Sputter depth profiling of cross-linked plasma polymers by Ar gas clusters

Overview

Thin polymer films are found in a wide range of devices and have many applications from use in semi-conductors, displays and solar cells to corrosion protection and packaging. Ion sources such as the Minibeam VI 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 cluster Ar_n^+ ions. Here we investigate the effect of the degree of polymer crosslinking on the Ar gas cluster sputtering process.

Introduction

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 require 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 magnitude 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 of functional groups in many of the systems studied.[3] However, the overall selectivity tends to remain fairly poor.

In this study we report on the sputter depth profiling 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. The degree of cross-linking may be inferred by the amount of 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.
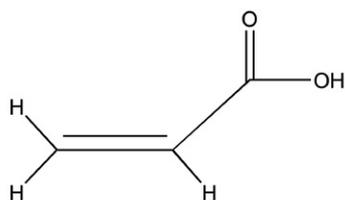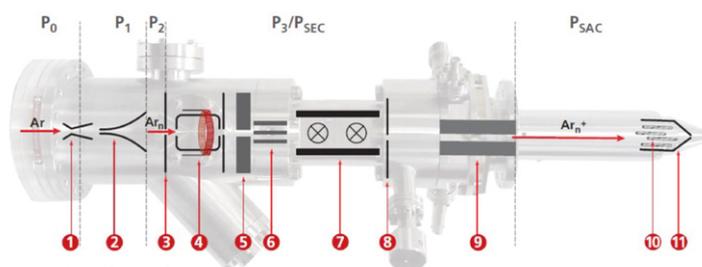

Figure 1: Acrylic acid monomer molecule.

The thin plasma polymer films were sputter profiled using Kratos' new Minibeam VI multi-mode Ar gas cluster ion source (GCIS), Figure 2. This ion source is designed to generate massive Ar clusters of up to 3000 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 dissipated within the first few nanometres of the sample surface.[12] 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 gentle removal of the top few nanometres of the surface without significant chemical damage of the underlying material.

Figure 2: Kratos' Minibeam VI multi-mode gas cluster ion source.

A schematic of the GCIS is presented in Figure 3. The ion source may be used in a number of modes: massive Ar_n^+ 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 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.
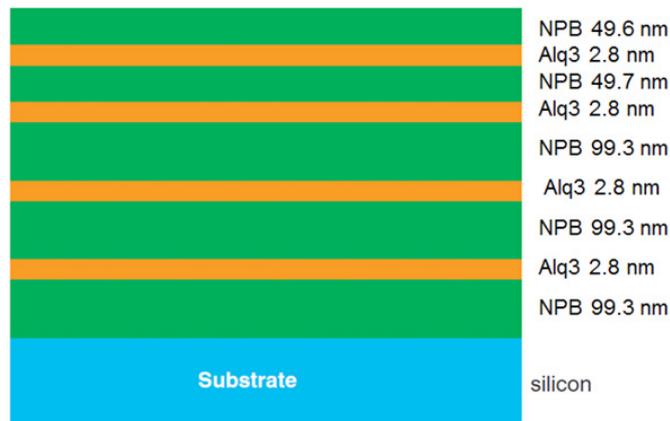

Ar GCIS schematics

1. de Laval Nozzle   5. Condenser Lens   9. Bend Plates
2. Skimmer   6. Alignment Plates   10. Quadrupole
3. Aperture   7. Wien Filter   11. Objective Lens
4. E.I. Source   8. Beam Monitor

Figure 3: Schematic of the Minibeam VI multi-mode gas cluster ion source.

To characterise the performance of the ion source a standard multi-layer polymer sample was profiled prior to the plasma polymers. The sample consisted of alternating NPB/ Alq3 layers and was provided by the National Physics Laboratory (UK) as part of the EURAMET project. The layer structure is shown schematically in Figure 4. NPB is a polymer containing C and H. Alq3 $[Al(C_9H_6NO)_3]$ delta layers contain 2.9% Al which may be used as a marker to elucidate the multilayer structure of the sample.

Figure 4: EMRP NPB/ Alq3 multilayer sample.

