



# *Surface Analysis Forum Newsletter No. 24*

**Spring 1998**




## *Contents*

Announcement of the forthcoming July Meeting of the Surface Analysis Forum

**"The Characterisation of Thin Layers and Depth Profiles by Angle Resolved XPS"**

*National Physical Laboratories  
Wednesday 15th July 1998*



***Report on the winter meeting of the Surface Analysis Forum***

**"Nano-Analysis"**

*Interface Analysis Centre, Bristol University  
Wednesday 7th January 1998*



*Including summaries of the invited lectures:-*

**High Spatial Resolution Analysis using Vintage Instrumentation!**

*Dr. RK Wild, Interface Analysis Centre, Bristol.*

**Image of Dopant effects using High Energy Resolution AES**

*Dr J Wolstenholme, VG Scientific*

**XPS and SIMS for surface Imaging Phase Separation in Polymer Blends**

*Dr. R Short, Sheffield University*

**New Developments in SEM**

*Dr. M El-Gomati, University of York*

**John Rivieré Prize**

**Probing the surface on the nano-scale spatially and as a function of depth**

*Dr. C Blomfield, Kratos Analytical*

**Angle Resolved XPS**

*"The development of a practical spreadsheet package for the average analyst"  
(and a taster for the Summer 1998 meeting at NPL)*

*Dr. P Cumpson, NPL*

Acknowledgements

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**Announcement of the forthcoming July Meeting of the Surface Analysis Forum**

*"The Characterisation of Thin Layers and Depth Profiles by Angle Resolved XPS"*

*National Physical Laboratories*  
**Wednesday 15th July 1998**

Dr. Peter Cumpson will host a new venture Surface Analysis Forum meeting, where the emphasis will be on the easy extraction of meaningful compositional depth profiles from Angle Resolved XPS. The morning session will discuss the theory and application of the technique, on ideal and real samples, while the afternoon session will involve the *hands-on* use of the latest software developed at NPL for UK users. Delegates will be shown how to use the PC software developed by Dr Cumpson, on computers set up for the UK Surface Analysis Forum. No prior knowledge of the use of PC's is required, beyond simple windows experience. Several well-established experts in the field will give review papers on the technique, prior to the workshop session.

More information including full programme, accomodation information and travel details is available [here](#).

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***"Nano-Analysis"***

**Bristol University - Wednesday 7th January 1998**

**Introduction & Welcome**

by Prof. GC Allen, *Dep.Dir. Interface Analysis Centre*

Professor Allen opened the meeting by reminding all the delegates of the previous UK ESCA Users meeting held at the IAC, at the Victoria Rooms conference facilities. The theme of that earlier meeting was also on high spatial resolution surface analysis. His main memory of that particular meeting was how cold the conference rooms were, and that there were two choices:

- *Hear the talks and freeze, or*
- *Have the jet heaters on and ignore the speakers!*

He was pleased to note that the current meeting was in a smaller warmer (*only slightly!*), conference room (in the Russian Language department) and that like the last meeting held in Bristol, it was very well attended.

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**"High Spatial Resolution Analysis using Vintage Instrumentation!"**

Bob Wild described how due to their limited budget, the IAC had been forced to look for alternative ways to get their hands on "state of the art" instrumentation. The policy that had adopted was the use of system upgrades, plus the use of considerable in-house expertise in the development of new instrumentation and software. In particular he showed the recent modifications to their 1984 PHI 595 Auger spectrometer (*figure 1*), and their "new" LMI-MS system, which was based on an old UHV chamber or two, a magnetic sector mass spectrometer removed from 20 year old GC/MS and a brand new FEI liquid metal ion gun. Both were now up and running, and producing excellent results.



Figure 1. 1984 Vintage PHI Auger Analyser at the IRC

The Auger spectrometer used the York Electron Optics Schottky Field Emission gun, which gave the system 100nm spatial resolution (for spectroscopy). The limit on the spatial resolution was set not by the electron gun, which would ultimately give 20nm spatial resolution, but by the stage vibration. This may be more difficult to resolve given the design of the instrument.

The mass spectrometer, also theoretically also had 20nm resolution, but again this was badly affected by machine vibration. However, the sensitivity of the instrument was exceptional, with polished sections of Inconel 600 showing boron segregation at grain boundaries. The maps were acquired in 1 second without O<sub>2</sub> dosing.



