



## Primary ion fluence dependence in time-of-flight SIMS of self-assembled monolayer of alkyl thiol molecules on Au(1 1 1)—Discussion of static limit

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### ARTICLE INFO

#### Article history:

Available online 8 May 2008

#### Keywords:

Static SIMS

TOF-SIMS

Soft materials

Self-assembled monolayer

### ABSTRACT

The nondestructive nature of static secondary ion mass spectrometry (SIMS) in the context of studies of self-assembled monolayers (SAMs) of organic molecules has been examined by measuring the primary ion fluence dependence of secondary ion signals with two well-known SAMs, C<sub>18</sub>H<sub>37</sub>SH on Au(1 1 1) and C<sub>18</sub>H<sub>37</sub>PO<sub>3</sub>H<sub>2</sub> on freshly cleaved mica. This SIMS analysis is challenging because the bonding nature is delicate and the areal molecular density is less than 10<sup>15</sup> cm<sup>-2</sup>. In SIMS, it is prevalently assumed that if the primary ion fluence is confined to not more than 1 × 10<sup>12</sup> cm<sup>-2</sup>, all secondary ion signals should not change by more than 10% and the practically defined static condition is satisfied. Our results from time-of-flight SIMS with the common primary ions of Bi<sub>3</sub><sup>+</sup>, Bi<sup>+</sup> and Ar<sup>+</sup>, indicate that this prevalent static assumption fails for both model SAMs. The SIMS results from the phosphyl case, which have been recently published, consistently display the evidence of bombardment-induced damage. In comparison, the thiol case presented here shows much more complex primary ion fluence dependence of SIMS signals. It is therefore concluded that practical static analysis should use primary ion fluence not more than 1 × 10<sup>11</sup> cm<sup>-2</sup> or should simply record and report the effects of primary ion fluence.

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### 1. Introduction

Static secondary ion mass spectrometry (SIMS), typically conducted with the time-of-flight (TOF) technique to yield high enough signals-to-noise statistics with a low primary ion fluence [1], is increasingly applied to study self-assembled monolayers (SAMs), bilayers and multi-layers of molecules in both natural biological materials and artificially engineered materials because the technique has an extremely high sensitivity and dynamic range. In general, SIMS promises to probe nondestructively the chemical nature of such a delicate layer having a mere areal molecular density of ~10<sup>15</sup> cm<sup>-2</sup> [2–4]. The emerging applications of SAMs and related molecular layers are very versatile [5]. For example, SAMs can serve as biomaterial interfaces in contact with living cells and biological fluids, towards the production of

biosensors and biochips [5,6]. They can also be used as building blocks in the fabrication of molecular diodes and transistors [5,7]. These emerging technologies highly depend on molecular level control achieved by varying the layer composition and the chemical nature of the molecules, particularly with the selection of the tail group to enable surface loading of proper chemical functionality for chemical or biological recognition. It becomes very clear then that accurate quantification and characterization of these molecular systems are required. However, their rather delicate nature makes them difficult to analyze.

In static SIMS of SAMs, the nondestructive mode of analysis is practically assured by setting a so-called static condition which for SIMS studies of common stable inorganic materials is set by limiting the primary ion fluence to not more than 1 × 10<sup>13</sup> cm<sup>-2</sup>. By convention, the static condition is satisfied when no secondary ion intensity changes more than 10% from the initial recorded data at the beginning of the SIMS experiment measured. Several groups [8,9] examined the static condition for polymeric materials susceptible to bombardment-induced fragmentation and other related changes, and indeed found that the primary ion fluence limit should be lowered to 1 × 10<sup>12</sup> cm<sup>-2</sup> for these “soft” materials.

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They also supported the philosophy of Delcorte et al. [10] that the conventional practice of setting a primary ion fluence limit as the universal static condition for all materials is convenient but risky.

