

Characterisation and Optimisation of a Polyatomic Ion Source for Organic Depth Profiling

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Sputter depth profiling of *inorganic* materials using X-ray Photoelectron Spectroscopy (XPS) has become a standard analytical technique. Generally the quantitative elemental and chemical depth distribution of species can be obtained from the sample surface to several microns into the sample relatively quickly with good interface resolution. It is obviously desirable to achieve the same performance on organic materials, however, there are several well known problems associated with sputter depth profiling of organics which has limited its application. The Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) community have pioneered the use of polyatomic ion sources (in particular C_{60}) to increase ion yields from organic materials. This use of C_{60} has been extended to XPS depth profiling and for some materials has shown good results. This paper discusses the characterization and optimization of another polyatomic species (that is showing considerable promise for XPS depth profiling of organic materials).

1. Introduction

The application of cluster ions as a primary ion source for ToF-SIMS analysis of organic materials has been developed over the last five years [1-6]. One motivation for the use of these cluster ions has been higher secondary ion yields when compared to atomic primary ions. For example, the use of C_{60}^+ ions has been shown to produce ~100 times increase in secondary ion yield over monatomic gallium sources with performance notably improved at higher mass [7]. A further advantage is that as the polyatomic clusters dissociate upon collision with the surface the initial energy is split among constituent atoms so the penetration of incident particles is less, reducing the ion-beam induced surface damage [8]. This is of particular importance for the analysis of organic and bio-organic materials and also of significance for application of XPS sputter depth profiling for this class of materials.

A recent study by Biddulph et al. [8] compared the use of C_{60} with C_{84} and coronene ($C_{24}H_{12}$) as the primary ion for use in SIMS. They concluded that coronene showed performance similar to C_{60} but that the hydrogen content of coronene during molecule emission may enhance proton transfer to organic molecules and increase the SIMS signal from these materials by relieving the matrix effect.

2. Development of the Cluster Ion Source

An ion source has been developed which is capable of running as either a polyatomic or monatomic ion source. In polyatomic mode an

electron bombardment source is used to generate polyatomic C_{60}^+ or $C_{24}H_{12}^+$ ions. For coronene, the powder is loaded into an oven and heated to *ca.* 170 °C to form a vapor which is then ionized by electron bombardment to create an ion.

- (A) sublimation oven
- (B) ionisation chamber
- (C) differential pumping
- (D) mass filter
- (E) source vacuum isolation valve
- (F) neutral suppression
- (G) focussing optics with retardation lens

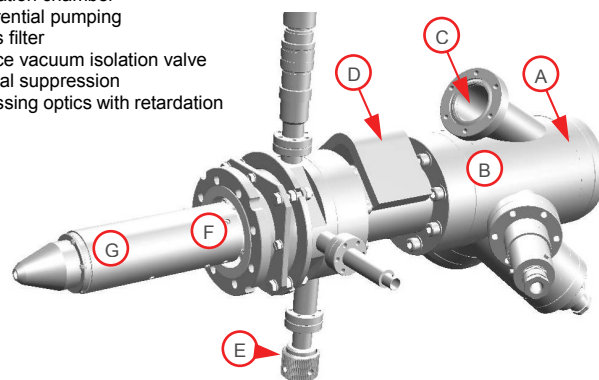


Fig. 1 Elements of the polyatomic ion source.

The $C_{24}H_{12}^+$ ions are extracted and collimated through an aperture. The ion source is capable of operating up to 20 keV for singly charged ions (equivalent to 40 keV for doubly charged ions) delivering a 300µm ion spot at the sample with typical currents of 1 – 40 nA. Ions are mass selected by a Wien filter which may also be used for beam blanking. The voltage on the Wien filter is scanned to select $C_{24}H_{12}^+$, $C_{24}H_{12}^{++}$ or $C_{24}H_{12}^{+++}$ ions. A plot of Wien lens voltage against sample current is shown in figure 2.

The lens column also includes a bend for suppression of energetic neutral atoms from the ion beam.

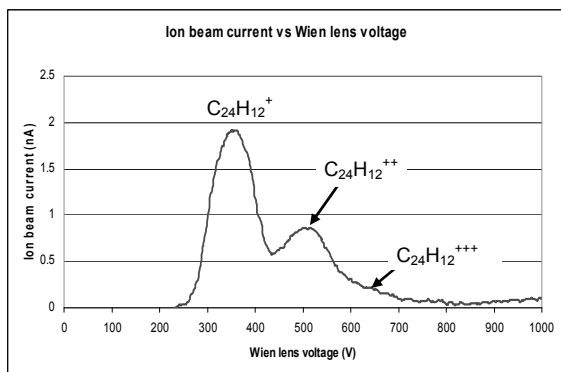


Fig. 2 Ion beam current as a function of Wien lens voltage.

