- 3-D Tapping Mode AFM images of Virgin, (A), and Etched, (B), PTFE.

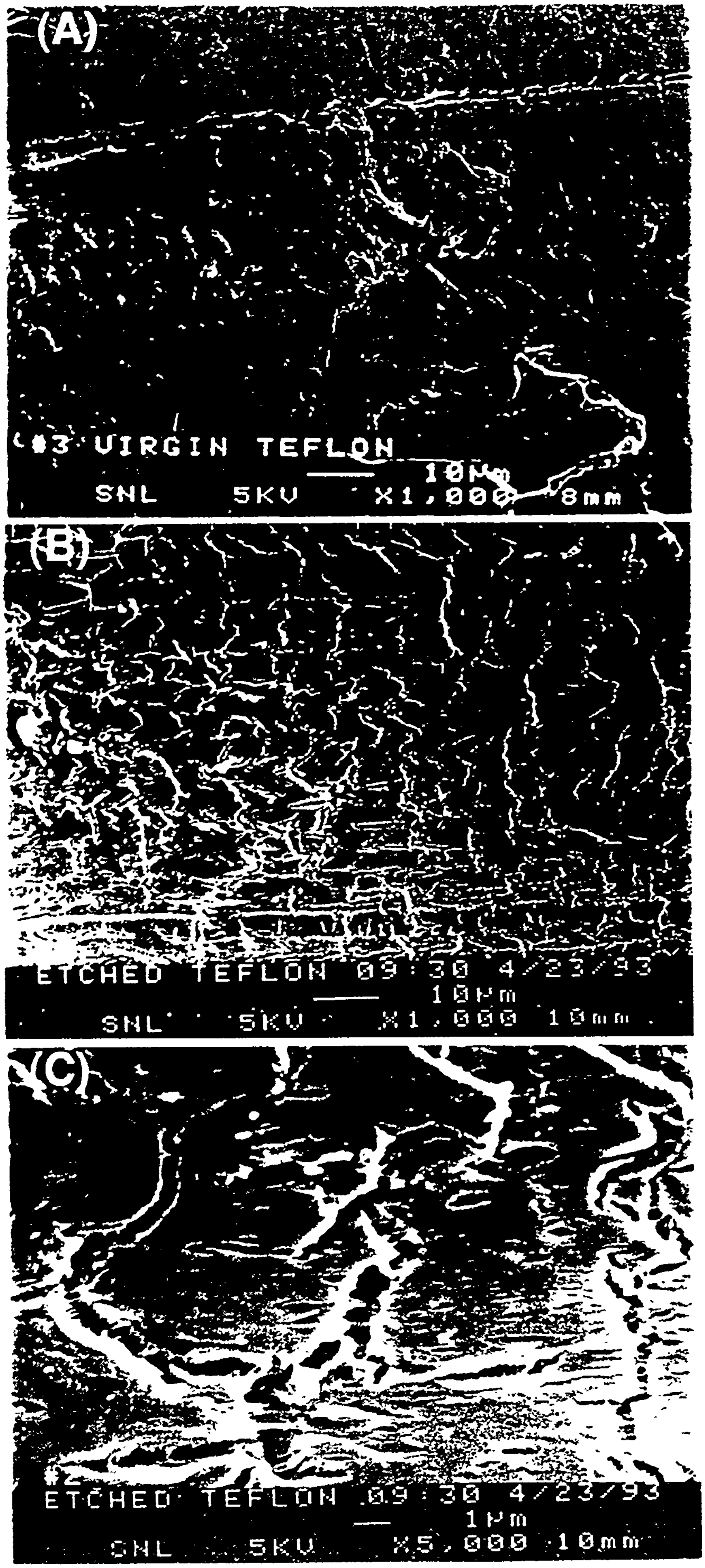
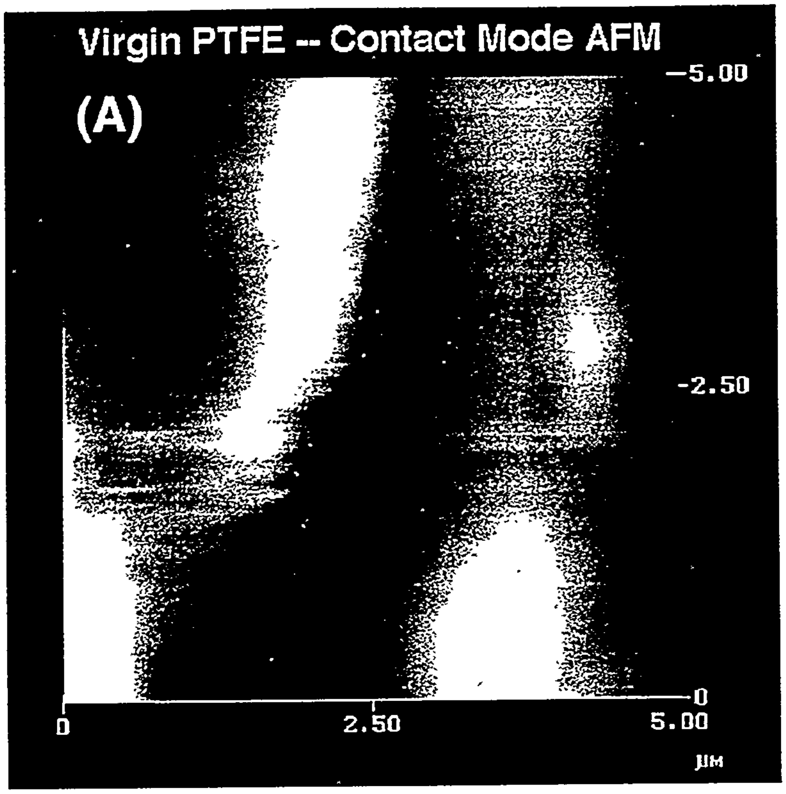

