Institution: University of Glasgow

Unit of Assessment: B9: Physics

Title of case study: DualEELS™: A key advance in electron spectroscopy in the electron microscope

1. Summary of the impact

DualEELS™ is a recent advance in Electron Energy Loss Spectroscopy (EELS) made possible by a successful collaboration between the University of Glasgow and Gatan, the world leader in electron spectroscopy systems for electron microscopy. The resulting Gatan GIF QUANTUM® and the ENFINIUM® electron microscope products, incorporating the novel DualEELS™ concept pioneered in Glasgow, have been a commercial success. Between the launch in 2009 and the end of 2011, 145 systems have been delivered to universities, research institutes and industry at a total market value of over US$7.5M. The market penetration of the DualEELS™ technique has been very high. In 2012, DualEELS™ units were delivered with over 70% of all GIF/EELS systems sold. These systems are used routinely for R&D, quality control and failure analysis in firms such as AMD, Intel and Samsung, and for development of the advanced materials and devices key to modern society in a wide range of industrial sectors.

2. Underpinning research

DualEELS™ is a recent advance in Electron Energy Loss Spectroscopy (EELS) in the Scanning Transmission Electron Microscope (STEM) made possible by a successful collaboration between Gatan and the University of Glasgow. In a technique known as spectrum imaging, an electron probe is scanned over an ultra-thin (<100nm) specimen with the signals of interest (e.g. an EELS spectrum, an x-ray spectrum, scattered electron intensities) recorded at each pixel. The information obtained from EELS includes local thickness, dielectric function, composition, local atomic environment, absolute numbers of atoms/area and absolute numbers of atoms/volume. Since the electron probe can be smaller than the interatomic spacing, such information can be extracted and mapped down to atomic resolution in a large range of scientifically and technologically important areas including semiconductors, data storage and catalysis.

In the energy loss range required to provide information on all elements (0 to 3kV), the dynamic range of the signal is very high ($\sim10^5$). Prior to DualEELS™, magnetic deflection coils were used to provide the shutter to control the number of electrons reaching the spectrometer, but their slow response time (msecs) limited the minimum exposure. Obtaining the entire spectrum required at least two scans with different optical conditions. This was not only time-consuming but presented serious disadvantages in maintaining the spatial registration of the data at the atomic scale.

Prof A J Craven (Lecturer, 1978-89; Senior Lecturer, 1989-92; Reader, 1992-98; Professor of Physics 1998-2012) recognised that a fast electrostatic shutter could control the exposure in a way that allowed the entire spectrum to be recorded without changing the optical conditions. With Dr W A P Nicholson (Research Technologist 1979-2005) and Dr J A Wilson (Postdoctoral Research Assistant [PDRA] 1999-2007), a prototype electrostatic shutter was developed. The results were reported in a 2002 paper [1], demonstrating the shutter had a time constant of 10nsec, allowing the system to settle to its full energy resolution in under 100nsec. The paper also showed that data could be recorded over the whole energy range of interest and proposed the concept of recording the entire EELS spectrum at each pixel in the spectrum image, the concept at the core of what has since become known as DualEELS™.

By 2005, there was significant interest among the scientific community in Glasgow's new concept. In the autumn of 2005, Gatan decided to undertake a major development of their spectrometer system and wished to incorporate the DualEELS™ concept. They collaborated with Glasgow University to develop a proof-of-principle DualEELS™ system to demonstrate the potential benefits for wider commercialisation and identify issues that needed to be addressed. The project capitalised on equipment already installed at the University of Glasgow and on the fast shutter developed by Prof Craven's research group. Gatan provided the software necessary to control the hardware and acquire and process the data.