Driven by the need of a sensitive technique for characterizing SAMs and devices fabricated with SAMs in our own research projects, we have begun to examine the effects of primary ion fluence on the secondary ion signals from SAMs. In this on-going investigation, we have chosen the SAM of octadecylphosphonic acid molecules ( $C_{18}H_{37}PO(OH)_2$ , OPA) on freshly cleaved mica and the SAM of octadecanethiol molecules ( $C_{18}H_{37}SH$ ) on Au(1 1 1) as our model SAM systems. We have selected these two SAMs as our model systems because they have been relatively thoroughly studied by us and other researchers [5]. In a recently published report [11], we show that the prevalent static limit of keeping the primary ion fluence not more than  $1 \times 10^{12} \text{ cm}^{-2}$  is not appropriate for SAMs like the phosphyl SAM model. More specifically, when the secondary ion intensities of large molecular ions were examined as a function of  $Bi_3^+$  (25 keV,  $45^\circ$ ) cumulative primary ion fluence, they were found to drop exponentially for both negative and positive secondary ion detection [11]. The intensity of  $C_{18}H_{37}PO_3H^-$  molecular ion, for instance drops by  $\sim 43\%$  when the primary ion fluence reaches  $1 \times 10^{12} \text{ cm}^{-2}$ , which is far more than the 10% limit. The consistent drastic drops in the intensities of large molecular ions support the hypothesis that the primary ion bombardment causes considerable damage of the SAM.

This article reports on the TOF-SIMS results as a function of primary ion fluence from the SAM model of  $C_{18}H_{37}SH$  on Au(1 1 1). The aim of this work is to examine if changes due to factors other than molecular damage are active. In this examination, the intensity changes of positive secondary ions as a function of primary ion fluence for  $Bi^+$  are compared with those of negative secondary ions under the same bombardment condition. To understand the role of surface-incorporated  $Bi^+$  on the secondary ion yield, we also compare the results with those from  $Ar^+$  bombardment. With atomic force microscopic measurements, we verify that sputtering or desorption of the SAM molecules is not a direct cause of the drastic changes of SIMS signals observed for primary ion fluence well below  $1 \times 10^{13} \text{ cm}^{-2}$ .

## 2. Experimental

All samples were prepared by first annealing Au(111) substrates (from Molecular Imaging) in a hydrogen flame then immediately immersing them in 1 mM 1-octadecanethiol (90%) ethanolic solutions for 24 h. The samples were then rinsed with pure ethanol and dried by nitrogen flow to remove weakly adsorbed molecules. The procedures routinely yield the well-known  $\sqrt{3} \times \sqrt{3}$  ordered molecular adsorption structure, as verified by scanning tunneling microscopy [5,12].

The analytical measurements were performed using a reflectron-type TOF-SIMS instrument (ION-TOF TOF-SIMS IV) operating with 25 keV pulsed  $Bi^+$  primary ion beam (10 kHz) at an incident angle of  $45^\circ$ . The primary ion beam was focused and scanned over an area of  $256 \mu\text{m} \times 256 \mu\text{m}$  delivering a cumulative ion fluence up to  $1.4 \times 10^{13} \text{ ions cm}^{-2}$ . The maximum fluence is about 100 times smaller than the number of molecules per  $\text{cm}^2$  in the SAM. The experiments were then repeated with  $Ar^+$  at 8 keV. To assure that no measurable changes in SIMS were caused by time variation of primary ion flux, we tracked the sample current during SIMS analysis of conductive samples and verified a steady condition. In addition, the analytical chamber was always kept at low  $10^{-9}$  Torr to reduce the risk of surface contamination.

The AFM measurements were performed in an ambient atmosphere using a XE-100 microscope from PSIA. The samples were scanned in a non-contact mode.

## 3. Results and discussion

In the phosphyl SAM case [11], we have found that although sputter-removal or desorption of the SAM molecules is not important, the SIMS signals of large molecular ions from the SAM drops exponentially as a function of primary ion fluence due to bombardment-induced damage of the SAM molecules. We also find this to be true for the present thiol SAM case. For example, our AFM examination of the SAM morphology before and after the SIMS measurements confirm that the SAM is virtually a complete coverage with no detectable void, and voids are gradually induced as the cumulative primary ion fluence increases (Fig. 1). The total loss of molecules amounts to  $\sim 7\%$  of the SAM. Since the molecular density is  $5.6 \times 10^{14} \text{ cm}^{-2}$ , the void formation yield is about 4 missing molecules per primary ion. In the context of examining the validity of less than 10% drop in SIMS intensity for a primary ion fluence of  $1 \times 10^{12} \text{ cm}^{-2}$ , the molecular density will only reduce by about  $0.04 \times 10^{14} \text{ cm}^{-2}$  due to void formation. This prelude justifies the focus of the remaining analysis of SIMS intensity changes in this article on molecular damage, ion yield and other factors.

