Improvement of metal adhesion to silicone films: a ToF-SIMS study

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Abstract—This report describes a fundamental study of strategies aimed at improving metal adhesion to poly(dimethylsiloxane) (PDMS) films. The considered routes involve, in particular, the 2 keV Ar$^+$ ion bombardment of the PDMS film, which proves to be very efficient, as indicated by the tape test. Complementary treatments include thermal annealing of the PDMS film and its cleaning with selected solvents. At each step of the study, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is used as a diagnostic tool for the assessment of the sample surfaces. Via a sample preparation procedure involving deposition of minute amounts of gold (20 nmol/cm^2) on the surface to enhance ionization (Metal-Assisted SIMS or MetA-SIMS), ToF-SIMS reveals the presence of short PDMS chains on the surface of the films. The Ar$^+$ ion bombardment/hexane-cleaning treatments of the films remove this oligomer overlayer and, thus, lead to a significant adhesion improvement of the titanium layer. Therefore, the ToF-SIMS results strongly support a scenario in which the adhesion of titanium to untreated films is limited by the presence of short, mobile oligomers on the PDMS surface.

Keywords: Adhesion; SIMS; metallization; poly(dimethylsiloxane); PDMS.

1. INTRODUCTION

Silicone rubber is routinely used for biomedical applications and, in several cases, the polymer surface has to be covered with a thin layer of a biocompatible metal such as titanium. The adhesion of a metal film to a silicone surface, however, constitutes a challenging issue.

Several strategies have been proposed over the years to enhance hydrophilicity or hydrophobicity of PDMS, and cell or coating adhesion to PDMS, including bombardment of the polymer surface by keV ions [1, 2], by laser beams [3, 4] and exposure to plasmas [1, 5–10]. The reasons why ion-bombardment and plasma-

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treatment strategies provide a dramatic adhesion improvement for metals have been discussed in the literature. In general, it is believed that the initial lack of adhesion is caused by the presence of a weak boundary layer (WBL) at the surface of the polymer. For instance, in the case of PDMS, this WBL is expected to result from segregation of low-molecular-weight chains in the surface region. In this hypothesis, the role of the plasma or ion-bombardment pretreatment is to eliminate the WBL *via* cross-linking [1]. Some indirect evidence of a cross-linked surface after pretreatment has been provided by electron micrographs.

In this paper, we show that the specific nature of the pristine and pre-treated surfaces can be elucidated using a novel and powerful chemical surface analysis procedure based on secondary ion mass spectrometry (SIMS). Recently, gold metallization has been introduced as a new sample preparation procedure for signal improvement in organic SIMS [11]. It was shown in that article and subsequent contributions that not only the quasi-molecular ion intensities but also the yields of positive and negative fragment ions were significantly improved by the metallization procedure [12–14]. With respect to the traditional cationization method used in SIMS, consisting in the deposition of dilute analyte solutions on clean metal surfaces [15–17], the so-called Metal-Assisted SIMS (MetA-SIMS) procedure has the distinct advantage that it can be applied to all types of samples, irrespective of their nature and thickness. In particular, real-world, bulk organic samples, often difficult to analyze by SIMS because of electric charging effects, prove to be excellent candidates for MetA-SIMS.

Using the MetA-SIMS procedure, it is demonstrated that the pristine PDMS surface is covered by an overlayer of low-molecular-weight oligomers. Cleaning the sample with hexane or bombarding it with 2 keV Ar^+ ions results in the disappearance of these oligomers. The adhesion improvement, however, is much higher with the latter treatment. It is our belief that Ar^+ ion-beam sputtering also creates reactive sites on the surface that eventually lead to a stronger binding of the evaporated metal.

2. MATERIALS AND METHODS

2.1. Material

2.1.1. PDMS film
The silicone film used in this study was MED-4750 from NuSil Technology (a division of Dow Corning). The elastomer is thermally cured using a Pt-catalyst to form a cross-linked network.

