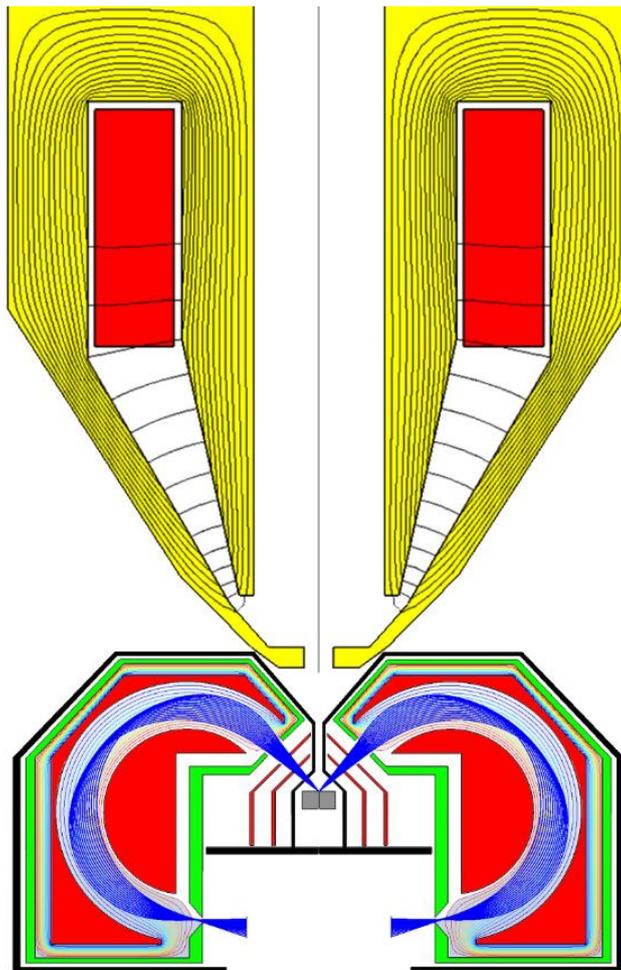


**International Workshop on
Secondary Electron Spectromicroscopy
and its Material Science Applications
Singapore, 6th -7th June 2019**



International Workshop on Secondary Electron Spectromicroscopy and its Material Science Applications

Venue: Eureka I & II, Level 6, Block E6,
5 Engineering Drive 1, Singapore 117608.
Electrical and Computer Engineering, NUS

Date: 6 June 2019 | Time: 9 am - 6 pm
7 June 2019 | Time: 9 am - 6 pm

Edited by

Prof. Anjam Khursheed,
Department of Electrical and Computer Engineering,
National University of Singapore

E6NanoFab



Organizing Committee

Prof. Anjam Khursheed,
Dr. Amit Banerjee,
Han Weiding,
Department of Electrical and
Computer Engineering,
National University of Singapore

HITACHI
Inspire the Next

Workshop welcome and introduction

It gives me great pleasure to welcome you to this International Workshop on **Secondary Electron Energy Spectroscopy and its Material Science Applications**. The workshop is in many ways, the first of its kind. Secondary Electron Energy Spectroscopy in the Scanning Electron Microscope (SEM) is a subject very much in its infancy, despite it having been proposed over 50 years ago in a seminal paper by Wells and Bremer [1]. Wells and Bremer illustrated the possible benefits of quantifying voltage, dopant and material contrast effects inside a SEM by using a SE energy spectrometer attachment. They used a modified Cylindrical Mirror Analyser (CMA) attachment, which although far from ideal, illustrated how much more information could be obtained through capturing the SE energy spectrum per pixel, as opposed to acquiring the usual SE detector image. That paper inspired the development of voltage contrast spectrometers, which led to the creation of commercial instruments known as Electron Beam Testers in the late 1980s. For over two decades, engineers and applied physicists collaborated together to perfect the technique of using SEMs to measure voltage signal waveforms propagating on the surface of Integrated Circuits.

From the mid-1990s, SEMs were proposed for mapping dopant concentration variations in semiconductor samples. However, unlike the prior experience aimed at quantifying the voltage contrast effect, quantifying the dopant contrast effect proved to be much more problematic.