Not unlike the phosphyl SAM case, we observe some rather drastic changes in SIMS signals as a function of primary ion fluence in the thiol SAM case and again the static condition of less than 10% change in SIMS signals for a primary ion fluence of  $1 \times 10^{12} \text{ cm}^{-2}$  is clearly violated. The violation is most obviously shown in the  $Au^+$  changes in Fig. 2(a) and  $C_{18}H_{37}S^-$  changes in Fig. 3(b). More specifically, the  $Au^+$  and  $C_{18}H_{37}S^-$  intensities drop by  $\sim 45\%$  and  $\sim 40\%$ , respectively, for the  $Bi^+$  fluence at  $1 \times 10^{12} \text{ cm}^{-2}$ , the changes are both much higher than the 10% limit. These are definitely not due to any system errors because the sample current during measurements was constant and the  $C^+$  intensity was also constant as shown in Fig. 2(a). To satisfy the 10% limit of SIMS intensity changes, the static condition requires a primary ion fluence not much higher than  $\sim 1 \times 10^{11} \text{ cm}^{-2}$ . This necessity of revising the prevalent static condition is consistently shown by the SIMS studies of both the phosphyl and thiol SAM models.

In comparison with the SIMS signal changes as a function of primary ion fluence in the phosphyl case [11], the changes in the

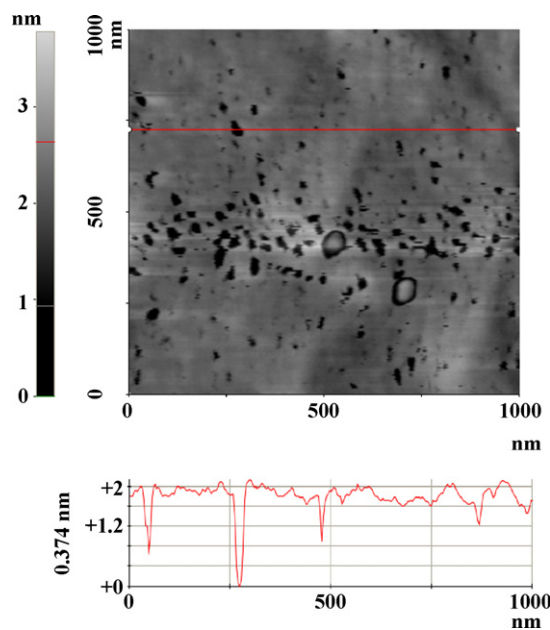
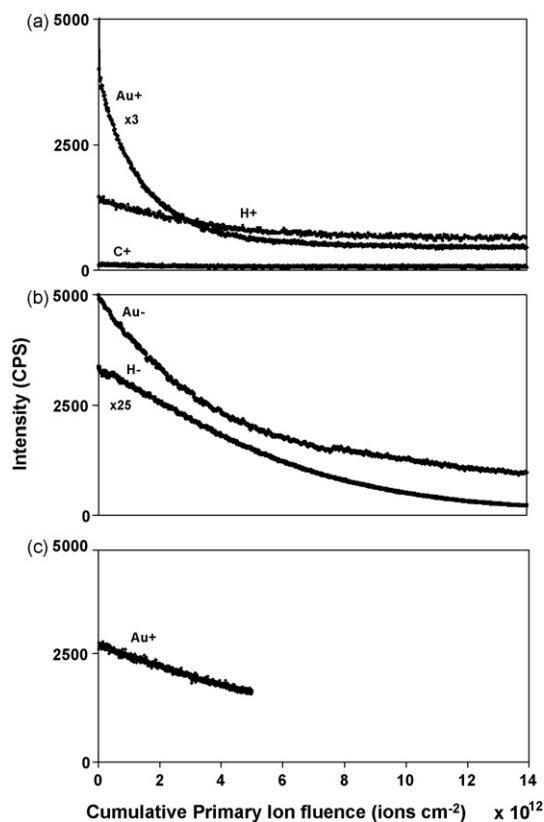