2.2. Methods

2.2.1. Film pretreatments
The Ar^+-ion-bombarded samples (1st series) were prepared using a 2 keV, defocused Ar^+ ion-beam, with a total ion fluence of 5×10^{15} ions/cm^2. The hexane-

Table 1.
Results of adhesion tests performed on Cu-metallized PDMS films with or without pre-treatment (hexane cleaning/Ar^+ ion irradiation)

	Pristine PDMS	Hexane-cleaned PDMS	Ar^+-ion-bombarded PDMS
Scotch® tape	–	+/–	+

+, deadhesion at the tape–metal interface;
–, deadhesion at the metal–PDMS interface.

cleaned samples (2nd series) were first annealed at 373 K for 1 h before rinsing for 2 min in pure hexane (p.a. grade, from Vel).

2.2.2. Film metallization
The metal evaporation (Ti and Cu for adhesion tests; Au for SIMS analyses) was carried out in an Edwards evaporator at an operating pressure of approx. 10^{-6} mbar and a deposition rate of 0.1 nm/s (quartz crystal monitor). For the adhesion tests, an adhesion promoting layer of Ti of thickness 15 nm was followed by a 100 nm layer of Cu.

2.2.3. Adhesion tests
After metallization, simple adhesion tests were performed for the three types of PDMS surfaces (pristine film, Ar^+-ion-irradiated film and hexane-cleaned film). Two kinds of tapes were used for the tests: Scotch® and Tesa®. The results of the Scotch® tape tests are summarized in Table 1.

2.2.4. Pretreatment for analysis
For MetA-SIMS analyses, the PDMS films were metallized by evaporating 20 nmol of Au per cm^2 on their top surface. This amount was shown to be the optimum with respect to secondary ion yield enhancement in the case of gold metallized polystyrene oligomer films [11].

2.2.5. Secondary ion mass spectrometry (SIMS)
The secondary ion mass spectra were acquired in a PHI-EVANS Time-of-Flight SIMS (TRIFT 1) using a 15 keV Ga^+ beam (FEI 83-2 liquid metal ion source; approx. 550 pA DC current; 22 ns pulse width bunched down to approx. 1 ns; 5 kHz repetition rate for the mass range 0–5 kDa) [18]. The experimental set-up has been described in detail elsewhere [19]. The ToF-SIMS spectra were obtained by collecting the secondary ion signals in the mass range $0 < m/z < 5000$ for the 600 s bombardment of a 180×180 μm^2 sample area, corresponding to a fluence of 3.5×10^{11} ions/cm^2. To further enhance the measured intensities, the secondary ions were post-accelerated by a high voltage (7 kV) in front of the detector.

3. RESULTS

The aim of this study was to elucidate the modifications occurring at the surface of a PDMS film after pretreatments, namely 2 keV Ar^+ ion bombardment and rinsing with hexane. For this purpose, a new sample preparation procedure for SIMS analysis (MetA-SIMS) is proposed. In the results, we first discuss the effects of the MetA-SIMS procedure on the measured mass spectra of pristine PDMS samples. Afterwards, the influence of Ar^+ ion bombardment is described and analyzed. Finally, the results of the Ar^+ ion irradiation procedure are compared to the chemical cleaning of the PDMS surface in pure hexane.

Before describing the details of the ToF-SIMS study, Table 1 summarizes the results obtained when performing the Tape test (Scotch®) for the three series of samples considered in this study (pristine PDMS film, Ar^+-ion-irradiated film and hexane-cleaned film). The results are best for the Ar^+ ion irradiated film (deadhesion at the tape–metal interface). In contrast, the metal film is almost completely removed by the tape for the pristine films. The hexane-cleaned samples show an intermediate behavior, with regions where the metal sticks and regions where it is torn away by the tape. Nevertheless, these samples remain conductive. In the discussion (Section 4), the results of this macroscopic test are tentatively explained using the wealth of information provided by the SIMS analysis of the samples.

