



Depth profiling studies of multilayer films with a C_{60}^+ ion source

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Abstract

A newly developed C_{60}^+ primary ion beam source for time-of-flight secondary ion mass spectrometry has been employed for depth profiling analysis of organic and inorganic multilayer films. In particular, the C_{60}^+ ion beam is used in the dc mode to sputter the surface for depth profiling while spectra are taken both with Ga^+ 15 keV and C_{60}^+ 20 keV projectiles between sputtering cycles. From C_{60}^+ bombardment of Langmuir–Blodgett films of barium arachidate, we find that cluster beams increase the secondary ion yields and ion formation efficiencies compared to monoatomic projectiles. For a 15-layer film, a barium arachidate fragment ion at $m/z = 208.9$ was monitored as a function of C_{60}^+ dose to determine that the sputtering rate is about 1.54 nm/s and that the film interface position can be determined with a depth resolution of 16 nm. For comparison purposes, a depth resolution of 8.7 nm was measured for a sample consisting of 66 nm of Ni and 53 nm of Cr on Si(1 0 0) at a C_{60}^+ beam energy of 20 keV. The neutral atom yield was monitored via laser postionization to avoid matrix effects. These experiments show great promise for the use of C_{60}^+ for depth profiling studies of multilayer targets.

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1. Introduction

Since the increased efficiency of cluster ion beams as projectiles for time-of-flight secondary ion mass spectrometry (TOF-SIMS) experiments on organic films has now been established [1–5], it is of interest to examine their behavior when attempting to depth profile through organic multilayer structures. This type of measurement is a particularly valuable measurement capability for a variety of devices in the nanotechnology world [6], but has not been possible

using atomic bombardment due to the rapid accumulation of chemical damage. With cluster beams, however, the idea is that the high sputtering rate removes accumulated damage at a rate that is comparable to its formation [7]. Recently, particularly high yields and efficiencies have been demonstrated for a range of organic compounds using C_{60}^+ ions as a projectile [8]. Here we explore the possibility of characterizing complex multilayer structures using this novel source.

We have chosen two multilayer samples: an LB film of barium arachidate and a sample consisting of alternating layers of Ni and Cr on Si (Ni/Cr/Si(1 0 0)) for C_{60}^+ depth profiling in order to investigate the depth resolution attainable with cluster beams. A TOF-SIMS instrument with both Ga^+ and C_{60}^+ beams

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has been utilized to compare the secondary ion yields, Y (number of secondary ions detected/number of primary ions incident on the sample), disappearance cross-sections (σ) and ion formation efficiencies ($E = Y/\sigma$) of the molecular ion ($\text{CH}_3(\text{CH}_2)_{18}\text{COO}^+\text{Ba}^+$) and its fragment ions of LB films of barium arachidate. These LB films have been chosen due to their ease of fabrication and control of thickness.

2. Experimental

A molecular overlayer of arachidic acid ($\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$) on a SiO_2 substrate was prepared by the LB technique with a Kibron μ Trough S-LB. Arachidic acid was dissolved in hexane:IPA (3:2) and spread on a subphase consisting of 60 ml of Millipore purified water (18.2 M Ω cm; 4 ppb organics) to which 10^{-4} M BaCl_2 , 10^{-4} M KHCO_3 and 10^{-7} M CuCl_2 to form barium arachidate. The addition of CuCl_2 is known to aid in the deposition of a large number of layers [9]. Silicon substrates were cleaned by piranha etch (3:1, H_2SO_4 : H_2O_2) prior to deposition to ensure a hydrophilic surface. Verification of thickness of 46.2 nm and number of layers of 15 was performed by ellipsometry.

Films were analyzed with a TOF-SIMS instrument equipped with both a Ga^+ 15 keV liquid metal ion source [10] and a C_{60}^+ 20 keV effusive source [8]. For each sample, experiments were performed with the C_{60}^+ ion beam in dc mode to sputter the surface in 5.8 s intervals with a primary ion dose of 8×10^{12} ions/cm² for depth profiling while spectra were taken with both C_{60}^+ and Ga^+ between sputter cycles at low ion doses of 10^{10} ions/cm² at an area of $300 \mu\text{m} \times 300 \mu\text{m}$. A large sputtered area of $500 \mu\text{m} \times 500 \mu\text{m}$ was used to avoid crater edge effects.

