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# Interfacial Chemistry of Titanium Films Deposited on PMDA-ODA Polyimide

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ABSTRACT Titanium was evaporated onto PMDA-ODA polyimide surfaces at room temperature up to total thicknesses of about five monolayers. The polyimide backbone is ruptured at both the oxygen ether linkage in the ODA and at the nitrogen imide linkage. The first fraction of a monolayer reacts with oxygen atoms in both the carbonyl and ether functionalities and forms a mixed oxide with titanium predominantly in the $Ti^{+3}$ oxidation state. Near one monolayer coverage, a carbide or mixed oxy-carbide species forms. Above one monolayer, nitrogen is strongly attacked and about fifty percent of the nitrogen reacts with titanium. The deposited titanium begins to take on metallic character only after the coverage has reached several monolayers. Heating at 575 K causes additional reaction. STM images obtained in air following heating show that the composite surface is substantially roughened.

## 1. INTRODUCTION

Good interfacial adhesion and chemical stability at the metal-polymer interface is important for the successful application of polyimides in microelectronic packaging [1-3]. In this paper we describe an experimental investigation of the initial stages in the interaction of titanium with a PMDA-ODA polyimide film as observed with x-ray photoelectron spectroscopy (XPS) and scanning tunnelling microscopy (STM).

The only previous study of the interaction of titanium with polyimide films is by Ohuchi and Freilich [4] who used XPS and several other spectroscopy techniques to characterize the properties of submonolayers. They conclude that at low coverages Ti interacts strongly with the polyimide and that charge transfer takes place via the carbonyl groups. Above an estimated one-third monolayer coverage, Ti-C bonds also form. Russat [5] has also reported results of a study of the interfacial chemistry of thin polyamic acid films which had been spin-coated onto air-oxidized Ti substrates and then heated to form polyimide. During the heating, he found that titanium suboxides and oxynitrides form below 350 °C and $TiO_2$ is reduced to TiO. Heating to 450 °C forms Ti-N, Ti-C, and Ti-N-O bonds at the interface.

In the present study, polyimide films were formed by a vapor deposition technique [6,7]. PMDA (1,2,4,5-benzenetetracarboxylic anhydride) and ODA (1,4-oxydianiline) are simultaneously deposited onto a substrate where they spontaneously react to form polyamic acid. This intermediate is then cured to form the PMDA-ODA polyimide. The vapor deposited polyimide is identical to the spin coated material as characterized by XPS although it may have substantially lower molecular weight [7].

We report results for much higher titanium coverages than used in previous studies and find that about one-half of the N bonds in the depth probed by XPS are broken. The Ti-polyimide interface is found to be unstable against heating to 575 K.

## 2. EXPERIMENTAL

The samples used in these experiments were prepared and initially characterized in an ultra-high vacuum (UHV) chamber equipped for x-ray photoelectron spectroscopy (XPS). The XPS system was built by Vacuum Science Workshop and consists of a dual anode (Mg or Al) x-ray source and an HA 100 hemispherical electrostatic analyzer. All data presented in this report were obtained in the constant pass energy mode with 25 eV pass energy. The energy resolution in this mode is about 1.6 eV as determined from the full-width half-maximum of the Cu $2p_{3/2}$ emission from a clean surface. The energy scale was calibrated using the XPS spectra of clean Cu, Ag, and Au.

XPS data for the Ti covered polyimide is shown after background subtraction using the procedure developed by Tougaard [8]. In some cases, the structure of the XPS lineshapes was decomposed using a non-linear least-squares fitting procedure [9] assuming each component to have a Gaussian lineshape.

A Digital Instruments Nanoscope I scanning tunnelling microscope (STM) was used to characterize the surface morphology. This instrument operates in air so that the samples had to be removed from the vacuum chamber and consequently exposed to air prior to imaging.