### Image of Dopant effects using High Energy Resolution AES

Dr J Wolstenholme, VG Scientific

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Figure 2. VG Microlab 310F

Dr. Wolstenholme showed results obtained from the VG Microlab 310F (*figure 2*), using an optimum spatial resolution of ~20nm (Au on C, *figure 3*), using a beam voltage of 10kV, and a spectral resolution of 0.05%. The project involved the careful examination of doped and undoped Si wafer specimens, noting possible 1) Beam Energy effects and 2) "Z" Stage Positions on the Si peak position. After completing a number of carefully controlled sets of experiments, it was concluded that there was no effect on peak position by these parameters!

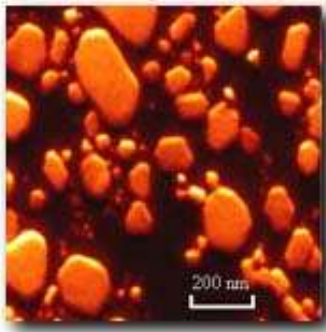


Figure 3. SEM of Au Particles on Carbon

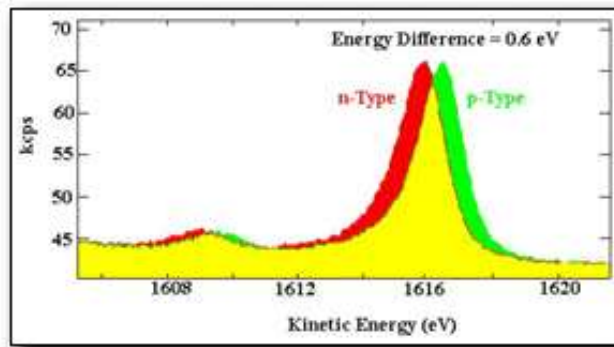


Figure 4. Si KLL Auger Peaks Shifts in High Resolution Mode (Note, Example is difference between n and p type doped Si)

Further experiments were then performed on in-situ fractured phosphorus doped samples, where it was clearly shown that there was a 0.7 eV peak shift (Si KLL) between the doped and un-doped material (*figure 4*). This difference could be used to generate AES maps of both regions and hence determine a diffusion profile of the region. The samples shift was also shown not to be sensitive to ion sputtering ( $\text{Ar}^+$ ) and could therefore be used on real samples.



## XPS and SIMS for surface Imaging Phase Separation in Polymer Blends

Dr. R Short, Sheffield University  
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Dr. Short gave an excellent presentation on the detailed examination of phase separation using a multi-technique/multi-instrument approach. Over a period of approximately 7 years his research group at Sheffield University had examined possible surface segregation phenomena in a PMMA/PVC blend. The work was part sponsored by ICI (Wilton) who had also contributed instrument time on their ESCASCOPE, Scienta ESCA 300 and PHI 7200 ToF-SIMS. Surface measurements were also made on the VG CLAM 200 (XPS) and VG Ionex IXL23LS ToF-SIMS at Sheffield University!

The work examined the possible segregation of a wide number of PVC/PMMA blends (0-80%), which were spin cast from THF. Quantitative XPS analysis of the surface (CLAM 200) indicated a slight surface excess of PMMA although, the results were always difficult to reproduce. Optical images of the polymers, however, clearly showed phase separation. Using the ToF-SIMS (IXL23LS) to generate elemental ion maps it was possible to show that the different phases seen in the optical micrographs (Cl<sup>-</sup> for PVC & O/OH<sup>-</sup> for PMMA). However, high spatial resolution XPS line scans made on the Scienta ESCA 300 indicated that there was a surface layer of PMMA on the PVC phase. This was shown by the O1s linescans across a sample section. ToF-SIMS molecular ion images (PHI 7200) and XPS images (ESCASCOPE) clearly confirmed these earlier results. The conclusions from the work were as follows:

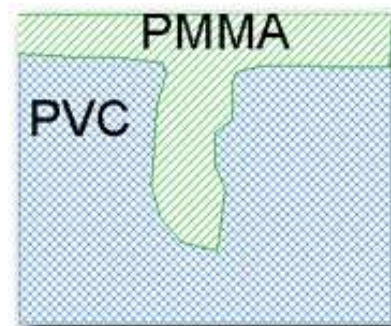


Figure 5. The surface of a spin cast PMMA/PVC blend (THF Solvent)

- In blends cast from THF, phase separation "extends to the surface", however,
- There is still a PMMA overlayer on the polymer blend.

