KRATOS ANALYTICAL
A SHIMADZU GROUP COMPANY

Applications Note

Sample rotation during depth profiling

MO460(A)

Keywords Polymers, GCIS, Shard, Zalar,

Overview

The aim of this investigation was to characterise the performance of the gas-cluster ion source (GCIS) for the depth profiling of thick organic multi-layer materials. The sample is composed of 25 repeating units of polystyrene (PS) and polyvinylpyrrolidine (PVP) PS = 288 ± 1.3 and PVP = 328 ± 7 nm on a glass substrate. It has been considered challenging to depth profile thick samples (>1 micron) of soft materials due to the changes which occur under sustained X-ray irradiation and bombardment of charged projectiles, however, in this study we describe a methodology to eliminate these issues. The use of fast acquisition, snapshot spectroscopy and rotation is discussed herein.

Introduction

Gas cluster ion sources are becoming more widely used to study polymer materials. Whilst very useful and valid chemical information can be obtained, it is often not possible to make observations to separate out subtle changes in etch rates or observe degradation of deep interfaces due to the crater / X-ray beam effects on the sample rather than intrinsic to the material or interface itself. Here we use well defined polymer multilayer materials, commonly used for optical filters and reflectors,[1,2] to propose optimized acquisition parameters for sputter depth profiling 'soft' multilayer materials.

We investigate XPS depth profiling of a challenging but well characterized 15 µm thick multilayer sample of PS and PVP (chemical structures shown in figure 1) using argon cluster etching. In this study the incident ion beam was used at a constant energy setting (10 kV, $Ar_{1000}{}^{+}$ equivalent to 10 eV per incident atom) and the sample presented without rotation, 'Zalar' (constant) rotation and 'Shard' (90 degree, stepwise cross etches) rotation. The effect of minimizing X-ray exposure was also investigated.

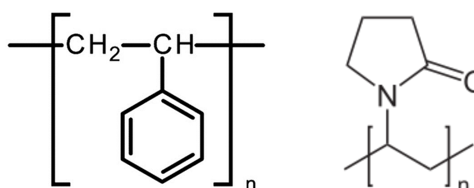

Figure 1: Chemical structures of PS (left) and PVP (right)

Discussion

For the initial depth profile an Ar_n^+ cluster size of n=1000 was chosen with an ion acceleration voltage of 10 keV. This mode is commonly used for depth profiling organic materials because the average energy per ion (10 eV) is above the threshold energy to break the polymer bonds. A raster size of 1 mm x 1 mm was chosen with an analysis area of 110 µm in the centre of the crater. Scanned spectra were acquired for the C 1s and O 1s regions with a total acquisition time of 120 s. In between depth profiles the X-ray source was turned off to limit exposure of the sample to the excitation source. From the profile shown in figure 2a) it is clear to see that the etching process initially works with the top 16 layers. The total etch rate for the first two layers was 164 nm/min. After 16 layers the resolution of the layer interface between the polymers begins to fade. Analysis of the C 1s and O 1s peaks after 20 layers showed the peak shape no longer represented either PVP or PS but a mixture of the two.

To further investigate whether the observed decrease in interface resolution was a symptom of the sample production process or of the analysis conditions, the use of Zalar [3] rotation was employed (figure 2b). It should be noted that for consistency the sample always returned to the original position and orientation for XPS analysis. Zalar rotation was initially developed as a solution to the formation of surface ripples formed under stationary ion bombardment. Theory explains the process of ripple formation as the effect of curvature dependent sputtering in the absence of viscous flow. Zalar rotation allows the smoothing effects of self-diffusion and viscous flow to dominate over the roughening effects. There is a marked improvement in the depth profile compared to stationary sputtering as many more layers are observed. In fact all 50 layers can be seen before the substrate is reached. However, blurring of the layers and an overall loss of interface resolution occur as the etch depth increases. A comparison of etch time for layers 1-6 and layers 42-48 shows that for the top layers each repeat period took approximately 270 s compared to 320 s for the bottom layers. This corresponds to an 18.5% increase in etch time per repeat period (despite the beam current remaining constant throughout the experiment).