The PMDA-ODA films were supported on a Ni(110) single crystal. The surface morphology of the Ni(110) substrate was characterized by STM prior to formation of the polymer film. The sample was cleaned by argon ion sputtering, followed by annealing for about one hour at 875 K in ultra-high vacuum. It was then cooled to room temperature, removed from the vacuum chamber and rapidly transported to the STM. Three typical images, all obtained from different 100 nm by 90 nm areas within one-half hour of removal from the vacuum chamber, are shown in Fig. 1(a)-(c). Although the surfaces are not completely flat, each image clearly shows that there are large flat regions on the surface. It should be kept in mind that the sample used for Fig. 1 had been transported through air and therefore was coated with a layer of oxide and probably contaminated with other adsorbed gases, including water molecules. Prior to coating with a PMDA-ODA film, the Ni crystal was cleaned by in situ cycles of argon ion bombardment and annealing.

FIGURE 1 GOES HERE

The PMDA-ODA films used in this study were prepared by in situ vapor deposition of PMDA and ODA molecules from separate sources as described previously [7]. At the start of a deposition, the sources are translated into the main vacuum chamber and positioned directly in front of the substrate. Upon completion of the deposition, typically 10 to 20 min, the sources are withdrawn into a separately pumped side chamber and a gate valve closed. The deposited layer is heated to 525 - 575 K to drive off excess ODA and to cure the polyimide. The resulting film is characterized by XPS to check that imidization is complete and that the film is thick enough to attenuate the Ni $2p_{3/2}$ emission by about 99 percent. Based on our previous studies, the resulting PMDA-ODA films are about 10 nm thick, continuous and conform to the substrate morphology [7,10]. STM images of the PMDA-ODA coated surface are indistinguishable from images of the substrate except for isolated small regions in which molecular order occurs [10].

Ti was deposited from an evaporation source consisting of a W wire basket heated by direct current. A deposition monitor was not available to calibrate the deposition rates but, based on attenuation of the XPS signals from the underlying PMDA-ODA film, the deposition rates are estimated to be between 0.5 and 1 nm/hr. The substrate was kept at room temperature (about 300 K) during deposition.

## 3. RESULTS

### 3.1. Deposition of Titanium at Room Temperature.

Ti depositions were carried out for for a total deposition time of 438 min. A complete set of Ti 2p, C 1s, N 1s, and O 1s XPS data was obtained after total deposition times of 4, 6, 10, 18, 78, 198 and 438 min. Following 10, 18, 198, and 438 min of deposition, the sample was allowed to stand in ultra-high vacuum overnight (for periods of 18, 24, 16 and 19.5 hr respectively) and a set of XPS spectra were obtained the following day prior to the next Ti dose. For C, N, and Ti there is no change in XPS lineshape. In the case of O, there may be a slight increase in the component near 530 eV perhaps due to reaction with water which was the major component of the residual background, but this increase, if real, is only just discernible above the noise level. We conclude that Ti interacts rapidly when deposited on PMDA-ODA at room temperature and that the reaction products are stable.

Although the Ti coverage cannot be accurately determined from our data, we can compare our measurements with the results of Ohuchi and

Freilich [4] who estimated their coverages using attenuation of the C LVV Auger signal. However, we emphasize that the coverage estimates made by Ohuchi and Freilich may have substantial uncertainties. Our Ti 2p emission after 18 min deposition is similar in shape to their 25 % monolayer result. Our C 1s emission has developed a distinct new peak at 281.5 eV by 78 min and corresponds to their 78 % monolayer case. The shake-up feature at 538 eV has been suppressed for our O 1s emission by 10 min compared to their 25 % monolayer data. Finally, the new N 1s feature at about 397.5 eV is comparable in relative intensity to their 52 % and 78 % data after a total 18 min dose. Taken together, this comparison indicates that our Ti exposure reaches one monolayer between 18 and 78 min and that our total exposure is therefore extrapolated to be between 6 and 24 monolayers.

### 3.2. Initial Ti interaction.

All of the XPS binding energies measured at low Ti coverages are in excellent agreement with the values reported by Ohuchi and Freilich [4].