The model of the surface is shown in figure 5. However, some questions remain unresolved, such as what is the thickness of the surface PMMA layer and is it uniform? Rob Short and his group will let us know in a few years time.

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## "New Developments in SEM"

Dr. M El-Gomati, University of York  
[mmg@ohm.york.ac.uk](mailto:mmg@ohm.york.ac.uk)

Dr El-Gomati described recent research at the University of York on the development of a combined Back-Scattered Electron Detector (BSED)/Cylindrical Mirror Analyser (CMA) fitted to an electron microscope which operates at low beam voltage (>20V) but retains spatial resolution! The system was shown to be highly effective in determining surface information and very surface sensitive (<10nm). The developments were driven by the semiconductor industries requirements for a rapid, high spatial resolution, low radiation analytical technique. Already the developments are very promising and the instrument may be commercial available in a few years.

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## John Rivieré Prize



Figure 6. Dr. Robert Wild Presenting Dr. Steve Evans with the 1998 Rivieré Prize.

Dr Dave Briggs addressed the meeting and thanked the delegates for the 1997 Rivieré prize presented to him at QSA 7 at Surrey University. The prize had been completely unexpected and he was grateful for the opportunity to thank the members of the Surface Analysis Forum for the honour. In an attempt to continue this tradition, Dr. Bob Wild then surprised Dr Steve Evans with the 1998 prize (*figure 6*). Steve was so surprised that he did not know what to say, but he has promised to make his acceptance speech at the July meeting at NPL!

The committee is indebted to the new Surface Analysis Forum official photographer, Dr Alan Carrick (Acolyte Consultants), for capturing the event for posterity.

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## "Probing the surface on the nano-scale spatially and as a function of depth"

Dr. C Blomfield, Kratos Analytical  
[Blomfield@kratos.co.uk](mailto:Blomfield@kratos.co.uk)

Dr Blomfield gave a presentation based on data obtained from the Kratos ULTRA (*figure 7a*), which offers both high spatial resolution spectroscopy (Images ~2 microns) with high spectral resolution (*figures 7b, 7c*) using the monochromator/charge neutraliser developed at Kratos analytical. The first example was ARXPS measurements on PMMA, using the high sensitivity of the spectrometer to differentiate

between the various tacticities of PMMA, (figure 8).