3.1. SIMS and MetA-SIMS mass spectra of a pristine PDMS film

The low mass range of the positive SIMS spectrum of a pristine PDMS film is shown in Fig. 1a. As expected, the characteristic peaks of siloxane polymers dominate the spectrum in this mass range (Si^+, m/z=28; $SiC_3H_9^+$, m/z=73; $Si_2OC_5H_{15}^+$, m/z=147; $Si_3O_3C_5H_{15}^+$, m/z=207; $Si_3O_2C_7H_{21}^+$, m/z=221, etc.) and the observed peak pattern mirrors the mass spectra published in the literature for PDMS [20, 21]. After gold evaporation (Fig. 1b), the fingerprint peak pattern of PDMS is almost unchanged, except for some intensity variation and the appearance of a strong Au^+ peak at m/z=197. In general, the intensities of the characteristic peaks are enhanced, especially for higher masses. For instance, the intensity of ions with a mass beyond 100 Da increases by an order of magnitude on average. Such large sensitivity enhancements also have been reported in previous articles [11, 22] for other types of organic samples and constitute the major interest of the method. The measured yields have been explained by the improved desorption/ionization induced by the presence of gold clusters in the top surface region of the films. The mass spectrum of Fig. 1b does not show any sign of degradation induced by the gold metallization procedure.