The most rapid changes take place during the first 18 min of the deposition and our spectra are very similar in shape to the low coverage spectra reported by Ohuchi and Freilich. The O 1s emission is the most strongly altered as shown in Fig. 2a. The O 1s peak from clean PMDA-ODA is a doublet [7,10,11] with the component at about 532 eV due to carbonyl oxygens and the shoulder at about 533.5 eV due to the ether O linkage in the ODA part of the polymer. A new low binding energy shoulder due to

FIGURE 2 GOES HERE

emission at about 530.4 eV is observed already after 4 min. If this peak is fit by three Gaussian components, each with the instrumental linewidth, the new oxygen state (530.4 eV) is found to contain about 27 % of the total intensity and the ratio of carbonyl oxygen to ether oxygen is unchanged from its clean surface value. We interpret this result to mean that Ti attacks both ether and carbonyl oxygen sites with about equal probability. This contrasts with Ohuchi and Freilich who, however, did not attempt a lineshape analysis. At least some of the Ti must be oxidized in order to produce the new oxygen state at 530.4 eV.

The C 1s lineshape also changes as illustrated in Fig. 2b. The carbonyl carbon emission (288.5 eV) is reduced by about 25 % and the high energy component of the main peak (286 eV), which is composed primarily of emission from carbons which are bonded either to nitrogen or to the ether oxygen [11], also looses intensity. These changes are consistent with the changes observed in the O 1s lineshape.

The N 1s signal is attenuated by about 25 % during the first monolayer of Ti deposition, but no new emission is observed indicating that N 1s does not interact directly with the initial Ti deposit. The N 1s line is at about 400.6 eV, in good agreement with previous XPS studies of polyimides and indicates no charging of this film.

The initial Ti deposit, shown in Fig. 3, has its 2 $p_{1/2}$ emission at 458.3 eV with prominent shoulders at about 455 eV and 457 eV. Clearly, at least three Ti valence states are present from the very onset of deposition. By the highest coverage, the 2 $p_{1/2}$ peak has shifted by about 4 eV to a binding energy

FIGURE 3 GOES HERE

of 454.4 eV that is more characteristic of metallic Ti. Comparison of this 4 eV shift with the results of Rocker and Goepel [20] lead to the conclusion that Ti initially reacts to form $Ti^{3+}$ with smaller amounts of lower oxidation states.

### 3.5. High Ti Coverages.

As Ti deposition continues, the O 1s signal continues to evolve. Figure 4a shows the spectrum following 198 min of Ti deposition. Curve fitting shows that the oxide state at 530.4 eV has increased to about 35% of the total signal and that the ether component (533.4 eV) is slightly reduced relative to the carbonyl component (531.9 eV) indicating that Ti may have a slight preference to attack the ether O site. The shake-up feature at 538 eV has almost completely disappeared.

FIGURE 4 GOES HERE

Figure 4b shows that the carbonyl carbon peak at 288 eV continues to decrease as Ti coverage increases, that a new feature appears at 282 eV, and that the intensity in the unresolved doublet continues to shift into the lower binding energy component. Unlike the O 1s shake-up, the C 1s shake-up feature (287 - 291 eV) remains strong. This is evidence that Ti does not interact significantly with the aromatic rings of the polymer.

The most dramatic changes at high Ti coverages are observed in the N 1s emission as illustrated in Fig. 4c. A strong new feature appears at a binding energy of about 397 eV and the Ni substrate Auger emission appearing at 407 eV is almost completely attenuated.

We interpret these results to show that Ti reacts to form carbide, oxide, nitride, and mixed compounds similar to those reported bu Russat [5] for polyimide coated Ti subtrates. The strong attack on nitrogen has not been previously reported since Ohuchi and Freilich did not use high enough Ti coverages to observe significant Ti-N interaction. Clearly, Ti attacks PMDA-ODA not only at the carbonyl functionality but also breaks the polymer backbone by reacting with the imide nitrogen atoms and the ether oxygen atoms.