Figure 7a. The Kratos Ultra

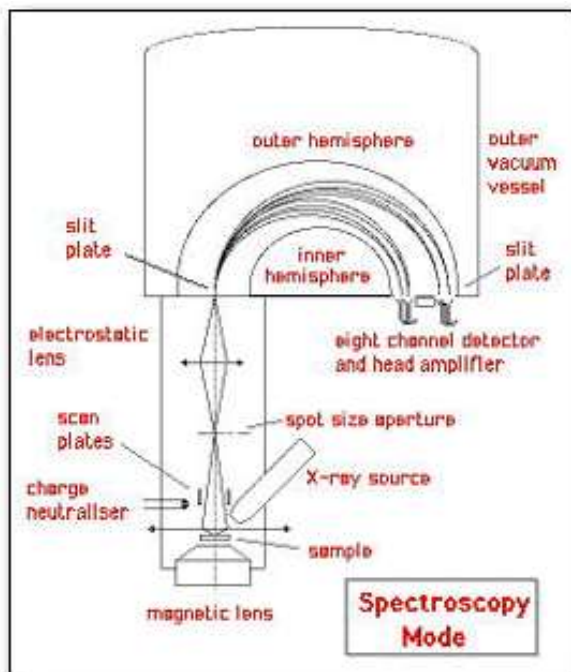


Figure 7b. Spectroscopy Mode

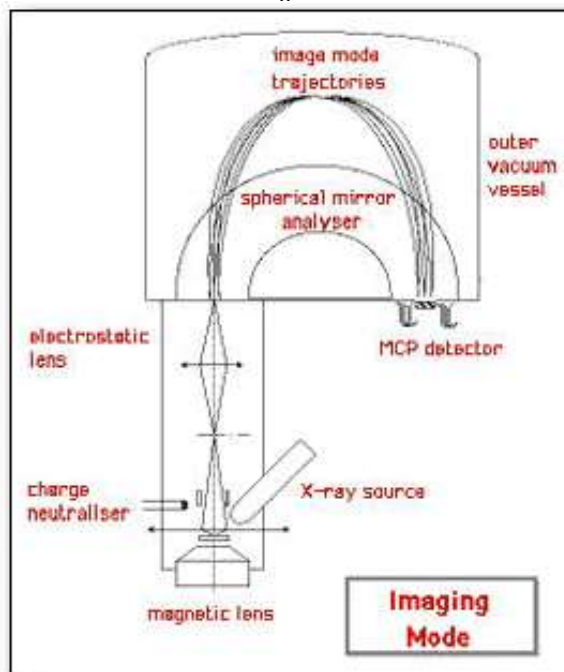


Figure 7c. Imaging Mode

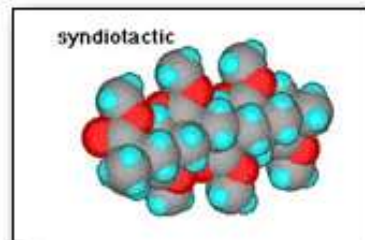
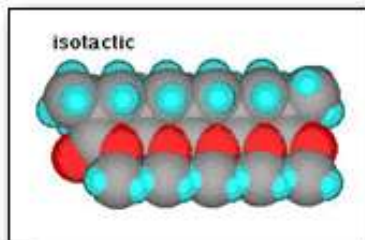
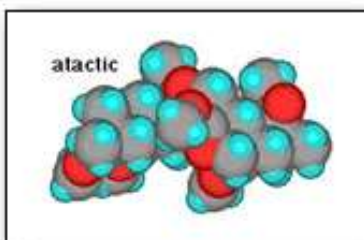


Figure 8. PMMA Tacticities

The system has sufficient sensitivity that good quality valance band spectra (suitable for chemical state determination) can be obtained in <20 minutes, (figure 9).

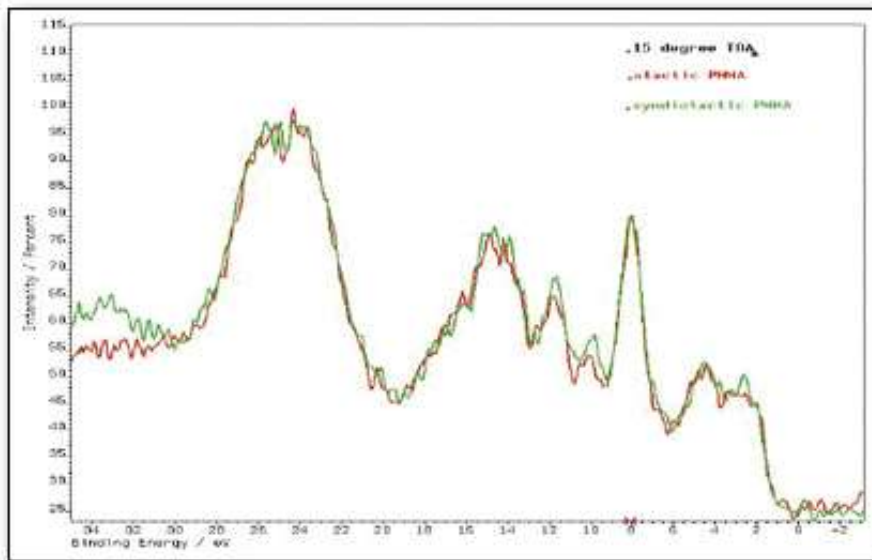


Figure 9. High resolution valence band spectra of two PMMA isomers, (*isotactic* in red, *syndiotactic* in green) overlaid and normalised at 8eV. 15 degree take of angle (close to grazing surface) spectra show a number of subtle differences.

Dr. Blomfield then showed several high spatial resolution examples on the oxidation of TiN films on steels. Using the new imaging machine, Chris was able to show the formation of  $\sim 100\text{m m}$  Fe/Cr Oxide islands in the surface of the TiN film. Instrument was then reset to take spectra from nominally a  $27\text{m m}$  area, in order to give a detailed chemical description of these features. The ultimate performance of the instrument at present appears to be around  $\sim 2\text{m m}$ , whilst retaining good spectrometer resolution. The examples shown by Dr. Blomfield were in general acquired in 2-20 minutes, which means the system can be used to tackle real problems within a realistic timescale.



