Institution:
The University of Manchester

Unit of Assessment:
UoA08 Chemistry

Title of case study:
Development and exploitation of a buckminsterfullerene, C_{60}^+ based primary ion beam system for secondary ion mass spectrometry (SIMS)

1. Summary of the impact

Pioneering research at the University of Manchester developed a primary ion beam system based on buckminsterfullerene C_{60}^+ for secondary ion mass spectrometry (SIMS) that has revolutionized the field by providing unprecedented insight into the 3D depth profiling of organic materials, and spawned the development of second-generation polyatomic sources. A commercial C_{60}^+ ion beam has been developed in collaboration with Ionoptika Ltd that has lead to: the sale of 70 units with value greater than £2m; the development of a new spectrometer with sales of £2.5m; the creation of five employment positions. Technology has been transferred to a Japanese instrument manufacturer contributing to £ tens of millions sales.

2. Underpinning research

The key Manchester researchers were

- Professor John Vickerman (Professor in Surface Chemistry 1970-to date)
- Dr Nicholas Lockyer (PDRA 1996-2000, Lecturer in Physical Chemistry 2000-2008, Senior Lecturer 2008 to date)
- Dr Daniel Weibel (PDRA 2000-2002)
- Dr Stephen Wong (PhD student 1997-2002)

SIMS is a very powerful tool for accurately analysing the chemical make-up of a solid material in order to build up a three-dimensional chemical map. The principle of the technique is to bombard the surface with a beam of ions (the primary ion beam) and then analyse the emitted particles (in the form of 'secondary ions') that is ejected from the sample, using mass spectrometry.
Previously, for in-depth or 3D analysis, SIMS had been limited to the analysis of inorganic materials due to the aggressive nature of the primary ion beam employed. Traditional primary ion beams based on Ar^+, Ga^+, Cs^+ and more recently Au_n^+ and Bi_n^+ cause significant damage to the underlying surface of the material, which restricted the amount of meaningful information that could be obtained to less than 1% of the sample surface.

Fundamental research in the late 1980's suggested that cluster molecules may serve as a more effective primary ion beam system than the simple atomic ions in use at the time. Research by the Vickerman group led to the development of a prototype C_{60}^+ primary ion beam system for SIMS . The C_{60}^+ primary ion beam is generated by ionising C_{60} molecules with a stream of electrons. The resultant positively charged C_{60}^+ particles are accelerated to collide with the surface of the sample. Through the first application of C_{60}^+ bombardment for practical SIMS analysis we demonstrated a ~1000 fold increase in secondary ion yields of 'molecular' ions enabling high sensitivity surface analysis [1]. This pioneering development yields sub-micron spatial resolution for examination of organic materials and systems in life sciences [2-5]. Moreover, a substantial reduction in bombardment-induced damage of the sample permitted up to 100% of the sample to be analysed providing unprecedented depth profiling of successive layers and 3D chemical imaging of organic materials [2,3] including the first 3D molecular SIMS analysis of a single biological cell [4]. Beyond SIMS, the rather gentle molecular erosion under C_{60} bombardment allows other 'surface analysis' methods including X-ray Photoelectron spectroscopy (XPS) to probe sub-surface chemistry.

3. References to the research

In 2004 JCV was awarded the Rivière Prize of the UK Surface Analysis Forum , in 2009 the Royal Society of Chemistry Theophilus Redwood Award ' and in 2012 JCV the Médaille Chevenard by the French Society for Metals and Materials for the contributions to the SIMS field including the work described in references 1-6 below. This research has been published in the topmost journals within the field of analytical chemistry and have each been highly cited. JCV and NPL have given between them 27 invited conference talks since the introduction of the C_{60} source in 2003.

Key Publications

1. D. Weibel, S. Wong, N. Lockyer, P. Blenkinsopp, R. Hill, J.C. Vickerman, A C-60 primary ion beam system for time of flight secondary ion mass spectrometry: Its development and secondary ion yield characteristics, *Analytical Chemistry* 75 (2003) 1754-1764. – 350 citations. DOI: 10.1021/ac026338o.
2. E.A. Jones, N.P. Lockyer, J.C. Vickerman, Mass spectral analysis and imaging of tissue by ToF-SIMS - The role of buckminsterfullerene, C-60(+), primary ions, *International Journal of Mass Spectrometry* 260 (2007) 146-157. - 68 citations. DOI: 10.1016/j.ijms.2006.09.015.
3. E.A. Jones, N.P. Lockyer, J.C. Vickerman, Depth profiling brain tissue sections with a 40 keV C-60(+) primary ion beam, *Analytical Chemistry* 80 (2008) 2125-2132. – 53 citations. DOI: 10.1021/ac702127q.

Other relevant Publications

4. J.S. Fletcher, N.P. Lockyer, S. Vaidyanathan, J.C. Vickerman, TOF-SIMS 3D biomolecular imaging of Xenopus laevis oocytes using buckminsterfullerene (C-60) primary ions, *Analytical Chemistry* 79 (2007) 2199-2206. 148 citations. DOI: 10.1021/ac061370u.
5. J.S. Fletcher, S. Rabbani, A. Henderson, P. Blenkinsopp, S.P. Thompson, N.P. Lockyer, J.C. Vickerman, A New Dynamic in Mass Spectral Imaging of Single Biological Cells, *Analytical Chemistry* 80 (2008) 9058-9064. – 86 citations. DOI: 10.1021/ac8015278.