The next parameter under consideration is X-ray exposure. Previous studies have shown polymer blends to degrade under X-ray exposure with spectra showing changes in peak intensities, positions and shapes. X-rays can cause electronic transitions in the material resulting in chemical changes with free radical reactions, cross-linking and structural reconstruction all possible degradation pathways. To explore this effect, snapshot spectral acquisition mode was used with 2 second spectra acquired per element (figure 2c). A clear improvement of the profile is seen with very little change in interface resolution or etch rate throughout the profile. This would imply that the broadening of layers and increase in etch time per layer discussed above was in fact due to X-ray exposure. A comparison of etch times for layers 1-8 and layers 40-48 shows there is a 7.4% increase over the depth of the sample which is a significant improvement from scanned acquisition.

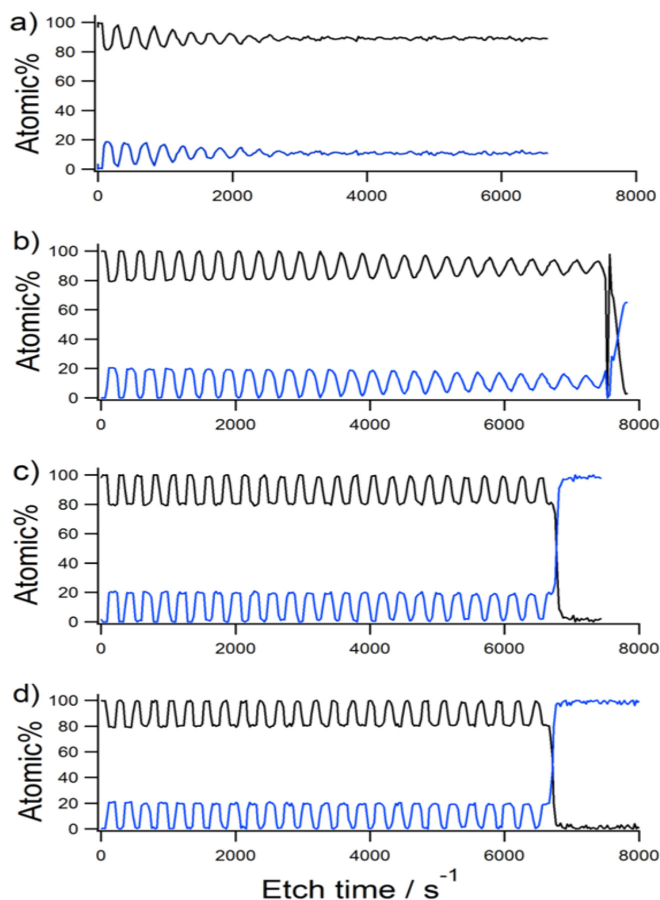

Figure 2: XPS depth profile of PS-PVP 50 layer sample using 'at%' of O (blue) and C.(black) a) Experiment 1; Standard 120s acquisition time and no rotation, b) Experiment 2: Standard 40s acquisition time and 'Zalar' rotation, c) Experiment 3: snapshot 4s acquisition time to minimize X-ray exposure and 'Zalar' rotation, and d) Experiment 4: 6s snapshot acquisition and 'step-wise' 90° rotation. (reproduced from [4]).

The final experimental parameter explored was rotation (figure 2d). A recent publication by Shard *et al* [4] highlighted the shortcomings of conventional Zalar rotation due to variations in ion dose across an etch crater when the rotational frequency is similar to or greater than raster frequency. Shard instead proposes a step-wise method employing 90° rotations between etches and no rotational movement during etching. This simple method assumes that any ripples will be removed by cross-etching, evening out any topography created by the ion bombardment.

Interestingly a small increase in interface resolution was observed using this method with even less blurring of layers and a change in etch rate throughout the stack of <5%. This slight but significant improvement indicates that the rotation and raster frequencies do indeed play a part in the absolute resolution of the profile, further highlighting the importance of experimental optimisation.

