Available online at www.sciencedirect.com
SCIENCE DIRECT
Applied Surface Science 252 (2006) 6533–6536
applied surface science
www.elsevier.com/locate/apsusc

Sputtering yields of PMMA films bombarded by keV C_{60}^{+} ions

I.L. Bolotin, S.H. Tetzler, L. Hanley *

Department of Chemistry, University of Illinois at Chicago, m/c 111, Chicago, IL 60607-7061, USA

Available online 3 May 2006

Abstract

A quartz crystal microbalance (QCM) has been used to determine total-mass sputtering yields of PMMA films by 1–16 keV $C_{60}^{+,2+}$ ion beams. Quantitative sputtering yields for PMMA are presented as mass loss per incident ion Y_m. Mass-lost rate QCM data show that a 13 keV C_{60} cluster leads to emission equivalent to 800 PMMA molecules per ion. The power law obtained for the increase in sputtering yield with primary ion energy is in good agreement those predicted by "thermal spike" regime and MD models, when crater sizes are used to estimate sputtering.

Keywords: Sputtering yield; Polymers; PMMA; Cluster; C_{60}; Secondary ion mass spectrometry

1. Introduction

Secondary ion mass spectrometry (SIMS) is the most widely used mass spectrometric technique for the surface analysis of molecular solids composed of organic, polymeric, and/or biomolecular species. Cluster ion beam are recognized as valuable sources for desorption of high mass ions in SIMS experiments when compared to atomic ions of similar or lower mass. Polyatomic projectiles also show promise for depth profiling of molecular solids.

Enhanced secondary ion yields – the number of sputtered ions produced per projectile or primary ion impact – improve the sensitivity of SIMS and expand its usage. Recent work has shown that polyatomic primary species enhance secondary ion yields compared with atomic primaries. Various degrees of enhancement have been reported, depending upon the type of projectile, target material and matrix [1–9]. For example, SF_5^+ ions will enhance the yields of organic ions emitted from many types of polymer films [8,10]. C_{60}^+ primary ion beams [5,11] have proven particularly effective for the characterization of organic films due to the significant C_{60}^+ yield enhancement for organic substrates [5,12]. For instance, at 10 keV incident energy, C_{60}^+ ion beams increase the yield of small proteins by at least a factor of 1000 relative to Ga^+ ion bombardment [5].

The reasons behind the unique properties of cluster beams are still not well understood. It remains unclear whether large enhancements are due to enhanced desorption, enhanced ionization, or both. In the case of molecular solids, this enhancement might also be due to reduced fragmentation during the desorption/ionization process. In recent years, several studies have been carried out to investigate some of the phenomena responsible for cluster-induced organic sample erosion. Molecular dynamics (MD) simulations of C_{60}^+ impact with kinetic energy 1–20 keV on graphite [13,14] and even on heavy metal substrates [15] show that a crater forms upon cluster impact and the cluster's kinetic energy is deposited into the near surface region. Determination of crater dimensions and the morphology of surface erosion provide a unique means of estimating total sputtering yields and testing theoretical models for material ejection. Nevertheless, data on total sputtering yields of organic materials bombarded by C_{60}^+ ions and on impact cluster dimensions remain limited.

This paper presents quartz crystal microbalance (QCM) measurements of the total sputter yield for spin-coated poly(methyl methacrylate) (PMMA) films induced by keV C_{60} clusters. The QCM allows measurement of sputter yields that are unaffected by ionization or fragmentation effects and directly comparable to MD simulations. It has been shown previously that the QCM can be used to study the etch rates of organic films by low-energy ion beams [16]. PMMA is used as model polymer since direct comparison can be made to previous work [10] where SF_5^+ was utilized as the primary projectile. Separate experiments are conducted to investigate C_{60} ion modification of PMMA thin films by X-ray photoelectron spectroscopy (XPS).

* Corresponding author. Tel.: +1 312 996 0945; fax: +1 312 996 0431.
E-mail address: lhanley@uic.edu (L. Hanley).

0169-4332/$ – see front matter
doi:10.1016/j.apsusc.2006.02.080

2. Experimental

Details of the instrumentation used for ion bombardment and photoelectron analysis have been described previously [10,17]. Briefly, the system consists of a differentially pumped ion source (Colutron) attached to a preparation chamber which is kept at a base pressure of 5×10^{-9} Torr. The ions are formed in an electron impact ion source, accelerated by 1–9 keV potential, mass separated by a Wien filter, bent 3° to remove fast neutrals, and guided by a series of lenses to impact the substrate at a normal angle. The experiments reported utilize a modification for a homemade C_{60} beam source in which C_{60} powder is loaded into a cylindrical reservoir where it is heated to inject vapour into the ionization region. The principal components of the primary beam consist of $C_{60}{}^{+}$ and $C_{60}{}^{2+}$. Using the mass filtering, pure $C_{60}{}^{2+}$ beam can also be selected, which effectively doubles the beam energy. A Faraday cup is used to obtain the true value of the total current and reduce the influence of secondary electrons. Although generally stable, the primary ion current exhibits a slow drift in value during a given measurement. Typical average ion currents are 40–900 pA over a 4 mm^2 spot.