### Angle Resolved XPS: –

*"The development of a practical spreadsheet package for the average analyst"*

Dr. P Cumpson, NPL.  
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Angle-Resolved X-ray photoelectron spectroscopy (ARXPS) can be used non-destructively to define the depth-distribution of chemical species. Often one needs a simple qualitative result, such as that "layer A" is above (or below) "layer B". In these simple cases one examines how the ratio of the two peak intensities changes as one tilts the specimen close to grazing emission. Sometimes one needs to use ARXPS quantitatively. This is often the case if chemical state information from the first 5nm or so is needed, since this is very rapidly destroyed by alternative depth-profiling methods involving sputtering. By acquiring spectra at a few different angles of emission we are typically trying to answer one of four types of question;

- Thickness Measurement (TM) - e.g. "What is the thickness of this aluminium oxide?"
- Depth Measurement (DM) - e.g. "What is the average depth of this low energy implant?"
- Layer Modelling (LM) - e.g. "What is the order of the layers in a complex oxide, and how thick are they?"

- Depth Profile (DP) - e.g. "How does the concentration of different oxidation states of carbon vary with depth over the first few nanometres in this bio-compatible material?"

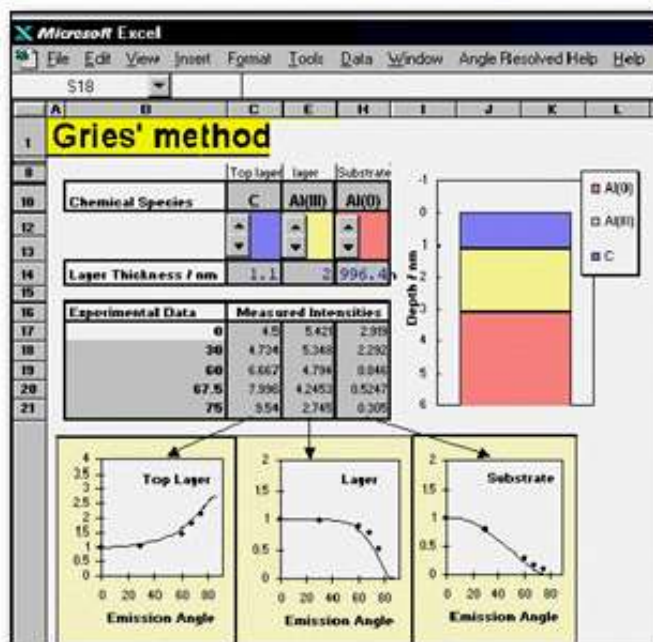


Figure 10. The NPL ARXPS Spreadsheet

At NPL we have reviewed the twenty or so different quantification algorithms proposed since 1974 for solving problems like these. One can classify them into families. Most recently we have developed a computer spreadsheet which allows one to apply the simplest and most reliable approaches to answer questions of this kind, and incorporate ones prior knowledge about the specimen. The use of some graphics and the standard "windows" user interface controls make the spreadsheet reasonably user-friendly. Prior knowledge turns-out to be extremely important, especially for the more challenging methods, which give a depth profile.

Comments from Surface Analysis Forum members at the Bristol meeting in January will help us refine the spreadsheet, to make it easy to apply to the widest possible range of typical samples. The July '98 Surface Analysis Forum meeting at NPL will include a "hands-on" computer-based workshop, focussing on how to apply the quantification methods available within the spreadsheet to typical sets of measured spectra.

## "Recent Advances in Scanning Probe Microscopy"

Dr. J Leckenby, TopoMetrix UK.  
[topometrix.uk@dial.pipex.com](mailto:topometrix.uk@dial.pipex.com)

Due to Dr. Readings unavailability, Dr. Leckenby gave a presentation on both the general use of AFM and the use of the CASM technique.

He reviewed the various modes of analysis such as:

- Contact
- Oscillating Cantilever
- Profile Mode

Dr. Leckanby then described in detail several examples of AFM studies on in-situ and ex-situ experiments such as the growth of oxide films on aluminium alloys, the corrosion of Cu and Fe, and the solvent etching of polymers. Further details of these particular examples can be found on the TopoMetrix website <http://www.topometrix.com/>

Two of examples, which Dr. Leckanby gave, were of the most recent advances in the use of AFM. One was the Layered Imaging experiment, which map surface compliance and



the other was Scanning Thermal Microscopy.