SEM dopant contrast research has so far been limited to probing idealised test *pn* junction specimens, and has typically involved making step dopant concentration measurements. An important element missing in over two decades of research dedicated to this topic has been its lack of instrument development. Not only has there been no reference to the original Wells and Bremer paper, but the fundamental question of whether a SE energy spectrometer attachment in the SEM is needed or not has not been critically discussed. One reason for this comes from the fact that SEM manufacturers have as yet, not made SE electron energy spectrometer accessories available, and almost all attempts to quantify dopant contrast in the SEM have so far relied on the use of SE detector systems as supplied by the SEM manufacturer. Very few researchers have attempted to build and test their own SE energy spectrometer attachments inside a SEM. The question of what can or cannot be achieved by using a SE energy spectrometer attachment inside a SEM is still a question that has, for the most part, been unanswered. Another problem has been created by overspecialised research communities not being aware of each other's research, which in this case involve the communities of SEM instrument engineers/applied physicists, SEM manufacturers, and material scientists.

The aim of this workshop is to bring together some material scientists, SEM instrument engineers/applied physicists, and a SEM manufacturer in order to discuss the question of what can be achieved by using an electron energy spectrometer in the SEM. The aim is to bridge overspecialised disciplinary gaps within our respective scientific communities that have so far prevented this question from being critically examined. It is a small and modest start, but hopefully, it will be one that will inspire some useful developments for material science research in the future.

I would like to thank Hitachi Hitachi High-Tech in Singapore for sponsoring all the food catering and for hosting the Workshop Dinner, as well as participating in the scientific programme. I would also like to thank my local team of researchers for assisting me organise and run this Workshop. To my international guests, I wish you a very productive, enjoyable and pleasant stay in Singapore.

Anjam Khursheed
Singapore June 6th 2019.

[1] Wells, O. C. & Bremer, C. G. Voltage measurement in the scanning electron microscope. *J. Phys. E.* **1**, 302 (1968).

Schedule for 6th June			
Time	Agenda	Speaker	Organization
9.15 am	Opening Address	Prof Anjam Khursheed	Cluster Lead, E6NanoFab L3 Metrology Lab
9.30 am	Welcome Address	Prof Aaron Thean	Director, E6NanoFab
9.45 am	SE Energy Spectrometer Attachments in the SEM and Semiconductor Characterization	Prof Anjam Khursheed	Cluster Lead, E6NanoFab L3 Metrology Lab
10.30 am	Material Analysis Using SE Energy Spectroscopy	Dr W Han	NUS
11:15 am	Tea Break		
11.30 am	Secondary Electron Spectroscopy For Imaging Semiconductor Materials Using a Fountain Detector	Dr Toshihide Agemura	Hitachi High-Technologies Japan
12:15 PM	Lunch Break		
1:45 PM	Confirmed Applications and limitation of SE Spectroscopy in Material Science	Prof Cornelia Rodenburg	University of Sheffield UK
2.30 pm	Energy Selective Electron Detection and Analysis in SEM for Determination of Dopant Concentration	Dr Filip Mika	ISI Czech Republic
3:15 pm	Tea Break		
3:30 pm	Secondary Electron Energy Filtered Imaging in a FE-SEM for Semiconductors	Mr Y. Yamazawa	Hitachi High-Technologies Japan
4:15 pm	Secondary Electron Spectroscopy with an ELSTAR Column: Current Challenges and Future Potential	Ms N. Stehling	University of Sheffield UK
7.30 pm	Workshop Dinner		

Schedule for 7th June			
Time	Agenda	Speaker	Organization
9.15 am	SIMS based Correlative Microscopy for Materials Science Applications	Prof H. Hoang	LIST, Luxembourg
10.00 am	A High Resolving Mass Spectrograph for an Investigation of Secondary Ions Formed at the Target of an Electron Microscope	Prof H. Wollnik	New Mexico State University, NM, USA
10:45 am	Tea Break		
11.00 am	Time Resolved SEM Characterization of Photoinduced Surface Voltages by Secondary Electron Contrast	Prof A. Tagliaferri	Politecnico di Milano, Italy
11.45 am	The Design of Pre-retardation Column Optics to Improve the Energy Resolution of Energy Analysers	Prof T. Zouros	University of Crete, Greece
12:30 PM	Lunch Break		
01.30 pm	Transmission EELS spectrometer attachments for SEMs	Dr Luo Tao	NUS
2:15 PM	Future collaboration/funding and book project		
03:15 am	Tea Break		
3:30 pm	Workshop sessions		
	Toroidal SE energy analyser attachment in a dual beam FIB-SEM		
	SE energy spectroscopy on the Hitachi Regulas SEM		
	E6 NanoFab tour		
6:00 pm	End of the Workshop		