The amount of material removed from the film during bombardment is determined using a QCM. The manipulator in a preparation chamber is modified to accommodate a 6 MHz quartz crystal (934-000, 14 mm, gold coated, Sigma Instruments with SQC 222 controller) probe, which is fixed to the opposite side relative to the sample holder. This geometry allows use of the same film sputtering conditions for an independent sample and the QCM crystal through a simple manipulator rotation, with the only geometrical limitation the requirement of an impact angle of 85° rather than 90°. Any slow drift in QCM frequency due to variation in C_{60} ion current or other effects is compensated for by analysis of several periods with the beam switched on and off. Differences in the QCM data for the on and off periods are statistically evaluated.

0.5–2% solutions of PMMA (Aldrich, average M_w = 15,000) in toluene are used for spin-coating at 3000 rpm for 30 s onto two types of substrates. Si wafers (Atomergic Chemical Corp., Si(1 0 0) p-type, boron doped) are hydrogen terminated with a minimum oxide by HF etching [18] and used for photoelectron spectroscopy. Samples for quartz crystal microbalance (QCM) analysis are prepared by spin-casting the solution onto the gold sensor crystals. The QCM samples are coated as thick as possible while maintaining a stable frequency in vacuum, but their absolute thicknesses are not determined. After coating, these samples are baked on a hot plate at 120 °C for 20 min.

XPS analysis is performed with a high-resolution monochromatic Al Kα X-ray source (15 keV, 25 mA emission current, VSW Rowland circle monochromator) and a 150 mm concentric hemispherical analyzer with a multichannel detector (VSW Class 150). The base pressure of the XPS chamber is 1×10^{-9} Torr. Samples are transferred from the ion bombardment preparation chamber into the analytical chamber without atmospheric exposure.

XPS show little to no changes in PMMA films upon ion bombardment. Small changes in the C_{1s} and O_{1s} spectra are observed by XPS, but these can be explained predominantly by differential charging effects. Regions of the PMMA film close to the crater formed by ion bombardment, where the film is thinner, undergo less charging during XPS. The thicker regions of the PMMA film, relatively unaffected by ion bombardment, undergo more charging during XPS. These results support the argument that PMMA films have no static limit in $C_{60}{}^{+}$ cluster SIMS, as little or no damage to the PMMA structure appears evident.

3. Results and discussion

Fig. 1 displays the QCM frequency response versus C_{60} ion fluences for bombardment of PMMA for two accelerated voltage (2 and 6.5 keV).

The flat regions of Fig. 1 show $\Delta f \approx 0$ Hz (corresponding to when the ion beam is off) and provides evidence for the high stability of the QCM. Three other regions show linear frequency increases as PMMA is sputtered during bombardment $C_{60}{}^{+}$ or $C_{60}{}^{2+}$. These are the regions analyzed by assuming that only PMMA is being sputtered here.

The response for rigid film on the quartz crystal to external perturbations follows the Sauerbrey equation [19], in which the change in frequency is inversely proportional to the mass change

$$\Delta f = -\frac{2 f_0^2}{A(\mu_q \rho_q)^{1/2}} \Delta m = -D \frac{f_0^2}{A} \Delta m = -(2.26 \times 10^{-6}\,\mathrm{cm^2/Hz\,g}) \frac{f_0^2}{A} \Delta m \quad (1)$$

where Δf is the change in frequency, resulting from a change in mass Δm; f_0 corresponds to the fundamental frequency of the crystal (~6 MHz); ρ_q and μ_q the density and the shear modulus of the quartz; D a constant for the crystal/film combination; A is the sensitive electrode area (~0.3 cm^2). The Sauerbrey equation holds for piezoelectric sensors such as the QCM when the

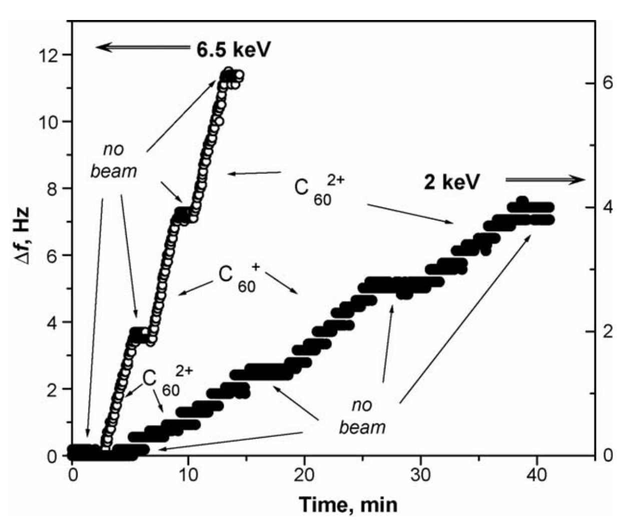

Fig. 1. Typical raw data obtained in sputtering measurements of PMMA by various accelerated potential (2 keV—solid circles, and 6.5 keV—open circles) of single and double charged C_{60} ions.