This ion source is also capable of running in monatomic gas mode. Typically Ar^+ ions are used for sputter depth profiling of metallic and inorganic materials and efficient differential pumping of the source region ensures a reasonable base pressure is maintained in the analysis chamber during this mode of operation.

3. Experimental

The ion source was mounted on the analysis chamber of a Kratos AXIS Ultra^{DLD} photoelectron spectrometer and was fully computer controlled from the Vision software. Coronene, purified by sublimation, 99% [Aldrich] powder was used in the ion source without further preparation. Various thin polymer films were provided by Nottingham University [9] by spin casting (3000 rpm for 1 min) from solution onto piranha etched silicon wafers. Film thickness was measured by spectroscopic ellipsometry at NPL [10]. The films investigated in this study were: 34.6 nm and 86.2 nm Polyacrylic acid (PAA) Mwt 50,000 (cast from water solution); and 41nm, 85nm, 134nm and 197nm Poly(lactic-co-glycolic acid) copolymer (PLGA) (cast from THF solution). The coronene ion source was optimized at 12 kV ion energy and the Wien filter set to select singly charged ions.

4. Results & Discussion

A review of the literature reveals that the C_{60}^+ erosion behaviour of Polymethylmethacrylate (PMMA), Poly(α -methyl)styrene (PAMS) and Polystyrene (PS) has been studied at various temperatures and compared with Ga [11]. Strong variations of erosion yields using C_{60}^+ are observed where the authors conclude that chemical

degradation mechanisms are operating. Such mechanisms are connected with the chemical nature of the polymer. This initially suggests that the polymer depth profiling with C_{60}^+ ions cannot be considered as a general tool for polymeric materials. It is well known that PMMA can undergo chain scission phenomena under ion irradiation.[11] Ion beam-induced degradation phenomena (e.g. depolymerisation reactions) if active under C_{60}^+ bombardment could explain the high erosion rates observed and would be compatible with the low level of damage left on the surface. In such a hypothesis the possibility of depth profiling polymers would be greatly limited since it would be strongly connected with the radiation chemistry of the particular polymer.

However, it has been shown that depth profiling of polymers is feasible. The high sputter yield and the very low penetration depth of C_{60}^+ ions sputter away the damaged region leaving a more or less undamaged surface behind for analysis. Published data [4] has shown that increased proton availability when using coronene ions may increase the formation of protonated secondary (sputtered) ions.

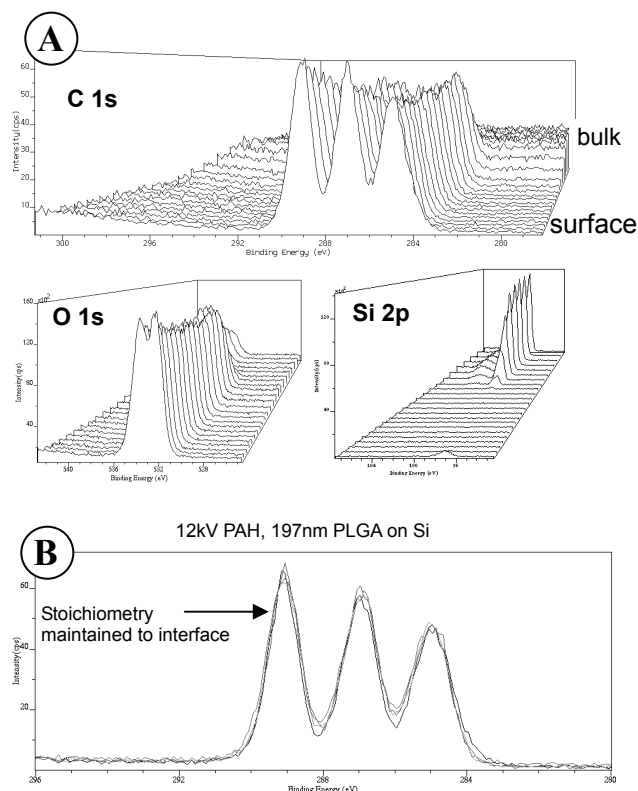


Fig. 3 (A) C 1s, O 1s and Si 2p high resolution XP spectra as a function of sputter time through 197nmPLGA thin film (B) Simple overlay of 4 C 1s spectra through PLGA film.