Biography of Speakers

Anjam Khursheed

Professor Anjam Khursheed is Director of the Engineering Science Programme at the National University of Singapore (NUS), and also a member of staff in the Electrical and Computer Engineering Department. His area of research lies in the subject of developing new kinds of focused electron/ion beam microscopes, energy spectrometers and sources. Anjam Khursheed obtained his BSC in Electronics and Physics from the University of Edinburgh, Scotland, in 1979, and went on to do a PHD there in the subject of Electron Energy Spectrometers for the Scanning Electron Microscope. From 1984 to 1987, he worked as an applied physicist at the High Energy Particle Physics Accelerator organization of CERN in Geneva, Switzerland (1984-7), where he worked on the design of high frequency electromagnetic cavities. He also worked on the subject of atomic clocks at the Politecnico di Torino, Italy (1992-1994). In 1995, Anjam Khursheed went to work at the National University of Singapore.



Han Weiding

Han Weiding is a Final-Year PhD student in the Department of Electrical & Computer Engineering, National University of Singapore, under the guidance of Assoc. Prof. Anjam Khursheed. His research interest involves Secondary Electron spectroscopy using an electron energy analyzer attachment in a Scanning Electron Microscope, and its applications in dopant and material contrast.



Toshihide Agemura

Dr Agemura joined the Instruments Division of Hitachi Limited (currently Hitachi High-Technologies Corporation (HHT)) in 1997 after his graduation from Nagoya University with a Master of Engineering on radiation detection measurement. He was a visiting research at the University of Tennessee studying under Dr David C. Joy from 2001 to 2003. He has experience in designing almost all units on a Fe-SEM column, including the source(gun) with UHV technology, electrostatic/magnetic lenses, detectors and so forth in his career with HHT. He also led new projects and managed the R&D group for FE-SEM and FIB-SEM. He engaged in a Doctoral course at the National Institute for Materials and Science (NIMS), as a partner of graduate school in the University of Tsukuba from 2015 and received his PHD in material science from this university in March 2018. He is currently a Diretive Manager of the electron microscope design department in HHT.



Cornelia Rodenburg

Cornelia Rodenburg (née Schönjahn) is Senior Lecturer in Materials Science and Engineering (MSE) and currently holds an Early Career EPSRC Fellowship during which her group has pioneered secondary hyperspectral imaging (SEHI). Prior to this she was Lecturer and held a Royal Society Dorothy Hodgkin Fellowship at University of Sheffield. Her first post-doctoral post was at the University of Cambridge in the Department of Materials Science & Metallurgy.



Her work has always been centered on developing a fundamental understanding of materials and systems often requiring innovative electron microscopy in combination with modeling. She has worked on semiconductors, steel, glass and ceramic coatings. Her current main interest is Secondary Electron Hyperspectral Imaging, applied to polymers or complex organic/inorganic materials in order to increase materials reliability or extract key information required for the reverse engineering of natural materials such as spider silk.

Filip Mika

Filip Mika is a senior researcher and Head of Microscopy and Microanalysis group at the Institute of Scientific Instruments of the CAS. He is a principal investigator of the team projects, management of laboratories, maintenance and operation of scanning electron microscopes. Institute of Scientific Instruments The Czech Academy of Sciences. His expertise is in the methodology of the scanning electron microscopy, in particular as regards imaging of insulators, imaging at low energies of electrons, the dopant contrast in semiconductors, mechanism of electron signal detection and generation (MC simulations). He works with MAGELLAN 400, TESCAN Vega 5130MM and JEOL 6700 SEM with EDX analyzer, Olympus confocal laser scanning microscope. Imaging of insulators with a method of non-charging scanning electron microscopy, imaging of materials at low energies of impacting electrons, design and construction of angular sensitive detector for studying of semiconductor contrast.



