Application Note

Ar_n^+ Gas Cluster Sputter Depth Profiling of Cross-Linked Plasma Polymers

MO393

Keywords:, plasma polymer, Gas Cluster Ion Source, thin film, depth profile

Overview

Thin polymer films are found in an enormous range of devices and have many applications from use in semi-conductors, displays and solar cells to corrosion protection and packaging. New ion sources such as the multi-mode Ar gas cluster ion source (GCIS) offered by Kratos have revolutionised the study of such organic thin films by depth profiling. As reported elsewhere the chemical composition of organic thin films may now be determined as a function of depth by a combination of XPS analysis and etching using massive Ar ions.

Plasma Polymerisation

Low temperature plasma polymerisation is well established as a versatile, economic route for the deposition of polymer coatings.[1] It is a clean, solvent-free technique, able to deposit coatings onto a wide range of substrate materials. The process of plasma polymerisation is discernible from conventional polymerisation by several important features:[2]

- The polymers formed lack a recognisable repeat unit;
- Polymer properties are highly dependent on the conditions of polymerisation as well as the initial monomer structure;
- Potential monomers do not retionquire a conventional polymerisable functional group such as a double bond.

The chemistry of plasma polymerisation is a non-thermal, non-equilibrium process and the electron temperature in non-equilibrium plasmas is several orders of magnitudes greater than the gas temperature[2]. Chemical reactions can take place at lower temperatures than would be possible under thermal conditions.

One of the limitations of the plasma polymerisation technique is that reactive processes such as ion bombardment, UV damage, and cross-linking reactions[2] in the plasma produce polymer networks with complex structures which often bear little resemblance to the precursor molecule. Therefore, one of the challenges has been to produce films containing high levels of chemical specificity. Variation of experimental parameters (e.g. input power[3,4] gas composition and pressure[5,6] substrate temperature[6-9] substrate position[10] nature of substrate[3,5] reactor dimensions[11] etc.) offers some degree of control over the stoichiometry. For example, it has been found that reducing the power supplied to the plasma increases the retention functional groups in many of the systems studied[3]. However, the overall selectivity tends to remain fairly poor.

In this study we report the sputter depth profile of acrylic acid plasma polymer which has been deposited with different degrees of cross-linking. The acrylic acid monomer molecule contains an acid group and a double bond, Figure 1.

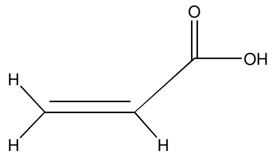

Figure 1: Acrylic acid monomer molecule

The degree of cross-linking may be inferred by the amount acid group retention in the polymer film as measured by XPS. It should be noted in this study no attempt has been made to distinguish between the carboxylic acid group (COOH) and the ester group (COOC). Both chemical groups have identical chemical shifts in the XPS spectrum.

The thin plasma polymer films were sputter profiled using Kratos' multi-mode Ar gas cluster ion source (GCIS), Figure 2. This ion source is designed to generate massive Ar clusters of up to 2000 atoms per cluster ion. These ions are accelerated by potentials up to 20 keV for sputter depth profiling of organic materials. Unlike monatomic ions, large cluster ions do not penetrate deeply into the subsurface region. The energy of the impact is deposited within the first few nanometres of the sample surface. As the total ion energy is shared by all atoms in the cluster, the energy per projectile atom (known as the partition energy) can be as low as a few electron volts leading to genital removal of the top few nanometres of the surface without significant chemical damage of the underlying material.

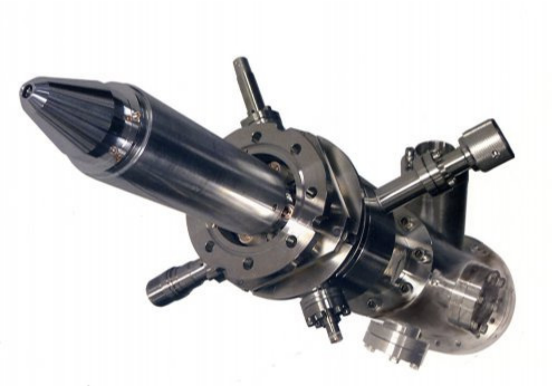

Figure 2 Multi-mode gas cluster ion source.