The Ti 2p emission after 438 min has evolved to a complex line shape which has significantly enhanced metallic character. We conclude that regions of metallic Ti begin to be stable once the coverage exceeds several monolayers.

The Auger emission from the Ni(110) substrate is continuously reduced in intensity during the deposition of the Ti overlayer. This demonstrates clearly that the net thickness of the Ti-polyimide composite is increasing and that the Ti containing layer does not contain thin regions.

### 3.6. Effects of Heating the Ti Film.

Following the total Ti dose of 438 min, the sample was heated to 575 K for 60 min and then cooled to room temperature. Figure 5 compares the O 1s, N 1s, and C 1s spectra for clean polyimide with the spectra obtained after heating at 575 K. Most simply stated, the changes in peak shapes observed during room temperature dosing are further enhanced by the heating. The fraction of higher Ti oxidation states also is increased by the heating.

FIGURE 5 GOES HERE

Figure 6 shows STM images obtained from four 100 nm x 100 nm

FIGURE 6 GOES HERE

regions of the surface after removing the heated film from the vacuum chamber. As in the case of the copper coated sample, the surface has been substantially roughened without increasing the signal from the Ni substrate. We believe that the fuzzy nature of these images is due to complete oxidation of the Ti upon exposure to air. This oxide forms a partially insulating layer which charges slightly during STM imaging.

## 4. DISCUSSION AND CONCLUSIONS

We have studied the interaction of thin Ti overlayers with PMDA-ODA films formed by vapor deposition. We conclude that Ti interaction is even stronger than reported in previous studies of spin coated films. The Ti films were deposited at 300 K up to thicknesses of about five-to-ten monolayers. The oxidation of some of the Ti during deposition of the initial submonolayer is achieved by chemical attack on the carbonyl groups as also reported by Ohuchi and Freilich [4].

Titanium appears to attack all oxygen and nitrogen sites on the polyimide molecular chain. Quantitative analysis of the XPS lineshapes is not possible due to their complex structure, the large number of valence states possible for Ti, and the possibility of formation of mixed oxides, carbides and nitrides. The initial submonolayer of Ti reacts with oxygen. At higher coverages, Ti attacks carbon and finally, at about one monolayer coverage, it begins to react with nitrogen. As might be expected, this sequence follows the heats of formation of Ti oxides, carbides and nitrides with the oxides being more stable [13].

STM measurements carried out in air, show that the surface of the annealed Ti covered polyimide films are much rougher than the underlying substrate. Future STM measurements should be done in ultra-high vacuum in both imaging and spectroscopy modes. This will eliminate any artifacts introduced in the present study caused by exposure of the samples to air and may also allow us to determine the distribution of electronic states and whether or not the metal uniformly covers the surface.

The Ti layer only begins to show metallic character after several monolayers have been deposited onto a room temperature polyimide film. However, heating the film causes additional reaction presumably by allowing Ti atoms to diffuse to new reaction sites. Thus, we find that the Ti-polyimide interface is very unstable at temperatures normally used in microelectronic device fabrication and packaging.

## 5. ACKNOWLEDGEMENTS

R. G. Mack built the deposition source and carried out the XPS measurements and E. Grossman obtained the STM images. This research was supported by the IBM Corporation, Endicott, NY.

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## FIGURE CAPTIONS

Figure 1. Scanning tunneling microscope images of uhv cleaned, air-exposed Ni(110). The images are from 100 nm x 90 nm regions and the length of the vertical bar in the center of the figure corresponds to 4 nm vertical distance.

Figure 2. (a) Comparison of (a) the O 1s and (b) the C 1s lineshapes from clean polyimide and after 18 min Ti deposition.

Figure 3. Comparison of the Ti 2p lineshapes after 4 min and 438 min depositions of Ti onto clean polyimide.

Figure 4. (a) The O 1s lineshape after 198 min of Ti deposition. (b) The C 1s lineshape after 198 min Ti deposition. (c) The N 1s lineshape after 438 min Ti deposition.