Yu Yamazawa

Mr Yamazawa joined Hitachi High-Technologies Cooperation (HHT) in 2008 after he graduated from Tokyo Institute of Technology with a Master of Engineering. The theme for his Master's was in the "Diffusion behavior of radiative materials in nuclear reactors". He was a visiting research at Osaka University under Associate professor Nishi from 2010 to 2011. He studied aberration correction for beam tilt in SEMs. Afterwards he returned to Hitachi where he went on to design electron optics of FE-SEMs and EELS. He is currently an engineer in the electron microscope design department in HHT.



Nicola Stehling

Nicola is a 3rd year PhD student in the Department of Materials Science and Engineering in Sheffield, UK. She completed a Master in Chemistry at the University of York, UK with a focus on chemical analysis and spectroscopy. She entered the world of materials research in her year in industry, where she developed and characterized polymer resins for the aerospace industry. At Sheffield, Nicola is applying and optimizing advanced SEM techniques including secondary electron energy spectroscopy to access compositional information of nanostructured materials, such as natural polymers.



Hermann Wollnik

Hermann Wollnik 1954-1964 studied at the Technical University Munich, and went to become a Professor at the University of Giessen, Germany between 1969-2001. Since 2002, he has been an Adjunct Professor at New Mexico State University, USA, and since, 2003, a Visiting Professor at KEK/RIKEN in Tokyo. He has over 300 articles in reviewed scientific journals and over 10,000 citations of published books and articles. He is one of the world's leading authorities in the subject of mass spectrometer design.



Hung Q. Hoang

Dr. Hung Q. Hoang is a researcher in the Advanced Instrumentation for Ion Nano-Analytics group at Luxembourg Institute of Science and Technology. His area of research lies in charged particle optics instrumentation and applications. He currently works on the energy/mass spectrometer design and development for SIMS based correlative microscopy for nano-analytics. He also carries out research on scientific instrumentation for field-portable and space applications. Hung Q. Hoang obtained his PhD in electrical engineering from the National University of Singapore in 2011. During his PhD, he worked on the development of miniature high-performance energy spectrometers for use in the scanning electron microscope for material and device inspection. From 2011 to 2013, he worked as a post-doc researcher at Luxembourg Institute of Science and Technology, where he worked on the design of a field portable mass spectrometer for hydrology applications. In 2013, Hung. Q Hoang became a permanent researcher at Luxembourg Institute of Science and Technology.



Alberto Tagliaferri

Alberto Tagliaferri is an Associate Professor in Department of Physics at the Politecnico di Milano. He graduated in Nuclear Engineering in 1996 and went on to be a visiting scientist for 10 years at ESRF synchrotron in Grenoble (FR). At the end of 2001 he took up a position as Researcher (Assistant Professor) at the Politecnico di Milano, Department of Physics, teaching Fundamental Physics. At present he carries at research on the development and application of ultrafast electron microscopy, joining the spatial resolution of electron microscopes with the temporal resolution of pulsed lasers. He leads a research team on the development of an original ultrafast scanning electron microscope, allowing the investigation of the dynamics of charge carriers at surface of materials and devices of interest in high speed electronics, sensors, light generation and solar energy harvesting.



Theo Zouros

Theo J.M. Zouros is a professor in Experimental Atomic and Molecular Physics in the Department of Physics, University of Crete, Heraklion, Greece. His research activity includes research in, the Physics of highly charged ions, Atomic collision physics with accelerators, Auger Electron spectroscopy of highly charged ions, Excitation and Ionization in ion-atom and electron-ion collisions, Charged particle optics and optimization of electron spectrometers and Photoionization of atoms using X-ray free electron laser beams.



Luo Tao

Mr. Luo Tao studied PhD in NUS from 2003 to 2009 in electron optics under guidance of A/Professor Anjam Khursheed. Mr. Luo has invented angle resolved back-scattered electron imaging technique for SEMs, and dynamic aberration correction technique for EELS spectrometers during his PhD studies. Mr. Luo worked for multiple international companies for semiconductor industry. Since 2015, Mr. Luo rejoined NUS in Khursheed group as a part time research fellow for researches in miniature electron columns.