In contrast, the influence of the MetA-SIMS procedure on the high mass range of the positive mass spectrum is dramatic (Fig. 2). While there were virtually no high mass ions in the SIMS spectrum of the pristine film (Fig. 2a), the gold-metallized film exhibits a distribution of intense peaks between m/z=800 and m/z=3500, as seen in Fig. 2b. The peaks in the distribution are separated by
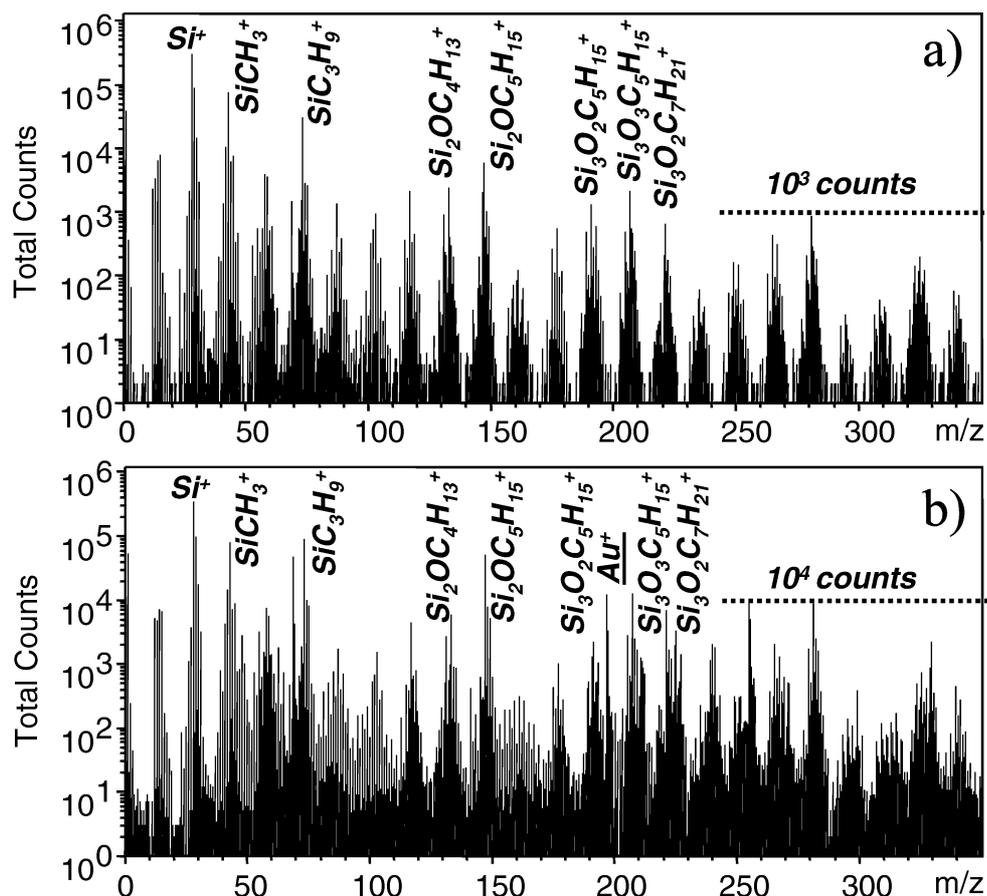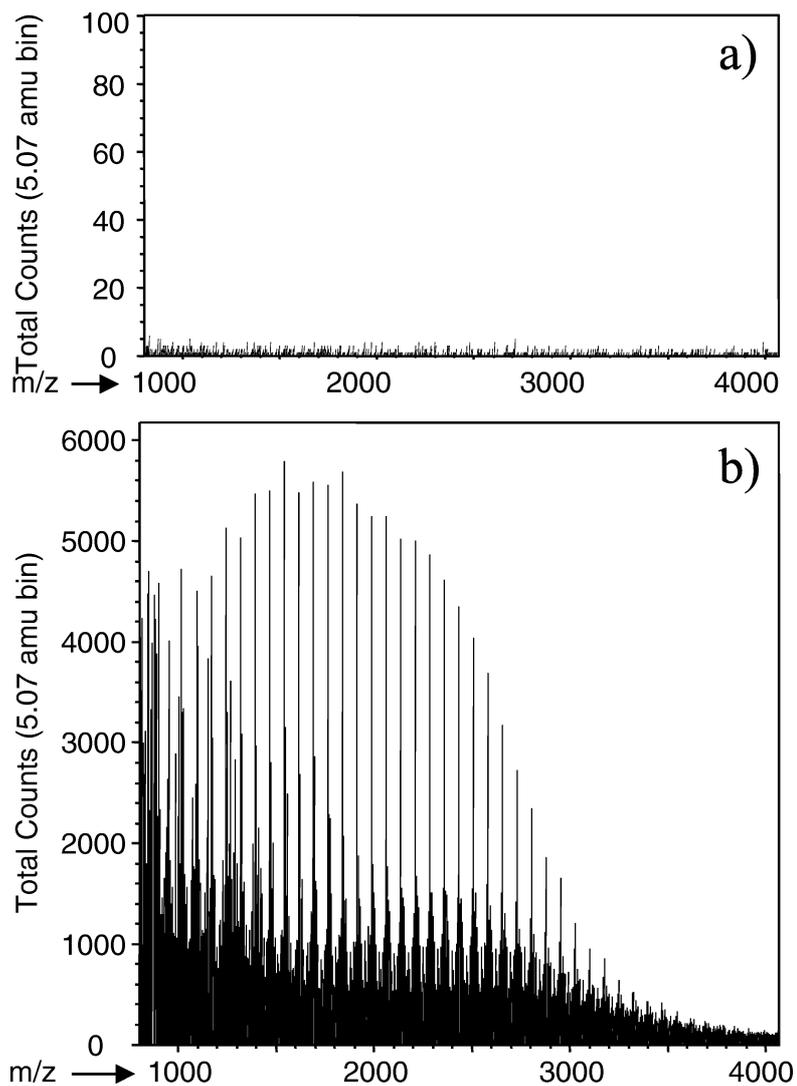
Figure 1. Fingerprint regions of the positive ion mass spectra of two PDMS films (logarithmic intensity scale). (a) Film 1, neat; (b) Film 2, after evaporation of 20 nmol/cm^2 of gold (MetA-SIMS).

74 Da, which corresponds to the mass of the dimethylsiloxane repeat unit. The observed distribution can be safely attributed to an overlayer of PDMS oligomers at the surface of the film. The results obtained after hexane cleaning of the film (see Section 3.3) also confirm that the appearance of oligomers is not an artifact of the gold metallization procedure but rather a direct effect of the Au-cationization (formation of a cation *via* recombination with a free Au$^+$ species) of the PDMS oligomers present at the sample surface. It should be noticed that an equivalent peak pattern is observed when short chains of PDMS are cast as a (sub)monolayer on a silver substrate [23].