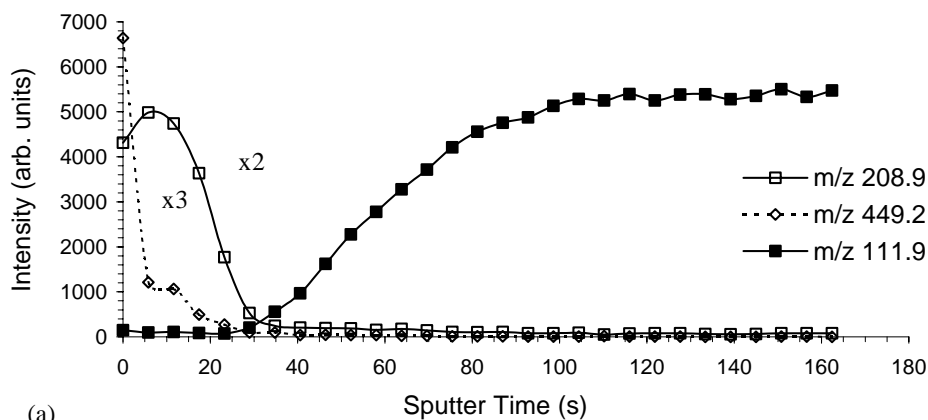
The Ni/Cr/Si(1 0 0) sample consisted of alternating layers of Ni (four layers at 66 nm per layer) and Cr (five layers at 53 nm per layer). The sample was sputtered with C_{60}^+ in dc mode for 20 s intervals with a primary ion dose of 5×10^{16} ions/cm² and analyzed with the C_{60}^+ ion beam. The Ni and Cr neutral atoms were ionized with 800 nm fs laser pulses with a peak power density of 8.5×10^{12} W/cm². Again, a large field view was used for sputtering to avoid crater edge effects.

3. Results and discussion

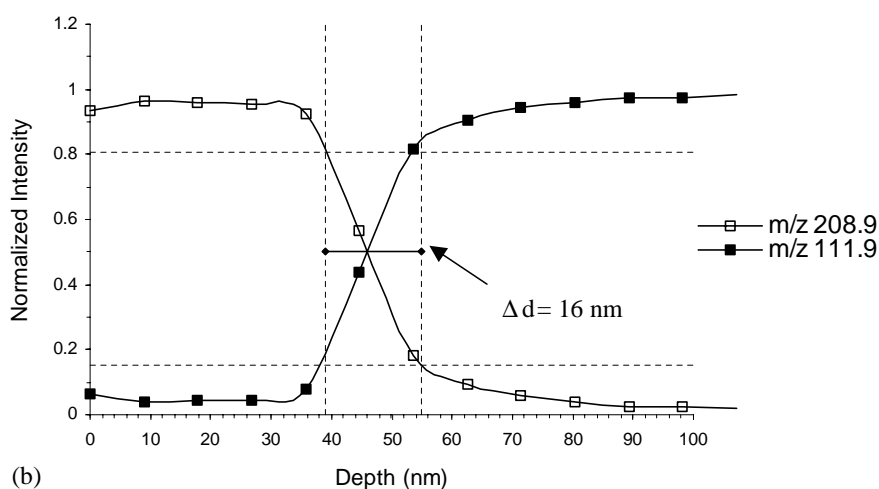
The 15-layer LB film of barium arachidate (BA) serves as an excellent model for C_{60}^+ bombardment of multilayer films since the physical properties are well-characterized, the possibility of molecular depth profiling can be assessed, and depth resolution can be determined by measuring the effective width of the BA/Si interface. The TOF-SIMS spectrum of this structure is reasonably straightforward. There is an intense molecular ion peak of $\text{CH}_3(\text{CH}_2)_{18}\text{COO}^+\text{Ba}^+$ at $m/z = 449.2$ and an equally intense fragment ion peak of $\text{CH}_2\text{CHCOO}^+\text{Ba}^+$ at $m/z = 208.9$. The lower mass range is dominated by Ba^+ and its hydroxide, easily recognizable from its complex isotope pattern. A series of Si cluster ions are visible after the LB film has been removed. In this work, we key on the Si_4^+ cluster ion at $m/z = 111.9$ since there are no isobaric hydrocarbon interferences at this mass.

The intensity of the key molecular ions as a function of C_{60}^+ dose is shown in Fig. 1. There is an abrupt onset of the Si_4^+ intensity after about 29 s of bombardment, signaling the removal of the LB film. The molecular ion intensity is observed to decay rapidly with dose and the influence of sample damage seems to rule out the use of this ion in monitoring the depth profile. The measured dose dependence indicates that there may be a plateau of this signal at sputter times between 6 and 12 s, but more detailed data are needed to clarify this point. The major fragment ion at $m/z = 208.9$, on the other hand, exhibits rather typical behavior for organic films bombarded with cluster beams [2,3]. The intensity actually rises slightly after the initial bombardment, stays approximately constant throughout a certain sputter time interval and then decays with a disappearance cross-section of 1×10^{-13} cm² until the silicon interface is reached at a C_{60}^+ dose of 4×10^{13} ions/cm².