(A)
#3 VIRGIN TEFLON
10µm
SNL 5KV X1,000 8mm
(B)
ETCHED TEFLON 09:30 4/23/93
10µm
SNL 5KV X1,000 10mm
(C)
ETCHED TEFLON 09:30 4/23/93
1µm
SNL 5KV X5,000 10mm

Fig. 1


Virgin PTFE -- Contact Mode AFM
(A)
-5.00
-2.50
0
0
2.50
5.00
µm

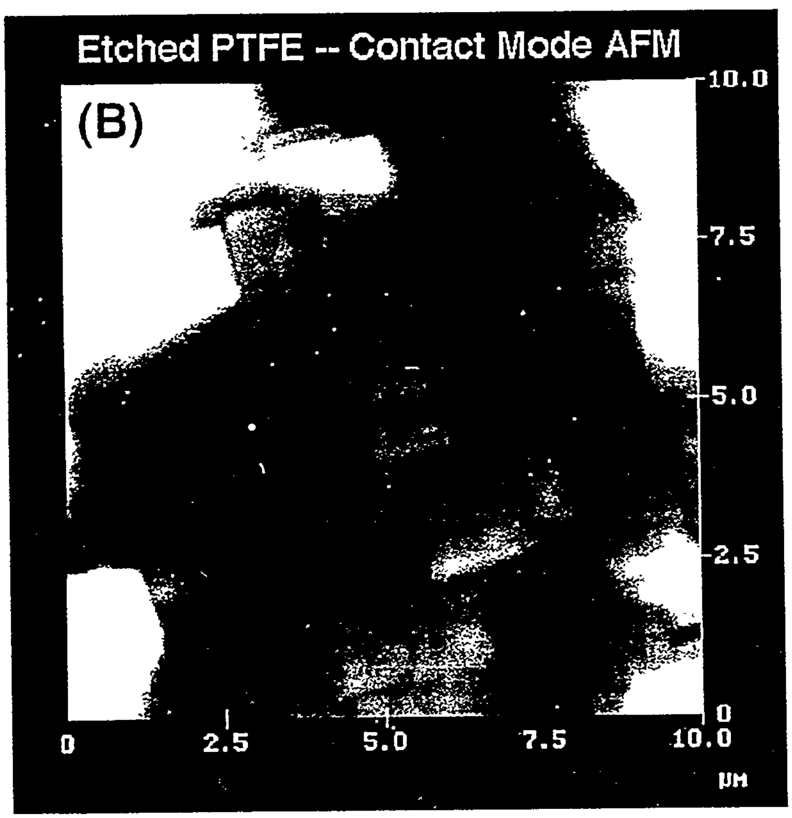

Etched PTFE -- Contact Mode AFM
(B)
10.0
7.5
5.0
2.5
0
0
2.5
5.0
7.5
10.0
µm

Fig. 2