The aim of this study is to characterise the performance of coronene as the primary cluster ion for sputter depth profiling polymer materials.

Figure 3 shows the high resolution spectra of C 1s, O 1s and Si 2p from a 197nm PLGA film on a Si wafer substrate as a function of sputter time. It is apparent from the representative overlaid C 1s spectra taken at the surface, sub-surface and PLGA/Si interface in figure 3(B) that the carbon chemistry is retained throughout the sputter process, with the implication that the surface analysed during XPS retains the chemistry of the bulk material. This lends support to the conclusions drawn from ToF-SIMS that cluster ion sputtering of polymer surfaces leaves very little surface damage. A typical elemental sputter depth profile through a PLGA thin film on Si substrate is shown in figure 4. It is noted that the C/O ratio is constant throughout the PLGA layer and that stoichiometry is maintained as evidenced by the high resolution spectra in figure 3. It is also noted that a thin native silicon oxide layer is removed at the interface with the Si wafer and PLGA thin film. The etch rate is calculated to be 15 nm/min for the $C_{24}H_{12}^+$ operating at 12 kV with 3.4 nA sample current. The etched crater was measured as 2.6 x 2.6 mm such that the total ion fluence to the interface was 6.7×10^{17} ion m^{-2} . For PLGA sputtered with $C_{24}H_{12}^+$ the volume removed per incident ion (yield volume) is 90 nm^3 which is similar to the yield volume report by Shard et.al. for C_{60}^+ profiling of PLA [13]. If a density of 1.2 g/cm^3 for the PLGA film is assumed, approximately 500 polymer 'repeat units' are removed per $C_{24}H_{12}^+$ ion.

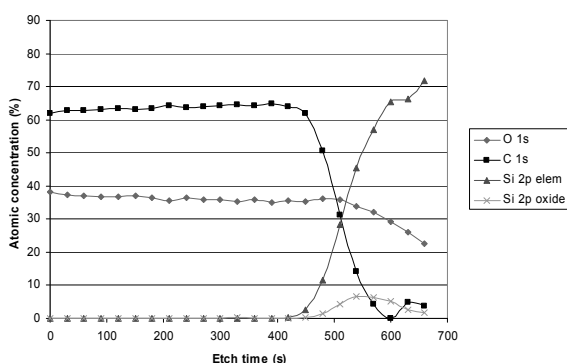


Fig. 4 Elemental depth profile through 134nm PLGA thin film on Si substrate.

Of great importance in sputter profiling is the constant removal of material during ion etching allowing the determination of material dependent etch rates and from this film thicknesses. Figure 5(A) shows the C 1s concentration as a function of

$C_{24}H_{12}^+$ sputter time for the four PLGA films of different thicknesses. Figure 5(B) shows the same data plotted as the time to the film/substrate interface against the PLGA film thickness determined by spectroscopic ellipsometry. The linear relationship between the PLGA film thickness and time to interface indicates that the sputter rate through the PLGA films of different thicknesses is constant under the sputter conditions used, at least up to the maximum film thickness used in this study. Whilst this is encouraging it should be highlighted that this is not always the case as shown by Shard et.al. [13] who conclude that C_{60}^+ sputter profiling of aluminium hydroxyl-quinolate (Alq_3) demonstrates a fluence-dependent sputter.

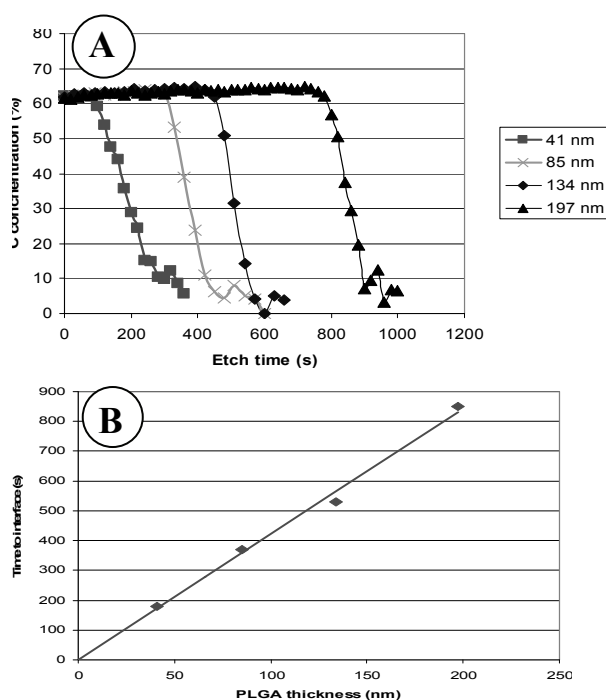


Figure 5 (A) carbon concentration as a function of sputter time for 4 different PLGA film thicknesses (B) time to interface versus PLGA film thickness.