Extended Abstracts

MAPPING MATERIAL SCIENCE PROPERTIES ON THE NANOSCALE BY SECONDARY ELECTRON ENERGY SPECTROMETERS IN THE SEM

A. Khursheed*, H. Weiding, and A. Banerjee

Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117583

*e-mail: eleka@nus.edu.sg

Over a period of around 20 years, approximately between 1970 to 1990, a wide variety of Secondary Electron (SE) energy spectrometer designs were integrated into the Scanning Electron Microscope (SEM) for the purpose of Integrated Circuit Electron Beam Testing Circuits [1,2]. These SE energy spectrometers enabled SEMs to quantitatively monitor changes in surface potential, and they were combined with different types of objective lenses, conventional magnetic ones, the retarding field type, and the magnetic immersion type. However, demand for Electron Beam Test equipment sharply fell after Integrated Circuits started to have ground cover planes, and now days, the use of SE energy spectrometers with SEMs is rare.

At present, SEM manufacturer's do not make SE energy spectrometer attachment accessories available, and it is up to individual researchers to make them for themselves. However, recent research shows that SE energy spectrometers inside SEMs can be used for a variety of different material science applications. Figure 1 shows a band-pass second-order electrostatic toroidal SE energy spectrometer attachment system for SEMs [3], and Fig. 2 presents experimental SE energy spectral signals captured from it on a test specimen having p -doped stripes in a n -doped silicon substrate, which was etched and then allowed to grow a 4 nm native oxide layer under controlled conditions. The results demonstrate how the SE energy spectral signal changes shape according the dopant regions and the presence of the native oxide layer. They point towards the development of a new possible method for mapping material science properties on the nano-scale in the SEM.

This talk will review different types of SE energy spectrometer designs, highlighting those that are most suitable to operate as SEM attachments, and will give examples of contrast mechanisms that can be quantified by them.

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- [1] J. T. L. Thong, *Electron Beam Testing Technology*, ch. 5, Plenum Press, 1993.
- [2] A. Khursheed, *Scanning Electron Microscope Optics and Spectrometers*, ch. 5, World Scientific, 2011.
- [3] A. Khursheed and H. Hoang, *Ultramicroscopy*, Vol. 109, (2008), pp104-110.