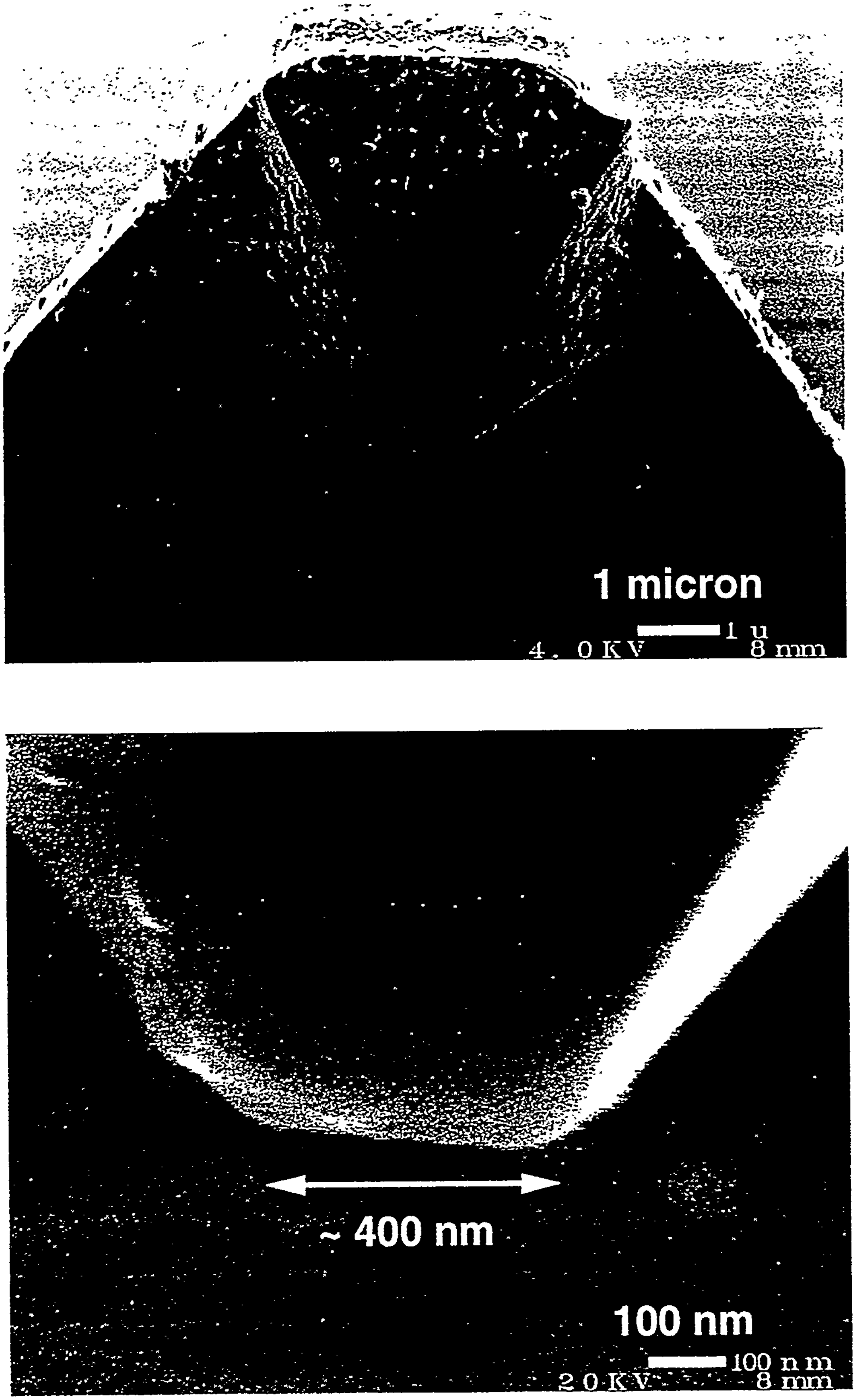
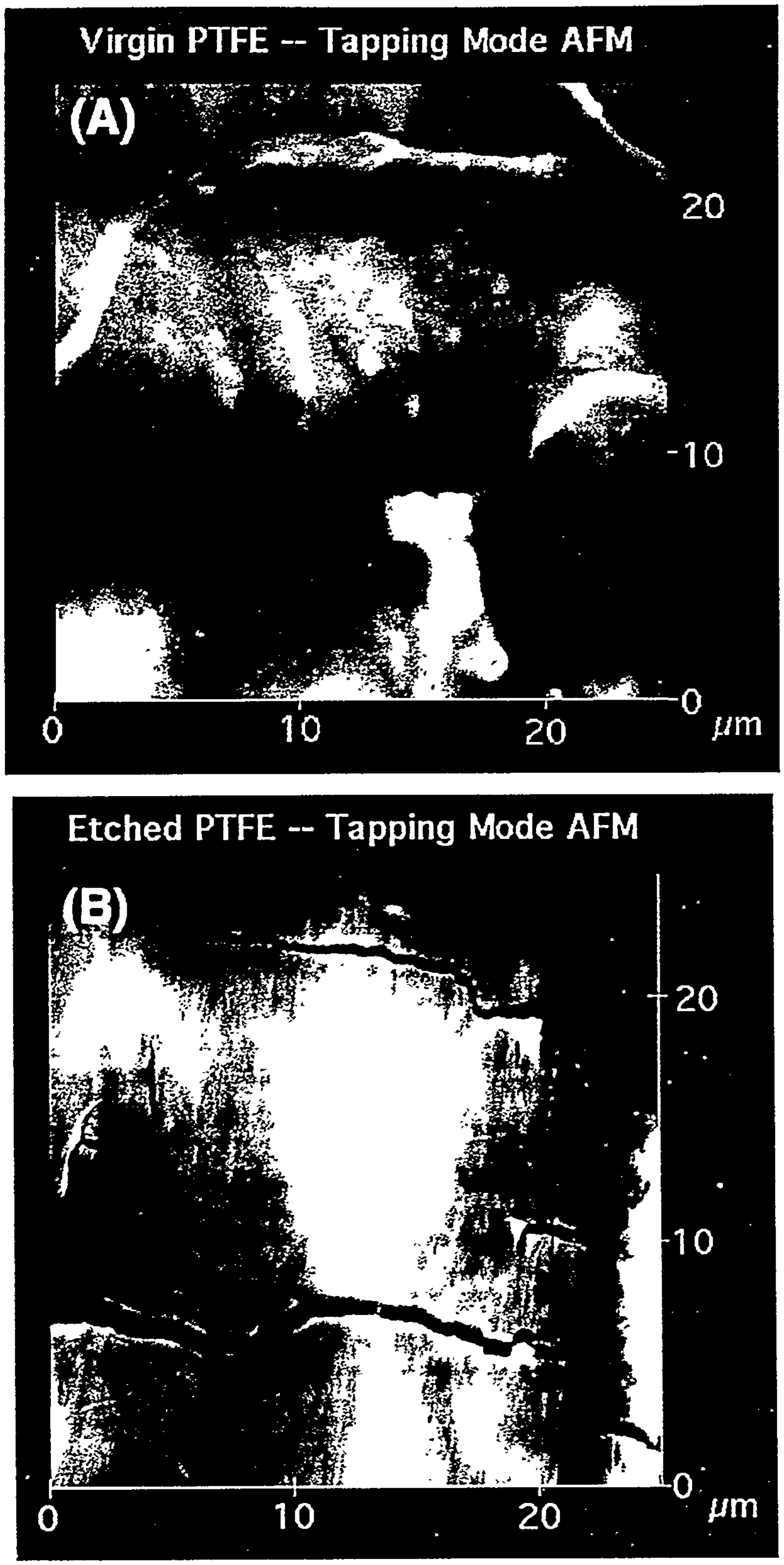


Fig. 3



Virgin PTFE -- Tapping Mode AFM
(A)
20
10
0
0
10
20
μm
Etched PTFE -- Tapping Mode AFM
(B)
20
10
0
0
10
20
μm

