

Polymer Communication

# Imaging of sub-surface nano particles by tapping-mode atomic force microscopy

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## Abstract

Time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy (XPS), and tapping mode atomic force microscopy (TM-AFM) were used to study the surface of a poly(*N*-vinyl-2-pyrrolidone) thin film containing nano silica particles. ToF-SIMS results illustrate that the topmost layer of the thin film consists of PVP and a small amount of poly(dimethyl siloxane) (PDMS). Nano silica particles are localized underneath this layer. XPS results suggest that the concentration of the silica particles increases as the sampling depth increases from 5.3 to 7.2 nm. TM-AFM phase imaging is shown to be capable of detecting the presence of these sub-surface nano silica particles. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** XPS; SIMS; TM-AFM

## 1. Introduction

It is well known that polymer surfaces play an important role in their applications such as adhesion, protective coating, friction and wear, microelectronics, and thin film technology. However, up to now, the term surface has not been well defined because a surface defined by one technique can be the bulk as revealed by another technique [1]. The most appropriate definition of a surface is the sampling depth of a solid measured by a particular technique. For time-of-flight secondary ion mass spectrometry (ToF-SIMS), only secondary ions coming from the top few layers of the surface atoms are analyzed. It is usually accepted that the sampling depth of ToF-SIMS is less than 1 nm when molecular ions are considered [2–5]. The sampling depth of X-ray photoelectron spectroscopy (XPS) can be varied from 2 to 10 nm by changing the take-off angle [2,6]. Atomic force microscopy (AFM) has been claimed to be very surface sensitive and has been used to measure surface features of polymer samples [7–9]. The combination of AFM, ToF-SIMS, and XPS allows us to obtain chemical and physical information at different sampling depths.

Recently, AFM has been recognized as a powerful surface characterization technique and has been widely used to study surface morphology of homopolymers [10–13], block copolymers [14–16], and polymer blends [17–26]. In addition, tapping mode AFM (TM-AFM) has been employed to determine the bulk morphology of polymer blends [27]. Even though TM-AFM is widely used, there are still many important issues that have not been explored extensively, such as sampling depth. The indentation depth has been shown to depend on the stiffness of the sample, the set-point amplitude ratio, and cantilever stiffness [28,29]. However, not much experimental work has been done to compare the sampling depth of TM-AFM with other surface analysis techniques. In this paper TM-AFM was used to detect nano silica particles underneath an ultra-thin polymer film. A comparison between the sampling depths of TM-AFM, SIMS and XPS was made.

## 2. Experimental

Poly(*N*-vinyl-2-pyrrolidone) (PVP) ( $\bar{M}_w = 360,000$ ) was supplied by Sigma Chemical Company and was used as received. Colloidal silica (Snowtex 40) was obtained from Nissan Chemical Industries, LTD. It contains 40 wt% SiO<sub>2</sub> particles. The average diameter for the SiO<sub>2</sub>

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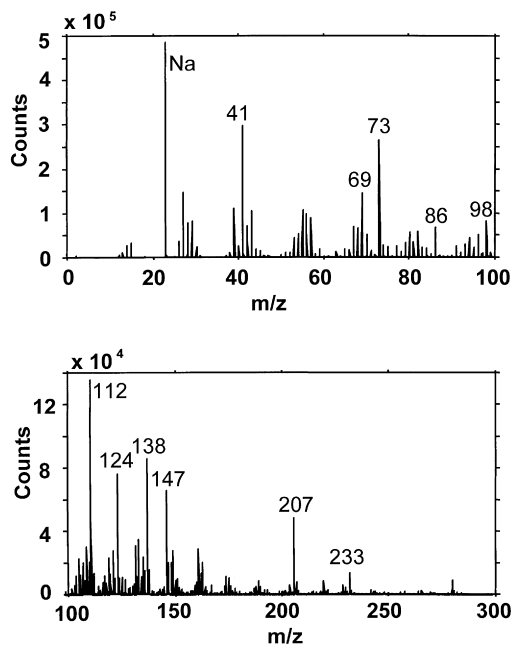


Fig. 1. Positive ToF-SIMS spectrum of the PVP/silica thin film surface.

particles is 10–20 nm [30]. A PVP/silica solution was prepared by adding 0.3 ml of SNOWTEX 40–10 ml of 3 wt% PVP water solution and the mixture was stirred overnight. Samples for ToF-SIMS and TM-AFM measurements were prepared by spin-casting the PVP/silica solution on silicon wafers and then dried in a vacuum oven overnight. The thickness of the film was measured to be approximately 80 nm by a profilometer.