Figure 5. Comparison of (a) the O 1s, (b) the N 1s, and (c) the C 1s XPS lineshapes from clean polyimide with those after heating the Ti covered surface to 575 K for 60 min.

Figure 6. Scanning Tunnelling Microscope images of a Ti covered polyimide surface obtained in air following heating at 575 K in vacuum. The images are from 100 nm x 100 nm regions and the bar in the center of the figure corresponds to 4 nm in the vertical direction.

FIGURE 1

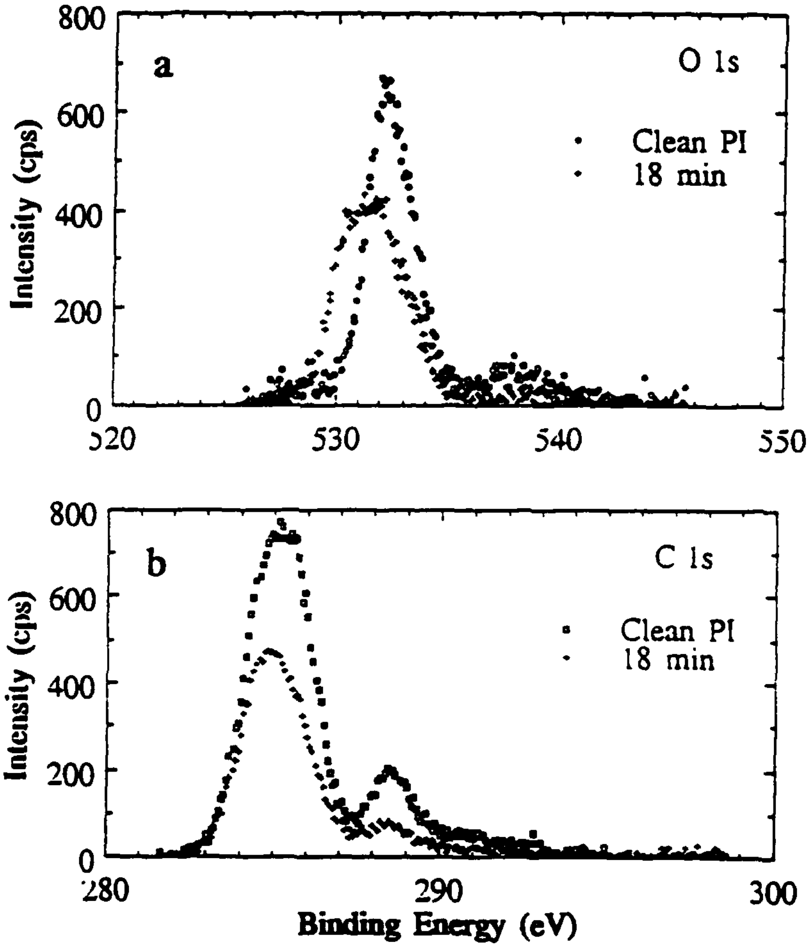


FIGURE TWO LINEL

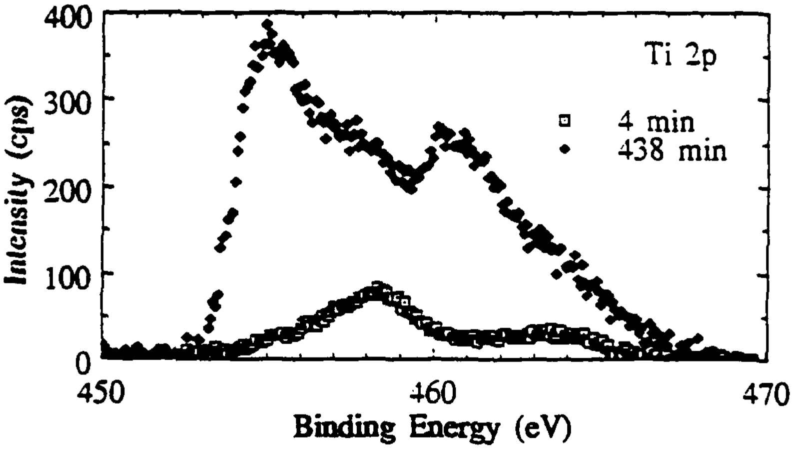
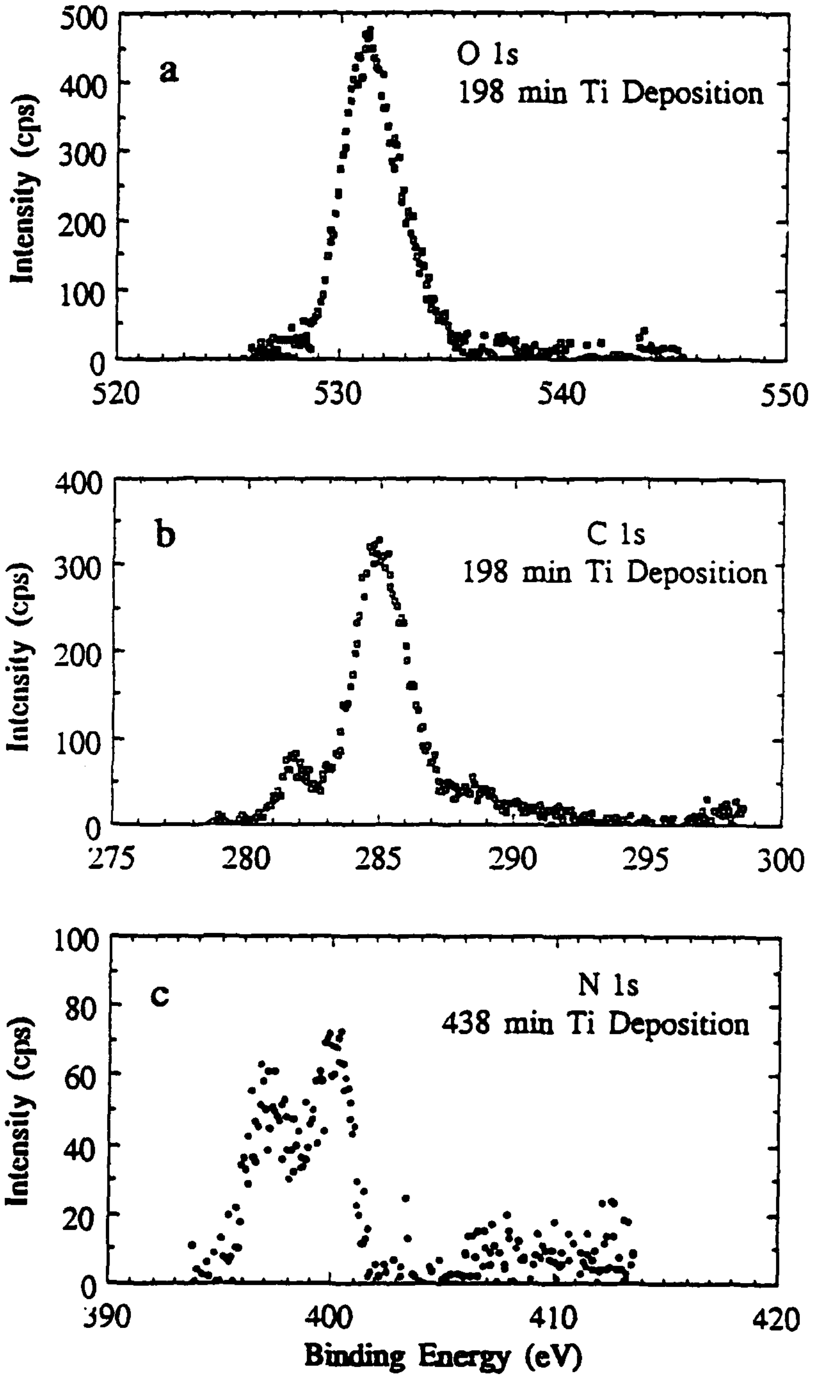