The ion source may be used in a number of modes: massive Ar cluster mode for depth profiling of organic samples; medium cluster, high energy mode for sputtering inorganic oxides; monatomic Ar mode for metals and other inorganic samples; and low energy He mode for ion scattering spectroscopy. In cluster mode large Ar$_n^+$ clusters are formed by the isentropic adiabatic cooling of Ar gas as it expands from high pressure into the vacuum of the source region through a de Laval nozzle. The Ar$_n^+$ clusters are then ionised by electron impact and accelerated along the ion column. A Wien velocity filter is used to narrow the sampled range of cluster size. The ions are accelerated up to a maximum of 20 kV, focused and rastered across the surface of the specimen.

To characterise the performance of the ion source a standard multi-layer polymer sample was profiled prior the plasma polymers. The sample consisted of alternating NPB/ Alq$_3$ layers and was provided by the National Physics Laboratory (UK) as part of the EURAMET project. The layer structure is shown schematically in Figure 3.

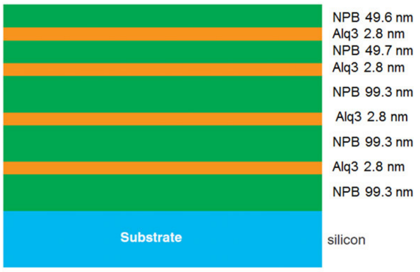

Figure 3 : NPB / Alq$_3$ multilayer sample.

NPB is a polymer containing C and H. Alq$_3$ [Al(C$_9$H$_6$NO)$_3$] delta layers contain 2.9% Al which may be used as a marker to elucidate the multilayer structure of the sample. The multilayer was etched with 5 keV Ar$_{1000}^+$ ions and the measured elemental composition of the sample displayed in Figure 4. Under these conditions the etch rate was 28 nm/minute and the ion does to the interface with the Si substrate was 8 x 10^{14} ions/cm^2. The Alq$_3$ layers were well resolved and the measured layer thicknesses reasonable given the XPS sampling depth.

Three plasma polymerised acrylic acid thin films (ppAA) were profiled using the GCIS. The ppAA were deposited under the following conditions:

- Sample 1: 10 W plasma discharge power, sample positioned 10 cm from the electrode.
- Sample 2: 10 W plasma discharge power, sample positioned 5 cm from the electrode.
- Sample 3: 50 W plasma discharge power, sample positioned 5 cm from the electrode.

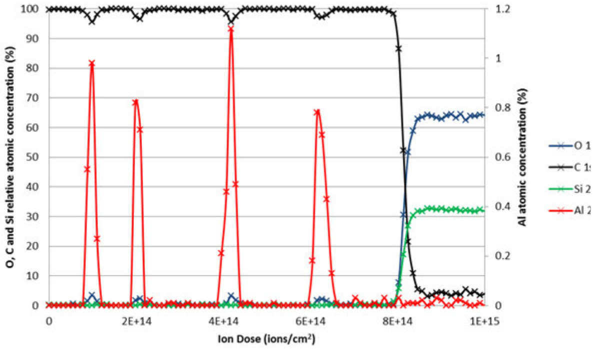

Figure 4 : NPB / Alq$_3$ multilayer depth profile.

The sample thicknesses of 46, 76 and 83 nm for samples 1, 2 & 3 respectively was measured by spectroscopic ellipsometary prior to profiling. XPS spectra from the C 1s core-level of the 'as received' surface demonstrates the various levels of acid group retention, Figure 5. As expected sample 1 retains the largest concentration of surface acid groups as this polymer was deposited under the most benign plasma conditions (low power, remote from the electrode). The least amount of acid group retention is observed for sample 3 (high power, close to the electrode).