3.2. Ar$^+$-ion-barbarded PDMS films

Positive mass spectra of Ar$^+$-ion-bombarded PDMS regions covered with 20 nmol/cm^2 of gold are presented in Figs 3 and 4. The high mass region shown in
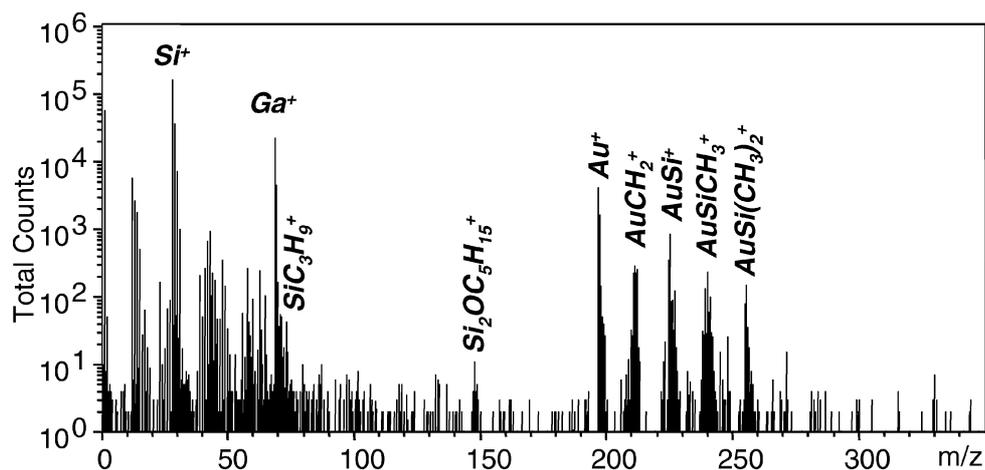
Figure 2. High-mass regions of the positive ion mass spectra of two PDMS films. (a) Film 1, neat; (b) Film 2, after evaporation of 20 nmol/cm^2 of gold. Note the distribution of Au-cationized PDMS oligomers.

Fig. 3a shows the disappearance of PDMS oligomers after the Ar$^+$ ion bombardment procedure. It is not clear from Fig. 3a whether these oligomers have been fragmented or sputtered away during the high fluence bombardment or whether they might have cross-linked to form a more compact network, preventing single molecule emission. The mass spectrum of Fig. 3b, however, measured at the edge of the irradiated area and encompassing both bombarded and pristine regions, provides some more information. In addition to the regular distribution observed
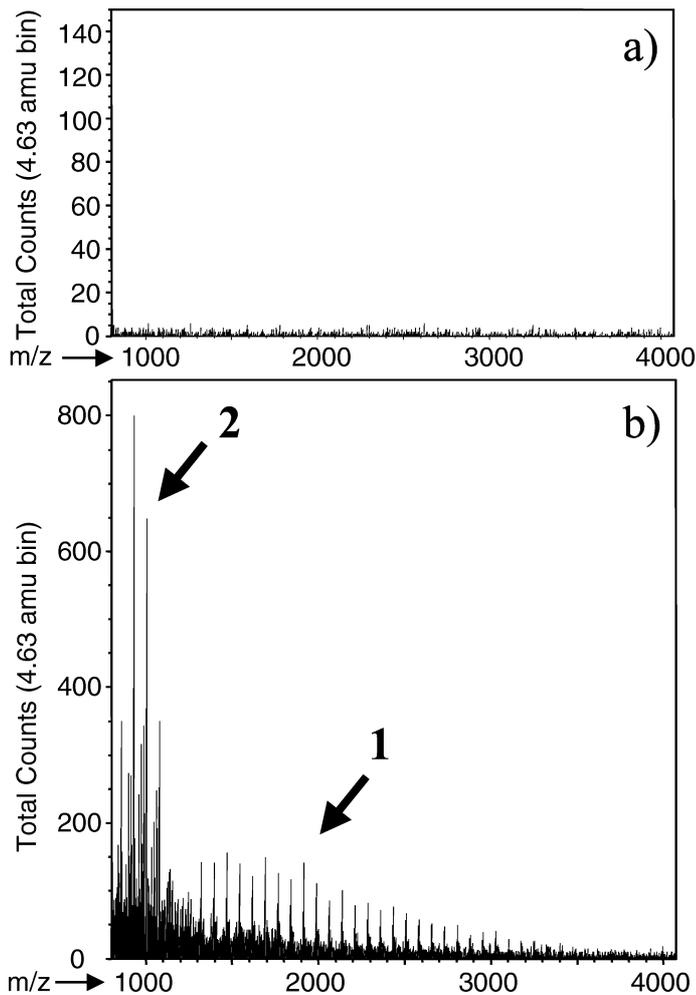
Figure 3. High-mass ranges of the positive ion mass spectra of a PDMS film locally bombarded with 2 keV Ar$^+$ ions and metallized with 20 nmol/cm^2 of gold. (a) Inside the Ar$^+$-ion-irradiated area; (b) edge of the Ar$^+$-ion-irradiated area. Distribution 1, initial oligomer distribution; distribution 2, ion-beam-induced fragments.