FIGURE 7 INSERT


a
O 1s
198 min Ti Deposition
Intensity (cps)
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100
200
300
400
500
520
530
540
550
b
C 1s
198 min Ti Deposition
Intensity (cps)
0
100
200
300
400
275
280
285
290
295
300
c
N 1s
438 min Ti Deposition
Intensity (cps)
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40
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100
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400
410
420
Binding Energy (eV)

Figure 4 [illegible]

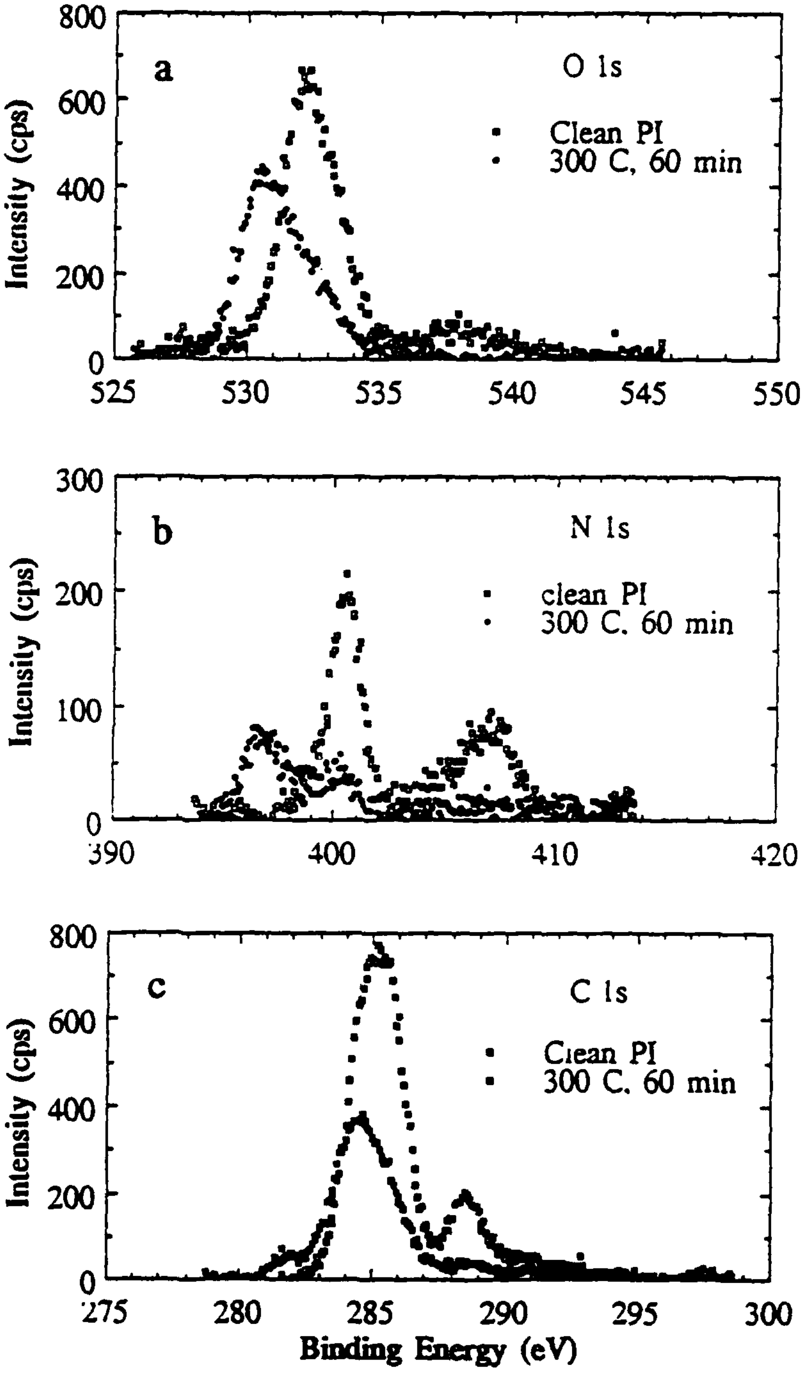

FIGURE 5 LINERT

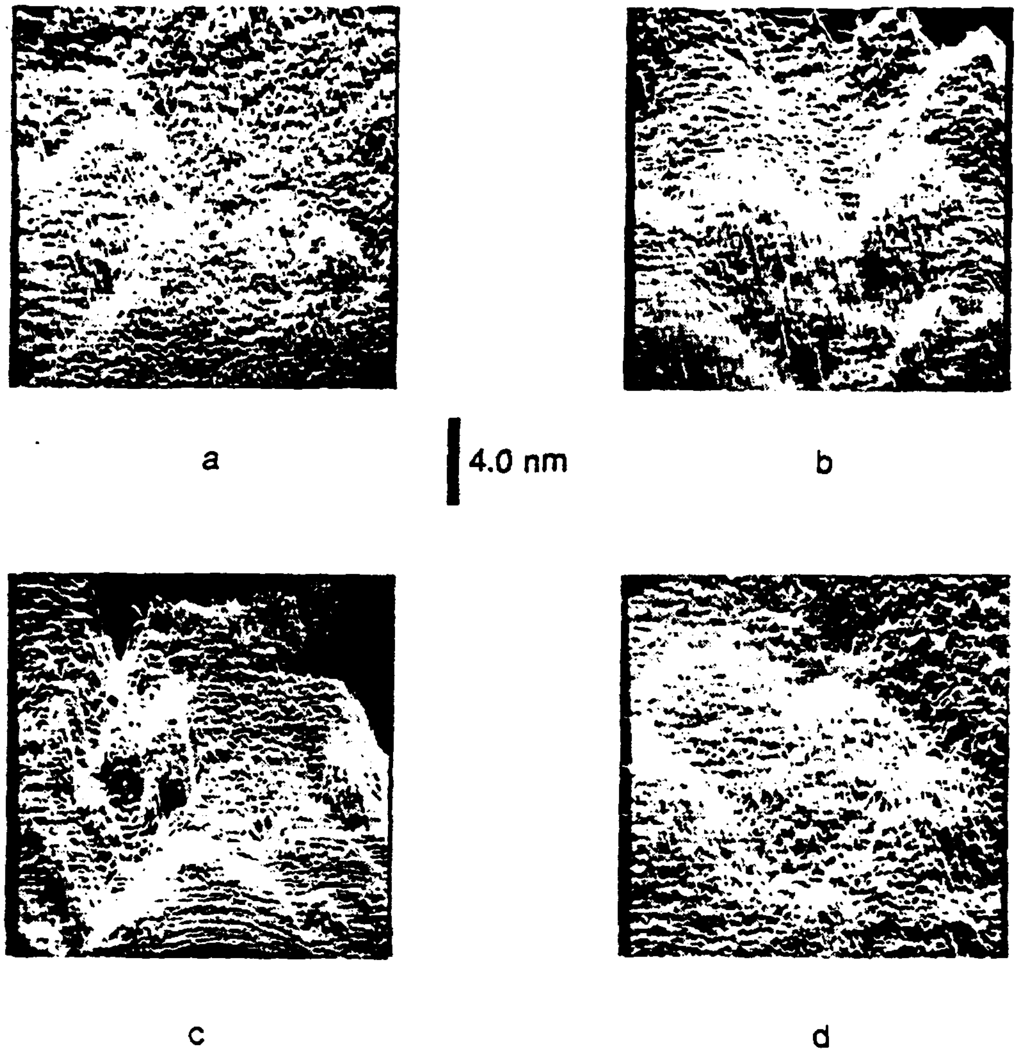

FIGURE 6

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