



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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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, C₁₈H₃₇SH on Au(1 1 1) and C₁₈H₃₇PO₃H₂ on freshly cleaved mica. This SIMS analysis is challenging because the bonding nature is delicate and the areal molecular density is less than 10¹⁵ cm⁻². In SIMS, it is prevalently assumed that if the primary ion fluence is confined to not more than 1 × 10¹² cm⁻², 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 Bi₃⁺, Bi⁺ and Ar⁺, 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 × 10¹¹ cm⁻² 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 ~10¹⁵ cm⁻² [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 × 10¹³ cm⁻². 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 × 10¹² cm⁻² 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°) 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° . 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 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

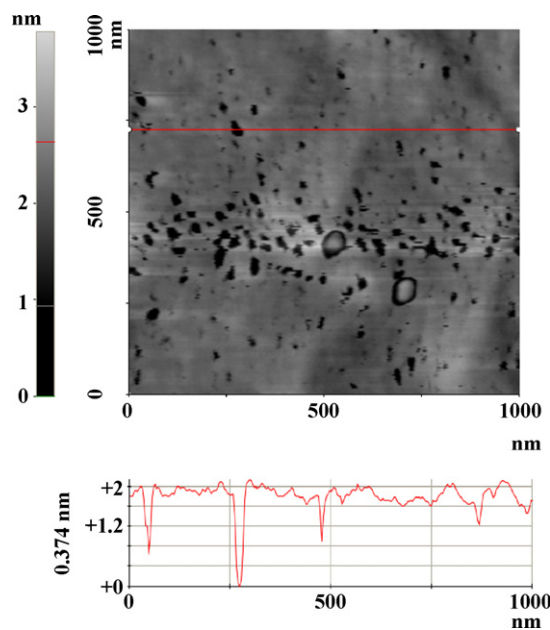


Fig. 1. AFM analysis of void (missing molecules) formation induced by $1.4 \times 10^{13} \text{ cm}^{-2} Bi^+$ bombardment of C18 thiol on Au(1 1 1).

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