The multilayer was etched with 5 keV Ar_{1000}^+ ions and the measured elemental composition of the sample displayed in Figure 5. Under these conditions the etch rate was 28 nm/minute and the ion dose to the interface with the Si substrate was 8×10^{14} ions/cm². The Alq3 layers were well resolved and display good interfacial resolution.
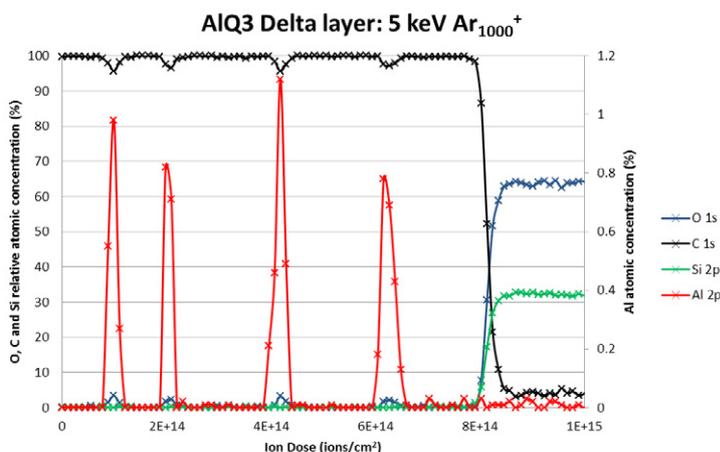

Figure 5: Alq3 / NPB Multilayer depth profile. O, C and Si concentration are plotted against the left hand Y axis while the Al concentration is plotted on the right hand Y axis.

Three acrylic acid plasma polymers (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.

The sample thicknesses of 46, 76 and 83 nm for samples 1, 2 & 3 respectively was measured by spectroscopic ellipsometry prior to profiling. C 1s XPS spectra of the as received surface demonstrates the various levels of acid group retention, Figure 6.
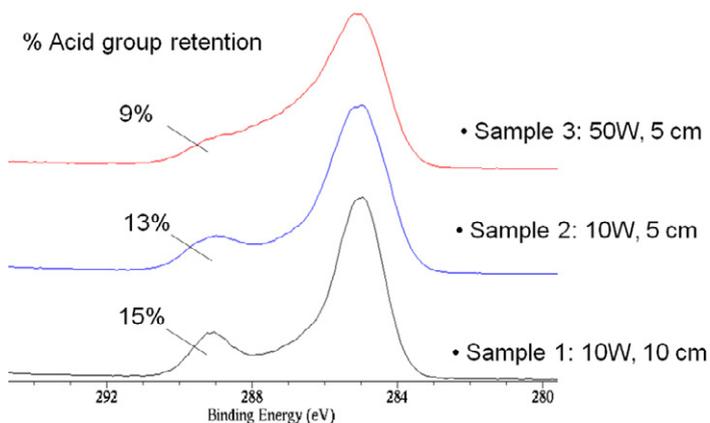
Figure 6: C 1s spectra of the ppAA as introduced surface.

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).

The ppAA's were sputter profiled using Ar_{1000} clusters at acceleration energies of 5, 10 and 20 keV. This gave partition energies of 5, 10 and 20 eV per atom. Results of the profile are plotted as yield volume (amount of material removed per cluster ion) against the partition energy (average energy per atom), Figure 7.
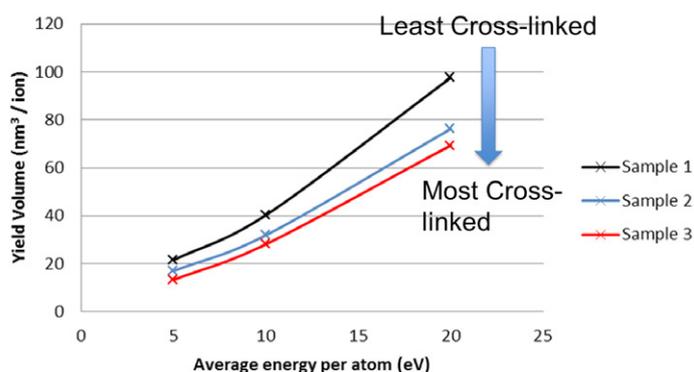
Figure 7: Depth profile of ppAA at different beam conditions.