### 1) Layered Imaging

In Layered Imaging, the user records the cantilever deflection through a partial or entire force distance curve for each pixel in an image. The actions are described in Figure 11 below.

- AB-Probe not in contact but approaching the sample, no attractive or repulsive force,
- BE-"Jump to Contact", due to attractive pull on cantilever
- CD-Upward motion due to sample deforming in response to cantilever, slope of curve indicates hardness.
- DE-Reverse of CD, and if CD' DE then indicates difference in elastic or plastic deformation.
- EF-motion of cantilever from surface to neutral deflection point, F=total adhesive force between probe and sample.

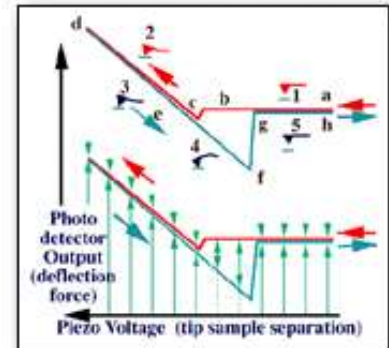


Figure 11. Force Distance Curve for SPM in Pulse Force Mode

An example of this type of experiment is shown below (*figure 12*), where recessed gum on a surface was examined using the SPM. The initial cantilever force was 0.14nN, then the tip was "pulled" away approximately 265nm from the surface.

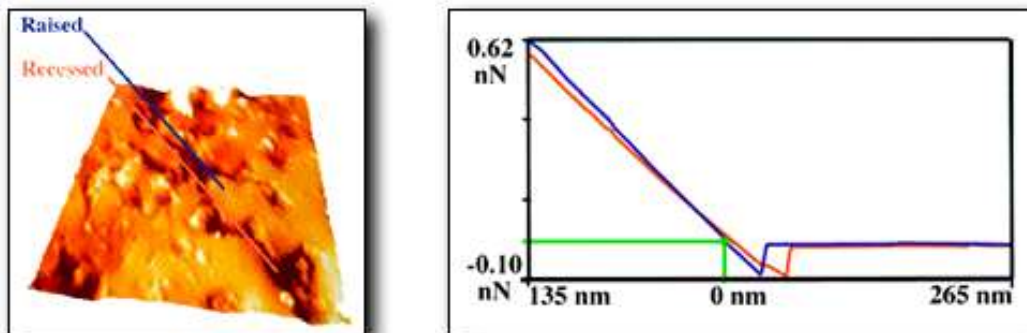


Figure 12 SPM Compression Experiment

### 2) Scanning Thermal Microscopy (SThM)

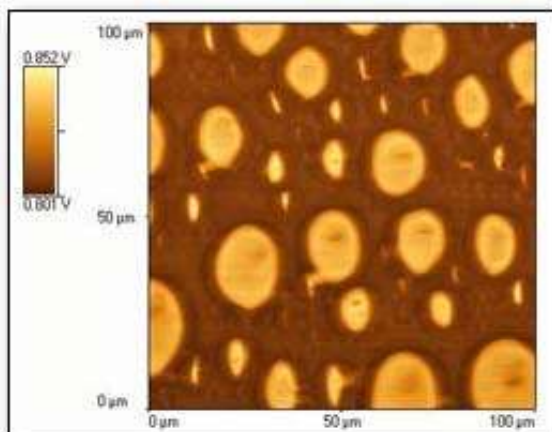


Figure 13. Polymer Blend at 40°C in the SPM


The image shows a polymer blend run at 40C in the SPM. Showing the two immiscible phases (PVC & PB). When the sample temperature is raised the two phases interact and merge. This experiment can be monitored in the SPM and the changes in dimension monitored as the process takes place. It is also possible to use the system to perform local DMA measurements on the specimens with a spatial resolution of around 200nm. This shows that SPM now yields chemical information at a very high spatial resolution, something only surface specific techniques have only really been good at until recently (and possibly TEM at

a push).



## Acknowledgements


The Surface Analysis Forum committee would like to thank Kratos, TopoMetrix and VG, for allowing data from their Websites to be included in the meeting report. All three Websites give many more examples of the latest instrumentation and there application.



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