ToF-SIMS measurements were conducted on a Physical Electronics PHI 7200 ToF-SIMS spectrometer equipped

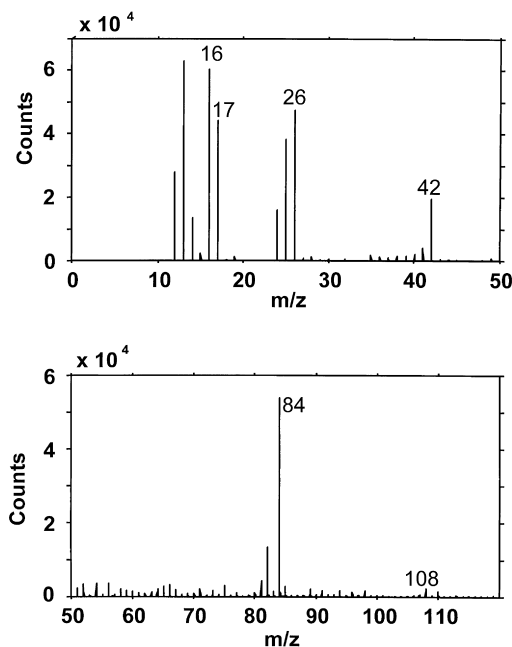


Fig. 2. Negative ToF-SIMS spectrum of the PVP/silica thin film surface.

with two ion guns ( $\text{Cs}^+$  for high mass resolution spectrometry and  $^{69}\text{Ga}^+$  for spatially resolved imaging) and a reflection ToF analyzer. Both positive and negative high mass resolution spectra were obtained by using an 8 kV  $\text{Cs}^+$  ion source. The scanned area was  $200 \times 200 \mu\text{m}^2$  and the total ion dose for each spectrum acquisition was  $< 4 \times 10^{11}$  ions/ $\text{cm}^2$ . In addition, a depth profile of the thin film was also obtained.

XPS measurements were performed on a PHI 5600 multi-technique system equipped with an Al monochromatic X-ray source. A pass energy of 23.5 and 187.85 eV was used respectively for obtaining the high resolution and survey spectra. In this study, the take-off angles used were 20, 45, and  $75^\circ$ .

TM-AFM images were obtained by using a NanoScope III MultiMode<sup>TM</sup>AFM (Digital Instruments) at room temperature. A Si tip with a resonance frequency of 300 kHz was used and the scan rate was 0.7 Hz. The sample/line was 512. The spring constant of the tip is about  $40 \text{ N m}^{-1}$ .

### 3. Results and discussion

#### 3.1. ToF-SIMS spectra

The surface of PVP/silica thin film was first analyzed by ToF-SIMS to determine the surface chemical composition. Fig. 1 depicts a positive ToF-SIMS spectrum of the thin film surface. Obviously, the spectrum is dominated by the characteristic fragments of PVP at  $m/z = 41(\text{C}_3\text{H}_5^+)$ ,  $69(\text{C}_4\text{H}_5\text{O}^+)$ ,  $86(\text{C}_4\text{H}_8\text{NO}^+)$ ,  $98(\text{C}_5\text{H}_8\text{NO}^+)$ ,  $112(\text{C}_6\text{H}_{10}\text{NO}^+)$ ,  $124(\text{C}_7\text{H}_{10}\text{NO}^+)$ ,  $138(\text{C}_8\text{H}_{12}\text{NO}^+)$ ,  $207(\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}_2^+)$ , and  $233(\text{C}_{12}\text{H}_{17}\text{N}_2\text{O}_2^+)$  [4,5]. In addition, characteristic fragments of poly(dimethyl siloxane) (PDMS) at  $m/z = 73(\text{C}_3\text{H}_9\text{Si}^+)$ , and  $147(\text{C}_5\text{H}_{15}\text{OSi}_2^+)$  [4,5] are also detected. However, it should be noted that the characteristic

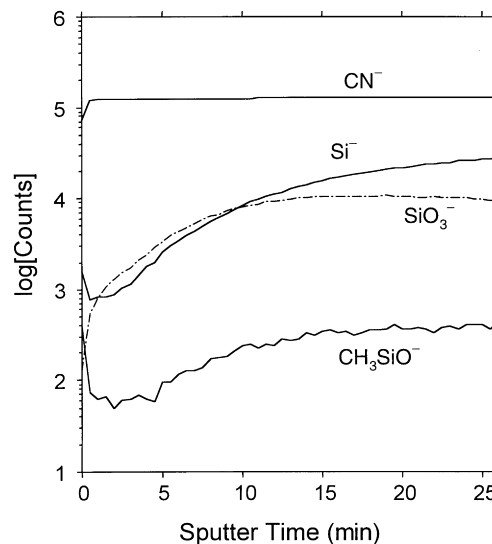


Fig. 3. ToF-SIMS depth profile of the PVP/silica thin film surface.