The normalized signal intensities as a function of depth into the sample are shown in Fig. 1(b). These intensities are computed by taking the ratio of a specific ion intensity to the sum of intensities at $m/z = 111.9$ and 208.9 at a specific dose. The time scale associated with the beam dose is converted into a depth scale by dividing the known thickness of the film of 46.2 nm by the time of 30 s associated with the half-way point of the barium arachidate normalized disappearance curve. This analysis also implies that



(a)



(b)

Fig. 1. (a) Depth profile obtained from a 15-layer barium arachidate LB film using C_{60}^+ bombardment and analysis. The characteristic molecular ion at $m/z = 449.2$ and the fragment at $m/z = 208.9$ were monitored. (b) Depth resolution of a 15-layer film of barium arachidate determined by monitoring the fragment ion at $m/z = 208.9$.

the sputtering rate of the film is about 1.54 nm/s and that the sputtering yield from the multilayer film is about 190 molecules per incident C_{60}^+ projectile. This analysis suggests that the depth resolution is about 16 nm, corresponding to five molecular layers after removal of a total of 15 layers of barium arachidate. Finally, we note that C_{60}^+ ion bombardment yields signal intensities that are 400–600 times larger than the corresponding yields obtained using Ga^+ 15 keV ions. Moreover, although the disappearance cross-sections are similar, the ion formation efficiency, Y/σ , is 100–200-fold greater with C_{60}^+ projectiles.

It is interesting to compare the behavior of molecular multilayer films to metallic multilayer films—where the issue of ion beam mixing rather than chemical damage is important. We have made preliminary investigations using a sample of Ni/Cr/Si(1 0 0) consisting of alternating layers of Ni (66 nm) and Cr (53 nm) as shown in Fig. 2(a). The neutral atoms were ionized with 800 nm fs laser pulses with a power of 8.5×10^{12} W/cm². Fig. 2(b) illustrates that the depth resolution is quite good at about 8.7 nm and it is possible to largely retain this resolution through nine layers. The sputtering rate of this source is about 0.2 nm/s.

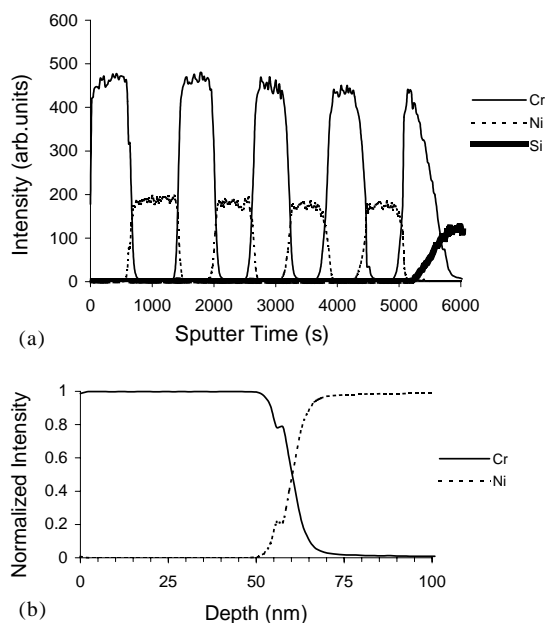


Fig. 2. (a) C_{60}^+ depth profile of a Ni/Cr/Si(1 0 0) sample consisting of five layers of Cr (53 nm per layer) and four layers of Ni (66 nm per layer) obtained from laser postionization with 800 nm fs laser pulses (data for the 4th Ni layer was not recorded and is sketched as a guide to the eye) and (b) depth resolution of the Ni/Cr/Si(1 0 0) sample.

4. Conclusion and future directions

Depth profiling with a polyatomic beam of C_{60}^+ is shown to be a feasible technique for an LB film of barium arachidate and a sample of NiCr. Furthermore, there is a 400–600-fold enhancement in secondary ion yields with C_{60}^+ bombardment of characteristic

fragments of barium arachidate. Future work will focus on tagging every five layers of arachidic acid with other metals besides Ba and then monitoring every five layers by the appropriate molecular and fragment ion of that particular arachidate molecule. This should allow for a more accurate analysis of the depth resolution.

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