The Glasgow team was led by Prof Craven and comprised Dr M MacKenzie (PDRA 2001-2008), Dr S McFadzean (Technician 1978-current), Dr Nicholson and Dr J Scott (PDRA 2001-2007). The results were published in 2008 [2]. The project demonstrated for the first time a system capable of recording a spectrum image which, at each pixel, gave the image signals, two EELS spectra (a low and a high energy loss range with very different signal levels) and an x-ray spectrum, while allowing all the existing features of the Gatan EELS system to remain available to the user. It demonstrated that the EELS spectrum could be accurately calibrated for energy, the multiple scattering removed, local thickness determined, signals from both low and high atomic elements recorded and the absolute number of atoms per area and volume extracted. It also identified an issue with the efficiency of the EELS acquisition which Gatan were subsequently able to overcome. This demonstration generated considerable interest in the potential market and resulted in the launch of the GIF QUANTUM® and ENFINIUM® systems. A GIF QUANTUM® forms part of the new Glasgow electron microscope system (obtained at a substantial discount) installed in 2012.

3. References to the research

[1] A J Craven, J Wilson and W A P Nicholson *A fast beam switch for controlling the intensity in electron energy loss spectroscopy*. Ultramicroscopy 92 165-180 (2002). doi: 10.1016/S0304-3991(02)00130-4 (The electrostatic shutter and DualEELS™ concept.) *

[2] J Scott, P J Thomas, M MacKenzie, S McFadzean, J Wilbrink, A J. Craven and W A P Nicholson *Near-simultaneous dual energy range EELS spectrum imaging* Ultramicroscopy 108 1586-1594 (2008) doi:10.1016/j.ultramic.2008.05.006 (The proof-of-principle DualEELS™ system and demonstration of the improved information extraction.) *

4. Details of the impact

The analysis and control of material properties down to the atomic scale is becoming increasingly important for a range of research and applications in both academia and industry. As a consequence, there is an increasing demand for laboratory techniques able to image materials and map their properties (e.g. composition and chemistry) down to atomic resolution. Aberration-corrected electron microscopy provides the atomic spatial resolution and information on structure, boundaries and defects, while EELS and x-ray spectroscopy provide information on the composition and chemistry in perfect spatial registration.

Gatan Inc. was established almost 50 years ago and is considered the world's leading supplier of analytical equipment and software for enhancing and extending the operation of electron microscopes. Gatan's products are designed to fit all major brands of transmission and scanning electron microscopes and to provide users with extended features ranging from specimen preparation to imaging and analysis. The company has extensive market penetration in industry and academia. Gatan supplies over 80% of all new EELS systems worldwide. In the general context of intermediate voltage (200/300kV) TEMs, Gatan analytical products are found on over 30% of all such instruments delivered in 2012.

Information obtained by DualEELS™ is crucial to the development of future materials and devices needed to provide the next generation of disruptive technologies that will allow the phenomenal improvement in performance seen in recent times e.g. as in Moore's Law in the computer field. The industries supplying computer components are key examples. The Si (O,N) gate dielectric layer in current Si-based MOSFETS used in applications such as computer CPUs has only ~5 Si atoms across it. The oxide layer in a spin tunnel junction used in the read head of a magnetic hard disc is only 5 to 10 atoms across. Hence development of new products and routine quality control and failure analysis for production of existing products in these multibillion dollar industries require techniques able to produce atomic scale information on the structure, composition and chemistry of the materials used. The importance of DualEELS™ in this field is demonstrated by a joint presentation by AMD and Gatan at the Electronic Device Failure Analysis (EDFA) Lonestar meeting in April 2013 entitled *"High-speed EELS Analysis of Semiconductor Devices"*. This presentation clearly demonstrates the major advantages provided by DualEELS™ in this area and explains its enthusiastic adoption by this sector.

Other sectors where materials analysis at the nanoscale is crucial and where DualEELS™ is being used include catalysis, ceramics and metals, among many others.

The main benefit of using EELS is the ability to obtain fully quantitative information about a wide range of material properties such as the local thickness, dielectric function, material bandgap, electromagnetic excitation modes of nanoparticles, relative composition, absolute number of atoms per area and per volume, the local chemistry and both the charge and magnetic state of ions. However, the ability to extract all this information is dependent on the acquisition of the whole energy loss range under the same experimental conditions to ensure accurate energy calibration and to allow correction for the effect of multiple inelastic events and for elastic scattering outside the spectrometer. DualEELS™ provides this capability for fast spectrum imaging. The fast shutter also makes operation of the whole microscope system much easier. For instance, the STEM imaging conditions can be set independently of the spectrometer conditions, which is crucial at atomic resolution, since any change in the optics requires the corrector to be re-tuned, which takes a very significant time.