on the pristine polymer, there is a more intense, low-mass distribution of PDMS chain segments in the range 800–1100 Da. This distribution of peaks is most probably the result of the fragmentation of larger oligomers induced by the partial Ar$^+$ ion bombardment in this region of the sample. The relatively high intensity of intermediate fragment peaks (between the major peaks of the distribution) also supports the idea of a quasi-random fragmentation of the polymer induced by physical sputtering. This result suggests that the picture of the events induced by the Ar$^+$ ion bombardment is probably more complex than just a straightforward cross-linking reaction [1].
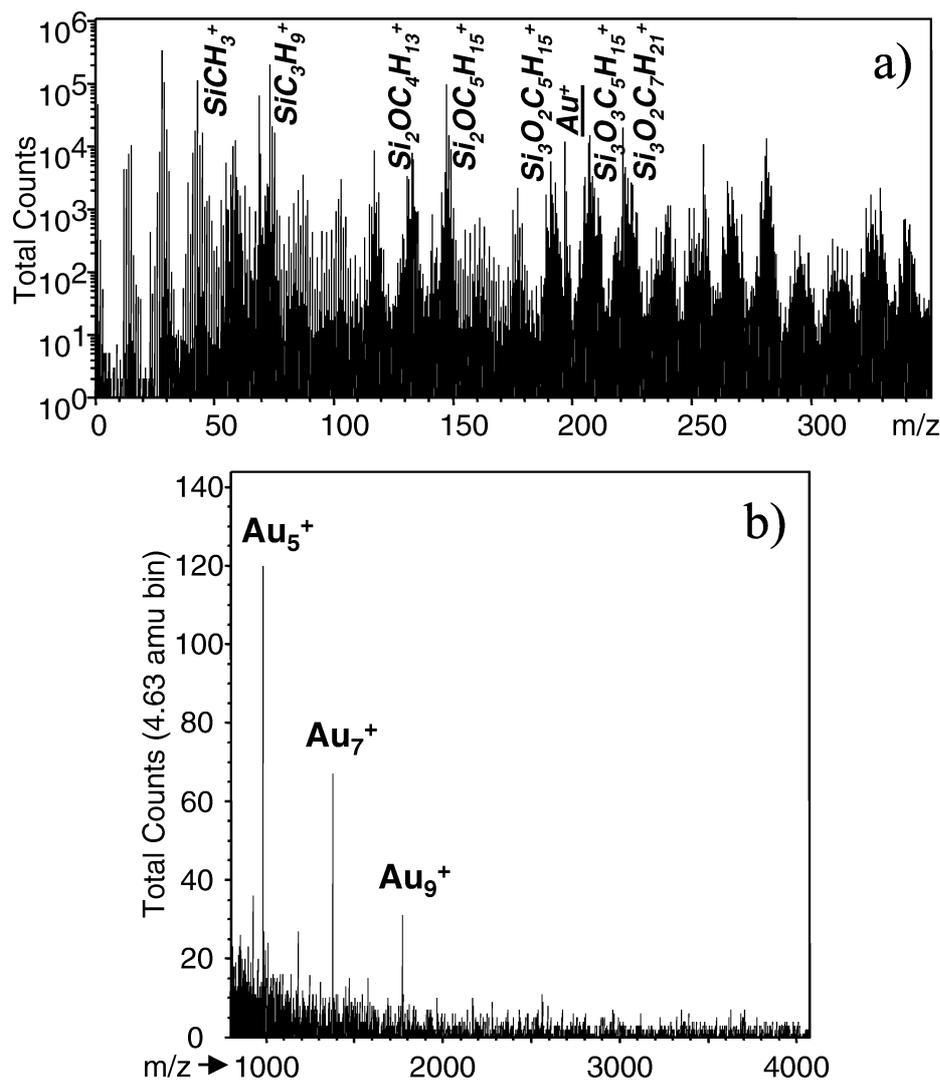
Figure 4. Fingerprint region of the positive ion mass spectrum of a PDMS film bombarded with 2 keV Ar^+ ions and metallized with 20 nmol/cm^2 of gold (inside the Ar^+-ion-bombarded area).