Figure 6 shows the effect of ion energy on the ion fluence required to reach the interface between the 85nm PLGA film/Si substrate. It is concluded that the ion influence required to reach the film interface decreased as the ion energy increased. This is further supported when the calculated yield volume is plotted against the ion impact energy. Figure 6(B) shows an approximately linear relationship between the amount of PLGA removed and the beam energies between 8 and 16 kV.

The sputter profiling of thin polymer films was extended to two other thin polymer films spun cast

onto Si wafer; Polylactic acid (PLA) and Polyacrylic acid (PAA). Film thickness was measured at 86 nm for PAA and 100 nm for PLA by spectroscopic ellipsometry.

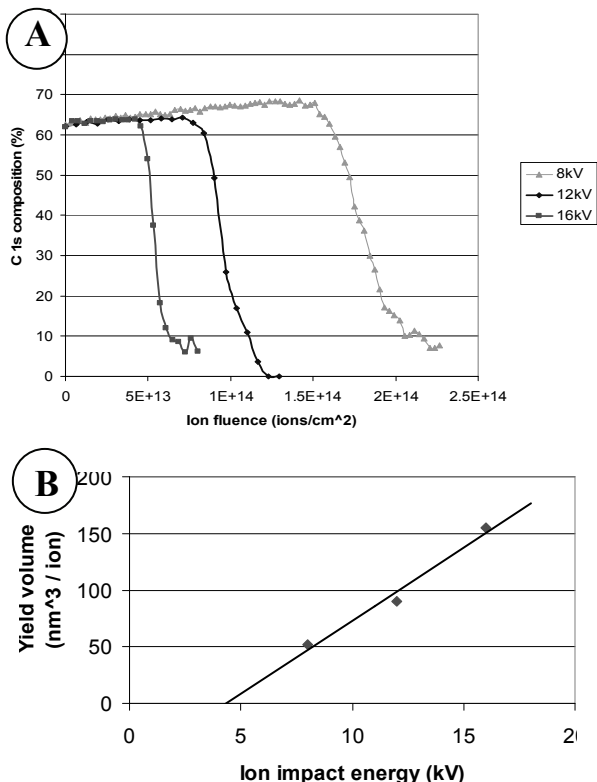


Fig. 6 (A) carbon concentration at different $C_{12}H_{24}^+$ ion acceleration voltages against ion fluence.(B) yield volume per ion versus ion impact energy.

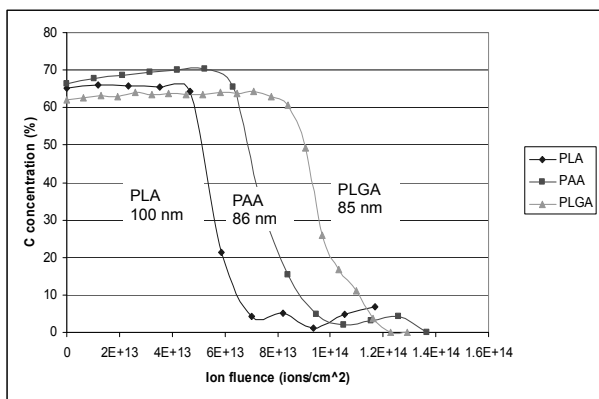


Fig. 7 carbon concentration at different $C_{12}H_{24}^+$ ion acceleration voltages against ion fluence.

Figure 7 shows a plot of the carbon concentration against total ion fluence to the thin film interface for PLGA, PLA and PAA. The yield volumes per $C_{24}H_{12}^+$ ion were calculated to be 90 nm³ (PLGA), 142 nm³ (PLA) and 117nm³ (PAA) which compares well to the value of 80 nm³ per 10

keV C_{60}^+ ion for PLA [13].

5. Conclusions

A new electron impact, mass filtered ion source suitable for monatomic or polyatomic sputtering has been developed for use on a high performance multi-technique X-ray photoelectron spectrometer. In this paper Coronene has been shown to have a similar behaviour to C_{60}^+ as an ion source for sputter depth profiling of organic materials.

The linear relationship between the PLGA film thickness and time to interface indicates that the sputter rate through the PLGA films of different thicknesses is constant under the sputter conditions used and that polyaromatic ion sources provide the capability of sputter depth profiling polymer materials with little or no change in stoichiometry.

6. References

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