In response to customer demand, in 2009 Gatan launched its GIF QUANTUM® electron spectroscopy system, the first instrument on the market to incorporate the Glasgow DualEELS™ concept and electrostatic shutter along with a range of other new innovative features from Gatan. Following the GIF QUANTUM® success, Gatan launched the ENFINIUM® system in 2011 to meet the demands of another, more specialised segment of the electron microscopy market. DualEELS™ in these systems can record over 1000 spectra/sec and so 1000 x 1000 pixel spectrum images can be recorded in as little as 20 minutes and smaller ones correspondingly faster. Thus data from regions containing key features such as precipitates, interfaces, boundaries or defects can be recorded down to atomic resolution in realistic times. As an example, such information is of particular relevance in the development of novel materials such as multiferroic oxides which couple electric and magnetic ordering with potential for sensors, actuators and data storage.

The GIF QUANTUM® and ENFINIUM® are extremely successful product lines for Gatan, resulting in an increase in the number of installation/maintenance engineers of ~10% worldwide and a similar increase in support staff in production. The list price for the GIF QUANTUM® is in the range US$510k - 820k depending on the model. Gatan sold over 65 GIF QUANTUM® systems to customers worldwide in 2010 and over 80 in 2011 and the numbers continue to rise. More than 70% of systems requested by customers in 2012 have the DualEELS™ options. In terms of sector breakdown, roughly 50% of systems are purchased by universities, 25% by research institutes and 25% by industry. The biggest segments of the industrial market are semiconductors (AMD, Intel, Samsung), data storage (WD, IBM, TDK) and catalysis (Michelin, Corning). Although the direct economic impact of Glasgow's research to Gatan is easily quantifiable, it is much harder to map how this has spread to the broader user community and how the technique has enabled not only new scientific discoveries but also improved processes and products in different industrial sectors.

While major companies in sectors such as semiconductors, data storage and catalysis can justify the purchase of DualEELS™ systems, many others require the information and analysis possibilities they offer. We give two examples of companies who have extended their capabilities using Glasgow's DualEELS™ system.

The zirconium alloy, Zircaloy, is of huge significance to the safe containment of highly radioactive nuclear fuels in power generation systems. Understanding the corrosion process at the nanoscale in Zircaloy is key input to predictive modelling of the safe operating lifespan of the current generation of nuclear reactors. In collaboration with Dr Gass of AMEC, we have used the DualEELS™ system in Glasgow to give previously unobtainable information on the reaction layers formed in the complex oxidation process by which Zircaloy corrodes in a pressurised water reactor. Using such information to validate predictive models of safe operating lifespan is a crucial step in achieving the aim of energy company, EDF, to extend the lifetime of the Sizewell B nuclear reactor by 20 years.

The second example is the study of precipitation in high manganese steels, in collaboration with ThyssenKrupp Steel Europe AG. Using our DualEELS™ system, we have developed a new technique that allows us to gain key information on the precipitate when in situ in the matrix. This not only gives information on the structure, composition and chemistry of nanometre sized precipitates but also their size in three dimensions, allowing their relationship to the surrounding steel matrix and its defects to be studied. Such information is essential to allow the development and validation of accurate models relating processing to nanostructure so that suitable precipitate distributions for optimal mechanical properties are achieved. This will play a key part in the development of high strength steels for the automotive industry leading to more fuel-efficient transport.

5. Sources to corroborate the impact

Product Manager – Analytical Instruments, Gatan Inc (can corroborate all claims related to the impact of research on the financial performance of Gatan, their market and customers).

Website: http://www.gatan.com/products/analytical_tem/ (DualEELS™ system and fast shutter)

Testimonial from Senior Consultant, AMEC, Clean Energy Europe (evidencing the importance of DualEELS in the study of Zircaloy) (available from HEI)

Testimonial from Research and Development, Modeling and Simulation Group, ThyssenKrupp Steel Europe AG (evidencing the importance of DualEELS in improving the performance of steel for the automotive industry) (available from HEI)