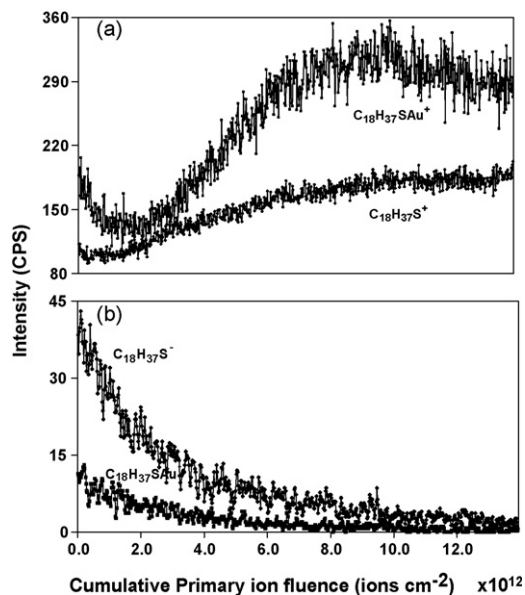
Fig. 1. AFM analysis of void (missing molecules) formation induced by  $1.4 \times 10^{13} \text{ cm}^{-2}$   $Bi^+$  bombardment of C18 thiol on Au(1 1 1).



**Fig. 2.** Variation of (a)  $\text{Au}^+$  and  $\text{H}^+$ ; and (b)  $\text{Au}^-$  and  $\text{H}^-$  intensities signals with primary  $\text{Bi}^+$  ion fluence for the case of C18 thiol on Au(1 1 1); and (c) the  $\text{Au}^+$  variation with  $\text{Ar}^+$  as the primary ion beam.

thiol case are much more complex. The non-monotonic changes of  $\text{C}_{18}\text{H}_{37}\text{SAu}^+$  and  $\text{C}_{18}\text{H}_{37}\text{S}^+$  in Fig. 3(a) show some facets of this complexity, and suggest that several factors influencing SIMS intensity are active and convoluted.

For example, if the  $\text{C}_{18}\text{H}_{37}\text{S}^-$  intensity changes shown in Fig 3(b) are compared to  $\text{C}_{18}\text{H}_{37}\text{PO}_3\text{H}^-$  intensity changes previously



**Fig. 3.** Variation of (a)  $\text{C}_{18}\text{H}_{37}\text{S}^+$  and  $\text{C}_{18}\text{H}_{37}\text{SAu}^+$ ; and (b)  $\text{C}_{18}\text{H}_{37}\text{S}^-$  and  $\text{C}_{18}\text{H}_{37}\text{SAu}^-$  intensities signals with primary  $\text{Bi}^+$  ion fluence for the case of C18 thiol on Au(1 1 1).

reported [11], with no prior knowledge of the other SIMS intensity changes in the thiol case, one may attribute the rapid drop, like in the phosphyl case, to bombardment-induced damage of the parent thiol SAM molecules during the SIMS experiment. One may also take the same approach used by the phosphyl case to adopt the concept of damage cross-section [1]. The damage cross-section for the parent molecule in the case of the thiol SAM by  $\text{Bi}^+$  at 25 keV (derived from negative SIMS) is  $\sim 3 \times 10^{-13} \text{ cm}^2$ ; in comparison, that for the parent molecule in the case of the phosphyl SAM by  $\text{Bi}^+$  at 25 keV (derived from negative SIMS) is  $2 \times 10^{-13} \text{ cm}^2$  [11]. Since the two types of SAM molecules have exactly the same  $\text{C}_{18}\text{H}_{37}$  alkyl chain, the similarity in their damage cross sections by the same bombardment condition is reasonable. On the other hand, the  $\text{C}_{18}\text{H}_{37}\text{S}^+$  intensity changes shown in Fig 3(a) cannot be explained by the same analysis approach and the peculiar non-monotonic changes, particularly the unexpected increase of parent ion molecular ion intensity in the primary ion fluence range of  $1-10 \times 10^{11} \text{ cm}^{-2}$ . This shows the presence of other factors which increase the positive molecular ion formation.