The Ar^+ ion bombardment strongly affects the fragmentation region of the mass spectrum (Fig. 4). In comparison with the Au-metallized PDMS sample (Fig. 1b), the irradiated sample displays a much simpler peak pattern. The characteristic peaks of PDMS have almost completely disappeared, indicating a profound transformation of the surface chemistry. The intensities of the $SiC_3H_9^+$ (m/z=73) and $Si_2OC_5H_{15}^+$ (m/z=147) peaks are more than three orders of magnitude lower. The major peaks remaining after irradiation are C^+, Si^+, Ga^+, Au^+ and a quite interesting series of ions beyond 200 Da. The most probable assessment for this group of peaks is: $AuCH_2^+$ (m/z=211) and $AuCH_3^+$ (m/z=212), $AuSi^+$ (m/z=225), $AuSiCH_3^+$ (m/z=240) and $AuSi(CH_3)_2^+$ (m/z=255). All these gold adducts were already present in the spectrum of the Au-metallized pristine sample. Their persistence in the spectrum of the bombarded sample shows that the irradiation step does not completely remove the specific molecular information of the PDMS repeat unit.

3.3. Comparison with hexane-cleaned surfaces

A batch of pristine PDMS samples was annealed at 373 K for 1 h and then cleaned for 2 min in pure hexane. The ability of hexane to dissolve low-molecular-weight PDMS chains is indeed well known [21]. The positive mass spectrum of a Au-metallized, hexane-cleaned PDMS film exhibits the characteristic fragmentation pattern of PDMS (Fig. 5a, compare to Fig. 1b), but shows no intact oligomers in the range 800<m/z<4000 (Fig. 5b). These spectra confirm two expectations. First, the high-mass distribution of peaks in Fig. 2b was indeed composed of oligomers, as opposed to long chain segments resulting from a bond breaking reaction, since they disappeared after a simple rinsing with the solvent. Second, the spectra indicate that hexane cleaning completely washes off the oli-

Figure 5. Positive ion mass spectra of a PDMS film cleaned in hexane (2 min) and metallized with 20 nmol/cm^2 of gold. (a) Fingerprint region, (b) high-mass region.

gomer overlayer without affecting the underlying film made of much longer PDMS chains. The high-mass spectrum also shows a distribution of gold ion clusters Au$_n^+$ with $5 < n < 10$, originating from the evaporated gold overlayer.

It is interesting to note that the surface of hexane-cleaned PDMS films is stable for several days under atmospheric conditions. To check their stability, samples were kept for five days in a Petri dish before gold metallization and SIMS analysis. Their spectra are identical to those of freshly metallized samples (Fig. 5). In particular, no oligomers migrated towards the clean surfaces.

4. DISCUSSION

Even though they do not provide a quantitative information, the simple tests performed with Scotch® and Tesa® tapes show that bombardment of the PDMS film with 2 keV Ar$^+$ ions induces a pronounced adhesion enhancement of the subsequently evaporated Ti and Cu layers (see Table 1). This observation is in line with the results reported in the literature [1]. The same tests indicate that a simple hexane-cleaning provides a lower but still significant adhesion improvement.