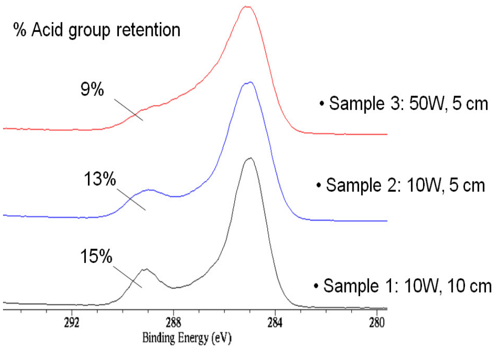

Figure 5 : C 1s spectra of the ppAA 'as introduced'.

The ppAA films were sputter profiled using Ar_{1000}^+ ions at acceleration energies of 5, 10 and 20 keV. This resulted in partition energies of 5, 10 and 20 eV per atom, Figure 6. As the partition energy increases the yield volume per ion increases in a pseudo linear fashion. In all cases the more cross-linked ppAA (sample 3) had a lower yield volume for a given ion energy.

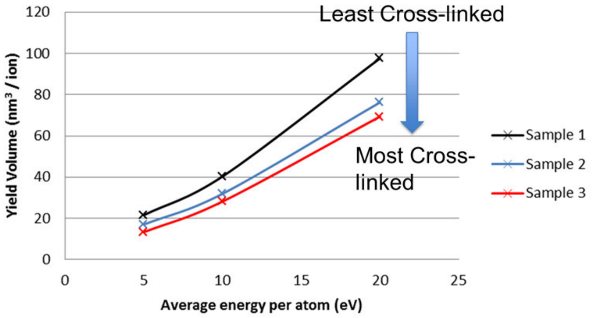

Figure 6: Depth profile of ppAA thin films at different beam conditions.

For all samples, and at all beam energies the chemical concentration of the ppAA did not vary through the film, this is demonstrated for sample 1 by a graph of the O concentration versus depth, Figure 7. Likewise the C chemistry of the films remained constant throughout the profiles at all beam energies. This is also demonstrated for sample 1 by a graph of the C chemistry versus depth at 5 eV partition energy shown in Figure 8. An overlay of the C 1s spectra of sample 1 from the surface and after an ion does of 8 x 10^{13} ions/cm^2 (nearing the interface with the Si substrate) shows that the ppAA is not chemically damaged during the profile.

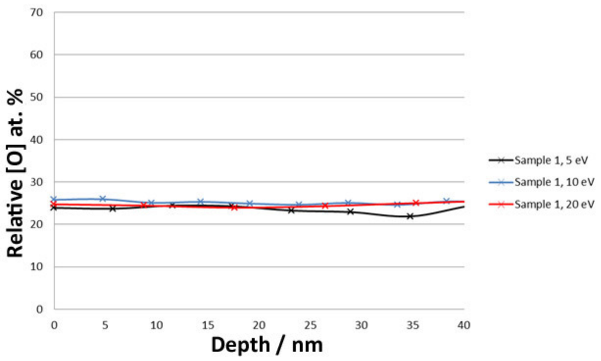

Figure 7: Oxygen concentration as a function of depth at 3 different beam acceleration voltages for sample 1.

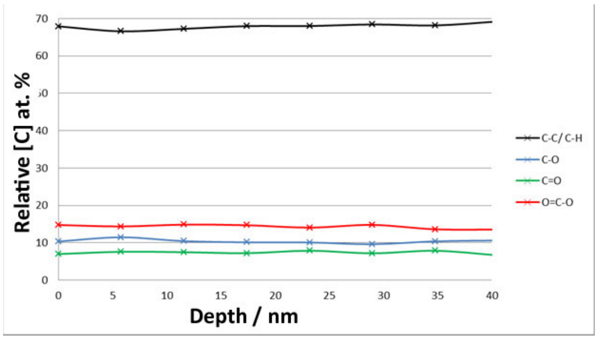

Figure 8: Carbon chemistry as a function of depth for sample 1 at a partition energy of 5 eV.

Conclusion

The multi-mode Ar_n^+ gas cluster ion source may be used to successfully depth profile through a range of organic samples with different chemical structures. In this study we have shown that the ion yield is dependent on the degree of cross-linking, specifically for acrylic acid plasma polymer. The chemical nature of the sample was not altered by the removal of surface layers by massive Ar_n^+ gas clusters. Furthermore, the ion yield was dependent on the acceleration voltage of the beam.

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