In the analysis of positive ion yields, it is well known [13] that secondary ion intensity is sensitive to charge exchange between the outgoing projectiles and the surface which leads to the general expectation that for a projectile with its first ion ionization potential ( $\alpha$ ) lower than the work function ( $\Phi$ ) of the matrix surface, its positive ion yield should be scaled exponentially with  $\Phi - \alpha$ . For the thiol SAM on Au(1 1 1), the SAM coverage is known to reduce  $\Phi$  from 5.3 to  $\sim 4 \text{ eV}$  [14] but the effects of  $\text{Bi}^+$  ion bombardment on  $\Phi$  of the SAM system are not known, other than that bismuth itself has a work function of 4.4 eV [15]. Switching the analysis attention to the  $\text{Au}^+$  and  $\text{H}^+$  intensity changes in Fig. 2(a), one can explain the exponential drop in intensity by assuming that  $\Phi$  is reduced gradually with an increase in cumulative  $\text{Bi}^+$  ion fluence, as  $\alpha$  of gold atom is 9.1 eV [15]. According to the charge exchange model, if there is a drop in  $\Phi$  of the SAM by the cumulative  $\text{Bi}^+$  fluence, the  $\text{Au}^+$  and  $\text{H}^+$  intensities should decrease due to the increase in neutralization probability. The slower intensity changes of  $\text{H}^+$  relative to  $\text{Au}^+$  as displayed in Fig. 2(a) can be explained by the fact that  $\text{H}^+$  can swiftly leave the surface and thus it is less sensitive than the slow moving  $\text{Au}^+$  to the increase in neutralization probability. However, the model would predict that if there is indeed a drop in  $\Phi$  by the cumulative  $\text{Bi}^+$  fluence,  $\text{Au}^-$  and  $\text{H}^-$  should increase; but the results shown in Fig. 2(b) contradict this prediction. In short, although changes in charge exchange induced by primary ion fluence may affect secondary ion intensities of this thiol SAM system, charge exchange alone cannot explain our experimental results.

To explain the drops in intensity for both  $\text{Au}^+$  and  $\text{Au}^-$  (also  $\text{H}^+$  and  $\text{H}^-$ ), one may postulate that the primary ion bombardment somehow enhances the bond strength of these two species with their chemical environment, and thereby reduces their emission probability via phenomena similar to those previously explained by the bond-breaking model [16]. In Fig. 2(c), we add the  $\text{Au}^+$  intensity changes with  $\text{Ar}^+$  (8 keV) as the primary ion. The  $\text{Au}^+$  intensity also drops (except that the drop is slower than in Fig. 2(a)). Hence, the bond-breaking effect is independent of bismuth chemistry. In fact, the surface concentration of bismuth even with a fluence of  $1 \times 10^{12} \text{ cm}^{-2}$  is still less than 1% of a monolayer. It is known that the H–C bond strength of H– $\text{CH}_3$  is 438.9 kJ/mol, and the strength increases to 462 kJ/mol for H– $\text{CH}_2$  [14]. Thus, one can argue that bombardment-induced damage of the alkyl chain either makes further H–C cleavage more difficult or introduces active carbon sites for recapturing recoiled/sputtered hydrogen projectiles. While these bond-breaking factors may indeed be active, they alone cannot explain the changes in Fig. 2 because the  $\text{H}^+$  and  $\text{H}^-$  drops in Fig. 2 are not observed in

the phosphyl SAM system which also has the same C<sub>18</sub>H<sub>37</sub> alkyl chain.

#### 4. Conclusions

In summary, a TOF-SIMS analysis using Bi<sup>+</sup> and Ar<sup>+</sup> primary ion beams of C<sub>18</sub>H<sub>37</sub>SH SAM on Au(1 1 1) was performed, and the results are compared with those from C<sub>18</sub>H<sub>37</sub>PO<sub>3</sub>H<sub>2</sub> SAM on mica. Taking the intensity changes for Au<sup>+</sup> and C<sub>18</sub>H<sub>37</sub>S<sup>-</sup> from Bi<sup>+</sup> bombardment of the thiol SAM as references, we find that the static condition for not more than 10% change of SIMS signals should require the primary ion fluence be less than  $\sim 1 \times 10^{11} \text{ cm}^{-2}$ . Unlike the phosphyl SAM model, the primary ion fluence effects on TOF-SIMS of this thiol SAM model cannot be described only by bombardment-induced damage of the parent SAM molecules. Changes in other ion formation and survival mechanisms are also active as a function of primary ion fluence; further work is needed to clarify them.

#### Acknowledgement

This work was partially supported by the NSERC Discovery Grant (Grant No. 327221 - 06 for Lau), NSERC-CONICET CIAM Grants (for Lau and Grizzi), NSERC USRA Grant (for Ghonaim),

Surface Science Western (SSW), Faculty of Science of the University of Western Ontario, and RENAMSI Argentina network.

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