Table 1  
Surface chemical compositions of the of PVP/silica thin film obtained by angle-resolved XPS

Take-off angle (°)	Sampling depth (nm)	Element (at%)					
		C	N	O	Si	Si1 (PDMS)	Si2 (SiO <sub>2</sub> )
20	2.6	76.2	9.9	12.7	1.2	0.5	0.7
45	5.3	75.2	11.3	12.2	1.3	0.3	1.0
75	7.2	73.9	11.3	13.1	1.7	0.2	1.5

fragments of SiO<sub>2</sub> are not detected in these spectra. These results suggest that no silica particles are detected on the surface, and only PVP and a small amount of poly(dimethyl siloxane) (PDMS) are present. The PDMS was probably transferred to the sample during drying in the vacuum oven.

Fig. 2 shows a negative ToF-SIMS spectrum of the surface. It is very clear that the spectrum is dominated by the negative characteristic fragments of PVP at  $m/z = 16(\text{O}^-)$ ,  $17(\text{OH}^-)$ ,  $26(\text{CN}^-)$ ,  $42(\text{CNO}^-)$ ,  $84(\text{C}_4\text{H}_6\text{NO}^-)$ , and  $108(\text{C}_6\text{H}_6\text{NO}^-)$  [4,5]. Similar to the positive ToF-SIMS spectrum, the negative characteristic fragments of PDMS at  $m/z = 59(\text{CH}_3\text{SiO}^-)$ ,  $60(\text{SiO}_2^-)$ , and  $75(\text{CH}_3\text{SiO}_2^-)$  are also detected [4,5]. But their intensities are quite low. Even though SiO<sub>2</sub> can produce SiO<sub>2</sub><sup>-</sup>, we believe that the SiO<sub>2</sub><sup>-</sup> is originated from PDMS instead of SiO<sub>2</sub>. This is due to the fact that other characteristic fragments of SiO<sub>2</sub>, such as SiO<sub>3</sub><sup>-</sup> and SiO<sub>3</sub>H<sup>-</sup> at  $m/z = 76$  and  $77$ , are not detected. Thus, the result from the negative ToF-SIMS spectrum confirms that only PVP and a small amount of PDMS are present on the surface of the PVP/silica thin film.

### 3.2. ToF-SIMS depth profile

In order to further confirm that only PVP and a small amount of PDMS are on the surface of the PVP/silica thin film, a ToF-SIMS depth profile was obtained and presented in Fig. 3. In this figure, CN<sup>-</sup>, SiO<sub>3</sub><sup>-</sup> and CH<sub>3</sub>SiO<sub>2</sub><sup>-</sup> represent respectively PVP, SiO<sub>2</sub> and PDMS. Si<sup>-</sup> comes from SiO<sub>2</sub> and PDMS. In accordance with this profile, several important facts are revealed. Firstly, as sputter time increases, the CN<sup>-</sup> intensity increases and then quickly attains a constant value, indicating that PVP is the matrix of the thin film. Secondly, the CH<sub>3</sub>SiO<sub>2</sub><sup>-</sup> intensity decreases significantly initially then reaches a constant value as sputter time further increases, implying that PDMS on the surface is removed by sputtering and a small amount of PDMS is still present in the bulk. Thirdly and more importantly, the SiO<sub>3</sub><sup>-</sup> intensity increases monotonically with sputter time at the beginning and then reaches a constant value. The increase in the SiO<sub>3</sub><sup>-</sup> intensity is attributed to the exposure of the sub-surface silica particles. Finally, the Si<sup>-</sup> intensity, due to the contribution of both PDMS and SiO<sub>2</sub>, first decreases then monotonically increases as sputter time increases.