As the partition energy increases the yield volume per ion increases in a pseudo linear fashion over the limited energy range investigated. In all cases the more cross-linked ppAA (sample 3) had a lower yield volume for a given ion energy. 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 8.
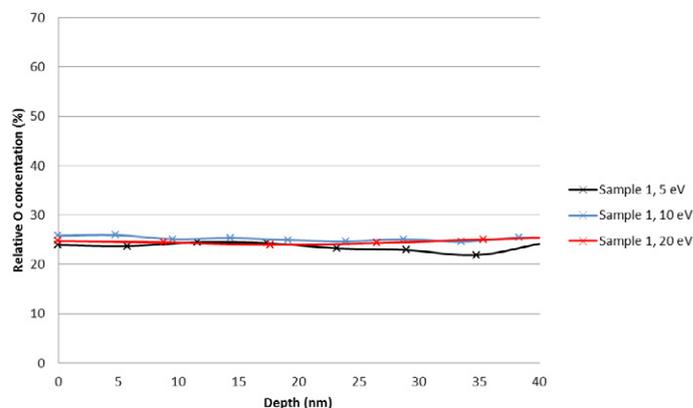
Figure 8: Sample 1 O concentration as a function of depth at 3 different beam acceleration voltages.

Likewise the C chemistry of the films remained constant throughout the profiles at all beam energies. This is again illustrated for sample 1 by a graph of the C chemistry versus depth at 5 eV partition energy, Figure 9.
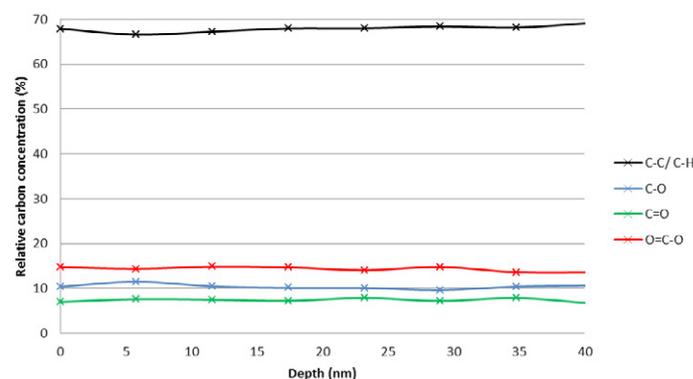
Figure 9: C chemistry as a function of depth for sample 1 at a partition energy of 5 eV.

An overlay of the C 1s spectra of sample 1 from the surface and after an ion dose 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 10.
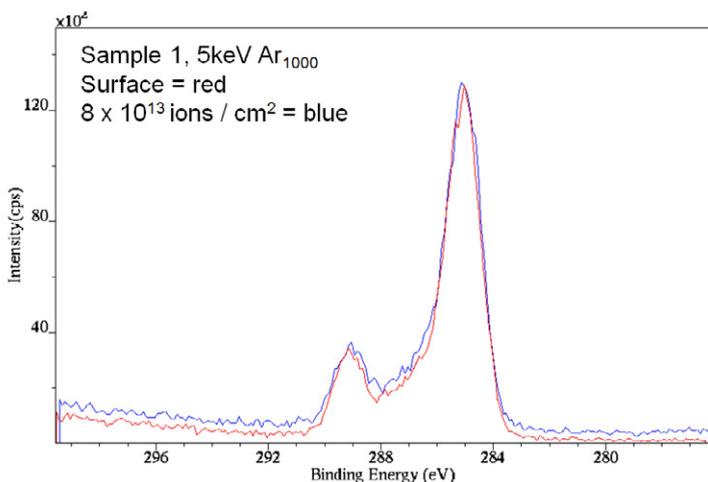

Figure 10: Overlay of C 1s spectra of sample 1 from the surface (red) and after an ion does of 8 x 10^{13} ions/cm^2 (nearing the interface with the Si substrate).

Conclusion

The multi-mode Ar 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 polymers. The chemical nature of the sample was not altered by the removal of surface layers by massive Ar gas clusters. Furthermore, the ion yield was dependent on the acceleration voltage of the beam.

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