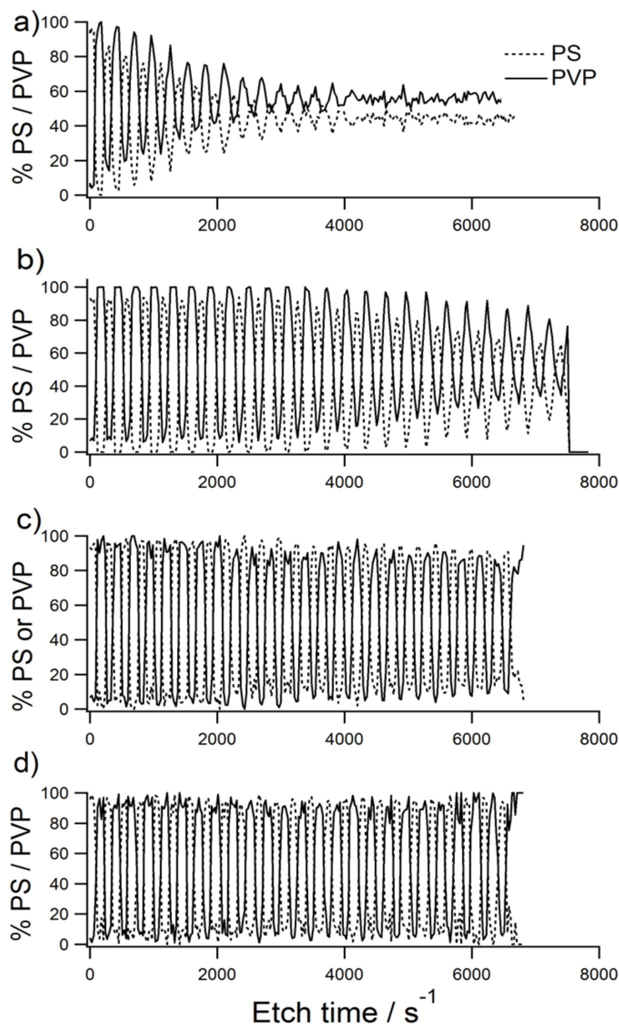

Figure 3: C 1s PS & PVP model peak fit profiles for all four experiments, a) Experiment 1; Standard 120s acquisition times and no rotation 50 b) Experiment 2: Standard 40s acquisition time and 'Zalar' rotation, c) Experiment 3: snapshot 4s acquisition time to minimize X-ray exposure and 'Zalar' rotation, and d) Experiment 4: 6s snapshot acquisition and 'step-wise' 90° rotation. (reproduced from [4]).

Figure 3 shows the sputter depth profile of the '50-layer' sample spectra based on modelling the C 1s peak shape. The C 1s spectra for the multiplayer samples were fitted with a set of model components based on the known polymer structure.

Figure 3 a) - d) show the profiles based on just the C 1s envelope for PVP and PS material. Comparing with the elemental profiles of figure 2, the C 1s profiles show the same behaviour, with the interface resolution degrading due to signal mixing caused by sample roughening for the non-rotated sample.

Conclusions

From this work it is concluded that it is possible to depth profile relatively thick polymer samples using GCIS 10 kV Ar_{1000}^{+} clusters and XPS. Reducing X-ray dose and using sample rotation markedly improves layer resolution and reduces changes to etch rates due to ion induced roughening.

Acknowledgments

Many thanks to Dr Emily Smith, Dr David Scurr and Dr Alex Shard for help and invaluable discussion on this topic.

References

[1] Bailey, J. & Sharp, J. S., Eur. Phys. J. E 33, 41–49 (2010).

[2] Farmer, D. J. *et al.*, Opt. Express 22, 15218–31 (2014) .

[3] A. Zalar, Thin Solid Films, 22, 1985, 223.

[4] E. Smith *et al.*, Surf. Interface Anal. Surface and Interface Analysis DOI:10.1002/sia.6250

MO442 Quantification of layer composition in compound semiconductors

MO393 Ar+ Gas Cluster Sputter Depth Profiling of Cross-Linked Plasma Polymers

Wharfside, Trafford Wharf Road, Manchester M17 1GP

Phone: +44 161 888 4400 Fax. +44 161 888 4402

www.kratos.com

Kratos Analytical Ltd, a wholly owned subsidiary of Shimadzu Corporation, has been manufacturing surface analysis instruments for over five decades. Throughout this period Kratos has continued to lead the development of new technologies relating to X-ray photoelectron spectrometers and associated accessories for surface and materials characterisation. All Kratos Analytical products are designed, assembled and supported from our headquarters in Manchester, UK.

Kratos Analytical Ltd has a policy of continuous product development and improvement and therefore reserves the right to make changes to specifications without notice.

© Copyright December 2019