In previous articles [1, 24], the explanation for the adhesion improvement subsequent to ion bombardment or plasma treatment of PDMS surfaces was based on the elimination of the WBL through cross-linking. To our knowledge, no direct evidence of the process was shown. Using the new development in static SIMS analysis (MetA-SIMS), our results unambiguously prove a series of points: (i) there is an overlayer of oligomers on top of untreated commercial PDMS films; (ii) this layer disappears after 2 keV Ar$^+$ ion irradiation of the surface but also after a simple cleaning of the surface with hexane; (iii) unlike hexane cleaning, the Ar$^+$ ion bombardment strongly modifies the chemistry of the top surface layer (disappearance of all large characteristic fragments of PDMS, Fig. 4); and (iv) the bombardment-induced modification of the surface involves creation of shorter oligomer chains as an intermediate stage (Fig. 3b).

From these observations, new hypotheses can be proposed. First, it is reasonable to think that the oligomer overlayer is partly or completely fragmented and sputtered away by the Ar$^+$ ion irradiation. This hypothesis is also supported by the common observation that PDMS oligomer contamination on other materials can usually be sputtered away by a very low primary ion fluence in SIMS analysis. Some of the oligomers might also cross-link, even though there is no direct proof of such a process. The drastic change in the fragmentation region of the mass spectrum after bombardment with Ar$^+$ ions, in particular, the disappearance of large characteristic fragments, could be an indication of cross-linking. Whatever its fate after Ar$^+$ ion irradiation, the oligomer overlayer is initially very thin and the cross-linking reaction should certainly affect the underlying high-mass chains, too. It should be noted, however, that the small Au-cationized fragments visible after pre-bombardment still contain CH$_3$ residues, which were believed to be eliminated by the cross-linking reaction [1].

In summary, our study demonstrates that the adhesion improvement observed after Ar$^+$ ion bombardment of PDMS is the result of a combination of factors involving both the removal of the so-called weak boundary layer made of oligomers and the severe chemical modification of the underlying, high-molecular-weight PDMS. In this respect, the observation that gold clusters appear in the positive mass spectrum of metallized, hexane-cleaned PDMS, but not in the mass spectrum of metallized, Ar$^+$-ion-irradiated PDMS, suggests a stronger interaction between the metal overlayer and the irradiated PDMS. The chemistry modification induced by the Ar$^+$ ion bombardment probably creates a surface that is more reactive towards the incoming metal atoms. For instance, Si–OH, –C=O and –COOH

groups might be introduced at the surface after reaction of the radicals formed under bombardment with the atmospheric O_2 and H_2O molecules [2]. Such an increase of reactivity could explain the much higher adhesion of metals to the Ar^+ ion bombarded PDMS surfaces in comparison to hexane-cleaned films.

5. CONCLUSIONS

This work unambiguously shows that commercial PDMS films are covered with an overlayer of kDa-range oligomers which limits the adhesion of metals evaporated on their top surface. This layer disappears after 2 keV Ar^+ ion irradiation, but also after a simple cleaning of the pristine films by hexane. However, the adhesion of titanium and copper layers on the surfaces is much higher when Ar^+ ion bombardment pretreatment is used. Our results indicate that this improvement is related to the chemical modification of the top layers of the sample and their increased reactivity towards the evaporated metal atoms.

From a methodological viewpoint, covering organic surfaces with minute amounts of gold induces a significant sensitivity enhancement for static SIMS analyses (MetA-SIMS). The positive fragment ion yields are, on average, enhanced by about one order of magnitude and the molecular ions become visible owing to an efficient ionization of the molecules *via* recombination with gold atoms. Such yield enhancements are promising for many problematic cases such as identification of kDa-range molecules on organic substrates and imaging SIMS applications where sensitivity usually constitutes a serious issue (e.g., polymer blends [25], polymers covered with additives [26], and cells and drug/biomolecule arrays [27]).

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