### 3.3. XPS results

The ToF-SIMS results indicate that there is a thin layer of PVP and a small amount of PDMS at the surface. To determine the thickness of this PVP layer, XPS was used. Table 1 shows the surface chemical compositions of the PVP/silica film obtained at different take-off angles. The sampling depths at different take-off angles were estimated by assuming an attenuation length of 2.5 nm. Fig. 4 shows an XPS Si 2p spectrum obtained at the take-off angle of 20°. The Si 2p spectrum can be fitted with two components: Si(1) at 101.5 eV and Si(2) at about 103 eV. Si(1) and Si(2) are attributed to PDMS [6] and SiO<sub>2</sub> [31], respectively. The Si 2p spectra obtained at two other take-off angles are also curve-fitted and the results are summarized in Table 1. It can be observed that the concentration of PDMS and SiO<sub>2</sub> decreases and increases, respectively as sampling depth increases. This result is consistent with the fact that PDMS is a surface contaminant and SiO<sub>2</sub> is found mostly underneath the surface. Also the SiO<sub>2</sub> concentration is found to increase more significantly as the sampling depth increases from 5.3 to 7.2 nm. The only plausible explanation for this result is that the concentration of the silica particles increases as sampling depth increases. The combined

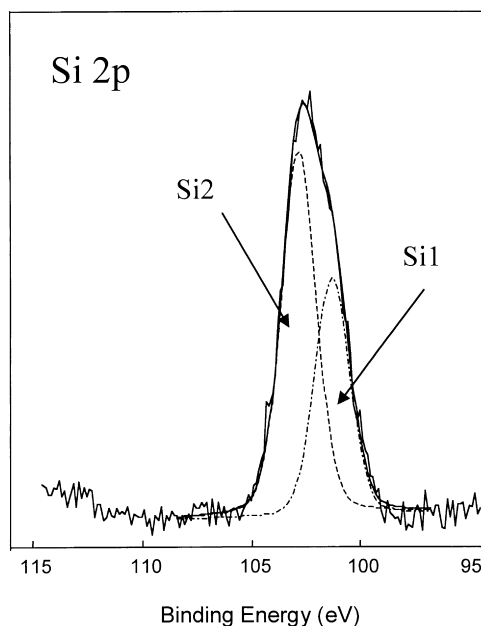


Fig. 4. XPS Si2p spectrum obtained at the take-off angle of 20°.

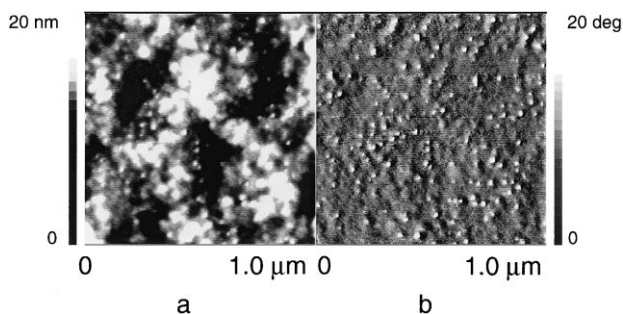


Fig. 5. TM-AFM images of the PVP/Silica thin film surface using a set-point amplitude ratio of 0.49. (a) the TM-AFM height image; and (b) the TM-AFM phase image.

ToF-SIMS and XPS results reveal the morphology of the film from the surface down to a depth of about 7.2 nm.

### 3.4. TM-AFM study

To test the capability of the TM-AFM to detect sub-surface structure, the height and phase images of the film surface were obtained. Our ToF-SIMS and XPS results on the PVP/silica film have shown that the silica particles are situated at a depth of about 5 to 7 nm from the surface. If TM-AFM can detect sub-surface structure, it may be possible to reveal the presence of the silica particles in the phase image of the sample because silica is much harder than PVP.

Fig. 5 displays the TM-AFM height and phase images of the PVP/Silica thin film surface, using a set-point amplitude ratio of 0.49. In the phase image, the bright dots are identified as nano silica particles because silica particles are much harder than PVP. The average diameter of these silica particles that ranges from 10 to 20 nm is in total agreement with the TEM results [30]. A careful comparison between the height and phase images reveals that the particles detected in the phase image do not completely correspond to the features observed in the height image. From the height image, some small silica particles can be observed and there are large features that show the morphology of the polymer at the topmost layer of the surface. Many more silica particles are seen in the phase image because TM-AFM can provide morphology information at the sub-surface region. This result is consistent with those of XPS and ToF-SIMS.

## 4. Conclusions

ToF-SIMS, XPS, and TM-AFM were used to study the surface of a PVP/silica thin film. ToF-SIMS results indicated that the topmost layer consists of only PVP and a small amount of PDMS. More nano silica particles are located at 5–7 nm underneath the surface. Our results clearly reveal that TM-AFM is capable of detecting the nano silica particles that are located at a sub-surface region.

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