Note: citation numbers taken from Web of Science (20/9/13).

4. Details of the impact

Context

Traditionally SIMS was limited primarily to the analysis of inorganic materials due to the aggressive nature of the primary ion beam employed, which caused significant damage to the underlying surface of the material and restricted the amount of meaningful information that could be obtained to less than 1% of the sample surface. In addition the low yield of diagnostic secondary ions limited the spatial resolution available in SIMS imaging of molecular materials

Pathways to impact

In 1998 Professor Vickerman at the University of Manchester secured 3-years EPSRC funding (£190k,) to develop a primary ion beam based on buckminsterfullerene C_{60}^+. Between 2000-2003, in collaboration with Ionoptika a commercial C_{60}^+ ion beam system was developed that is protected by 3 patents. The C_{60}^+ ion beam system has both enabled the development of the next generation of secondary ion mass spectrometers and Ionoptika to establish itself as the world leading manufacturer and supplier of commercial C_{60}^+ ion beam systems.

In addition, further funding from RCUK and Ionoptika Ltd was secured to evaluate the capabilities

of the C_{60}^+ ion beam and more recently to develop a high-resolution time-of-flight SIMS instrument that fully exploits the unique capabilities of C_{60} for the study of biological and similarly complex chemical systems. The C_{60}^+ primary ion beam technology experienced immediate and rapid growth from a specialist academic research interest to influence the whole direction of SIMS and XPS analysis and establish a whole new field of organic materials depth profiling in life-sciences and materials science. Applications for chemical imaging of tissues and in disease research have brought intense interest from the medical community, according to the Director of the National ESCA and Surface Analysis Centre for Biomedical Problems in the USA [A]. Such was the paradigm shift in the research field that within 5 years of our introduction of the C_{60} source almost every SIMS lab in the world was seeking to follow our lead [B].

Impact

Commercial C_{60}^+ primary ion beam systems for SIMS that were developed at Manchester in collaboration with Ionoptika have led to the sale of ~70 C_{60}^+ ion beam units during 2008-2013 with revenue >£2m that created 5 employment positions [D]. Furthermore, the new ion beam technology has been incorporated into a completely new type of Secondary Ion Mass Spectrometer that fully exploits the capability of the C_{60}^+ ion beam system. In 2012 two new C_{60}^+ SIMS instruments were sold to the US and Sweden with associated revenues of £2.5m [D]

Additionally, technology transfer to Ulvac-Phi inc, a Japanese manufacturer of XPS and SIMS instrumentation also included the C_{60}^+ion beams in their systems at an early stage, giving them an initial competitive advantage in the organic surface analysis market and contributing towards instrument sales of several £10m's of instrument sales [C]. C_{60}^+ bombardment resulted in new, enhanced analysis protocols adopted across many sectors including the semiconductor industry, chemical industry, biotechnology industries, automobile companies, and drug companies, in addition to governmental and academic research labs. The CEO of Omicron (formerly from Ulvac-Phi) is of the opinion that all of these organisations were able to use cluster beam analysis to develop new products that could be life-changing for many people. (D). Subsequently all other manufacturers of SIMS instruments for molecular analysis have adopted C_{60}^+ ion beams in their systems.

The breadth of impact is illustrated by the diverse range of important application areas including tissue and cell imaging, atmospheric sciences, drug delivery, anti-bacterial coatings, polymer composites, biomaterials, microelectronic fabrication, organic electronics and nanoparticles, according to a Fellow at the National Physical Laboratory [E]

"The pioneering work at Manchester has revolutionised the imaging capability, especially in 3D, for SIMS and XPS. It has had a diverse impact on many industrial sectors as well as fundamental scientific understanding and has led to an important boost in the UK instrument sector." [E]

As a direct result of the success of C_{60}^+ ion beams for SIMS analysis a number of alternative second-generation polyatomic ion beams are under development including Ar_n^+ and $(H_2O)_n^+$ (where $10<n<5000$). We are currently developing this technology with Ionoptika Ltd.

5. Sources to corroborate the impact

A. Director, National ESCA and Surface Analysis Center for Biomedical Problems, University of Washington. Evidence on the benefits of the C_{60}^+ion beam system in organic and bio-organic research.

B. Evan Pugh Professor of Chemistry, Penn State University. Evidence as to the impact of the C_{60}^+ ion beam system on the direction of SIMS research and application.

C. Managing Director, Ionoptika Ltd. Information on the commercial benefits of the instrument - the number and value of ion beams manufactured and supplied.

D. CEO, Omicron, Japan. Evidence of the impact of the development in the Japanese analytical instrument market.

E. Director, National Centre of Excellence in Mass Spectrometry Imaging, National Physical Laboratory, Teddington UK. Evidence of wider impact of C_{60}^{+}ion beam.