Fig 4

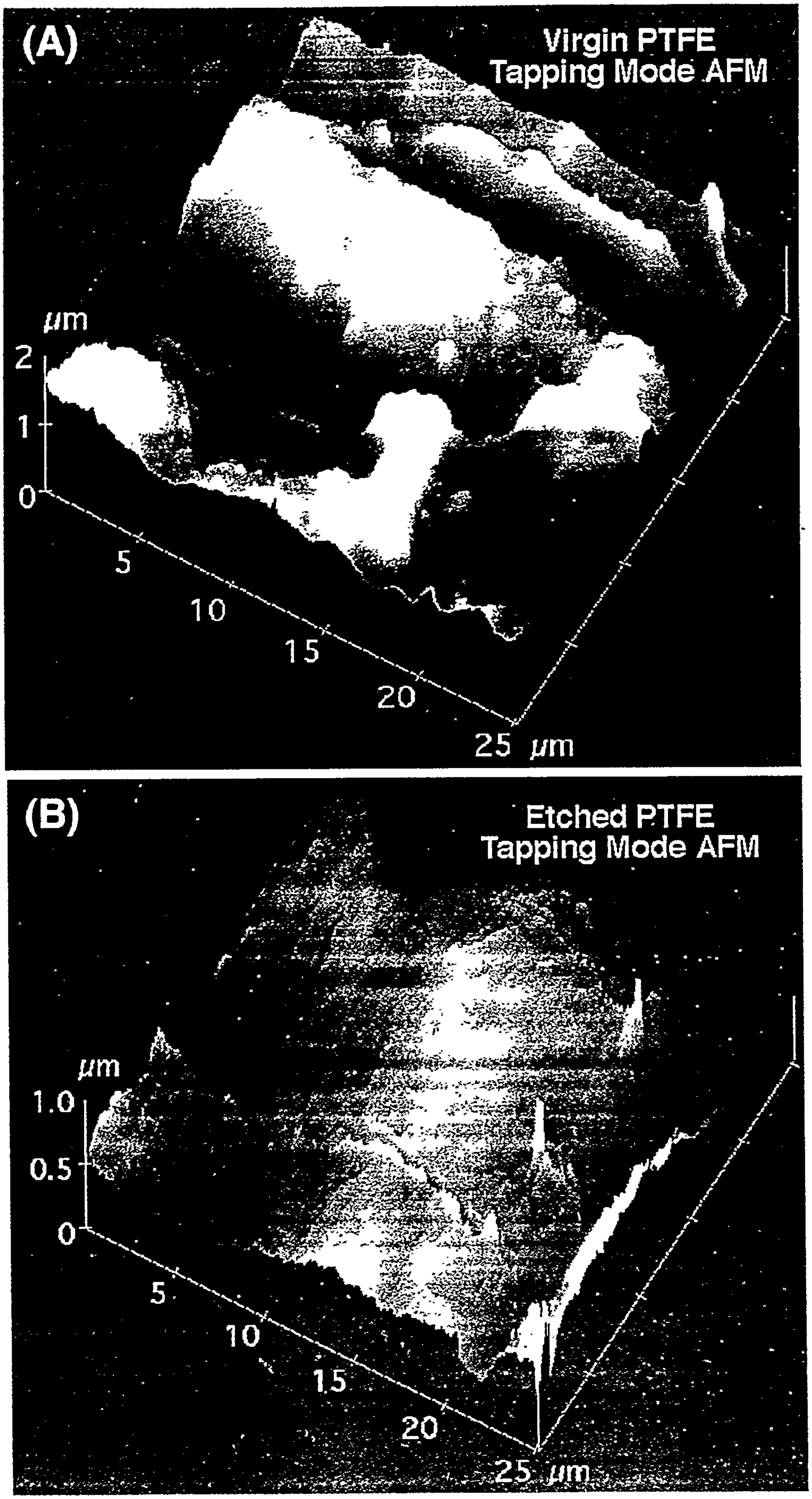

(A)
Virgin PTFE
Tapping Mode AFM
μm
2
1
0
5
10
15
20
25 μm
(B)
Etched PTFE
Tapping Mode AFM
μm
1.0
0.5
0
5
10
15
20
25 μm

Fig. 5