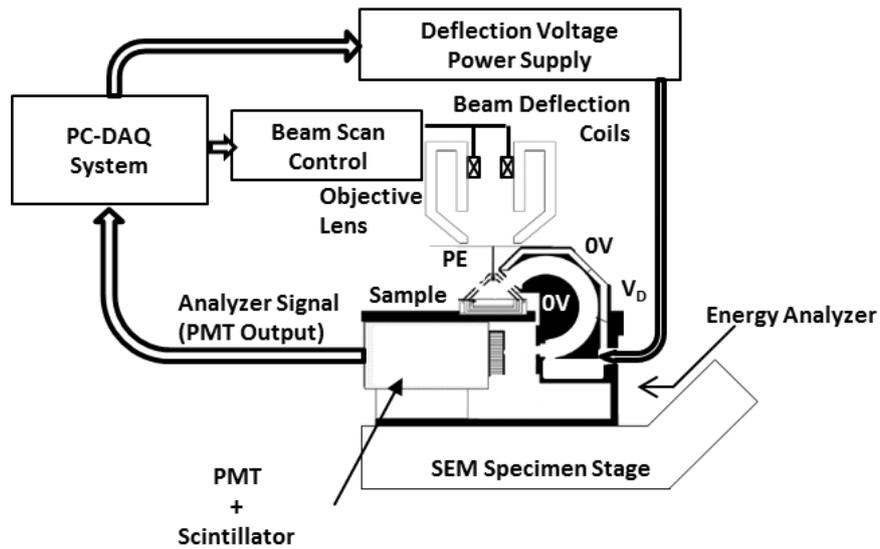


Figure 1: A second-order toroidal SE energy spectrometer inside a SEM

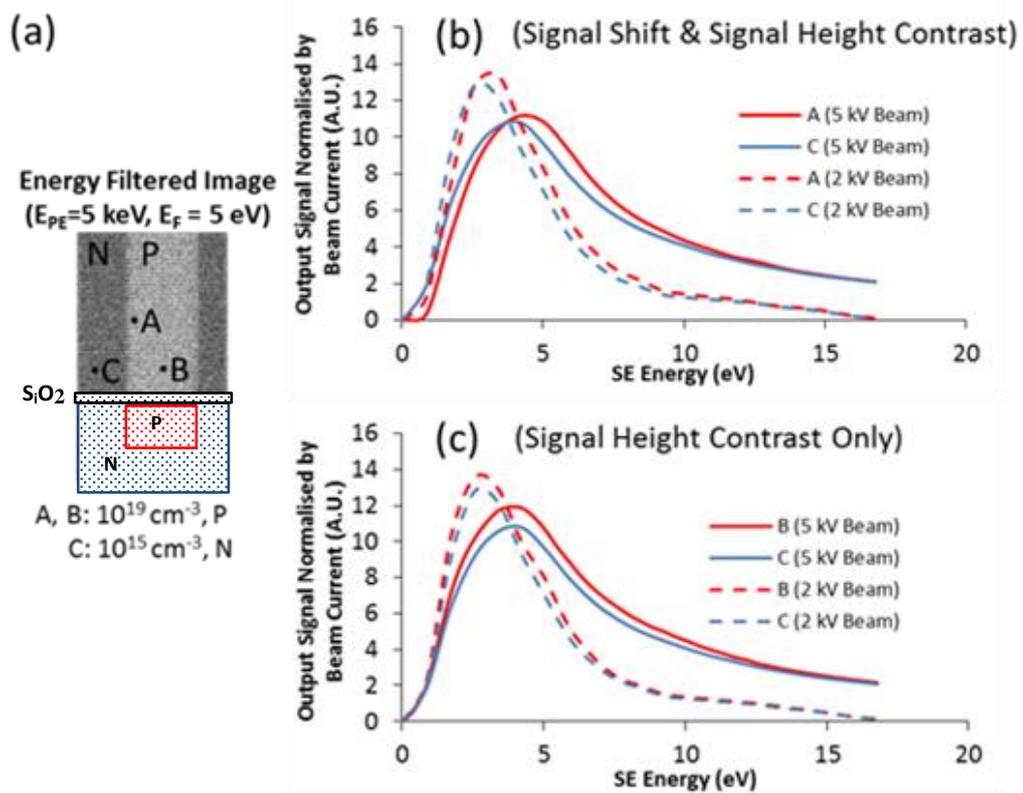


Figure 2: Experimental results on a *p*-doped stripe in a *n*-doped silicon substrate test specimen in the presence of a 4 nm native oxide layer

(a) SEM image (b) At the stripe edge (point A) (c) At the stripe centre (point B)

MATERIAL CONTRAST OF METALLIC SAMPLES WITH FULL-RANGE SCATTERED ELECTRON ENERGY SPECTROSCOPY IN THE SEM

H. Weiding*, A. Banerjee and A. Khursheed

Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117583

*e-mail: elehwe@nus.edu.sg

For decades, elemental surface information has been acquired by various electron energy spectroscopy methods such as Auger electron spectroscopy (AES) and X-Ray photoelectron spectroscopy (XPS) that utilize electrons emitted from a sample due to an electron/photon beam striking it. Their requirement for very high vacuum conditions make them unsuitable for use with the Scanning Electron Microscope (SEM). Backscattered electrons (BSE) are known to contain material information as well, where the backscattered coefficient [1,2] or Full Width at Half Maximum (FWHM) of the backscattered electron spectrum [3] have been correlated to specimen atomic number. Secondary electron energy (SE) spectra have up to now, been largely disregarded, except in areas such as topological, voltage and dopant contrast.

Full-range scattered electron energy spectra covering both the secondary electron and backscattered electron energy range can potentially provide a more complete material characterization tool. However, obtaining accurate spectra with minimal contamination requires the use of a spectrometer with high signal-to-noise characteristics. Figure 1 shows an experimental SE energy spectral signal $E.N(E)$ of a gold sample obtained by a band-pass second-order electrostatic toroidal SE energy spectrometer attachment system for SEMs [4] and is fitted with its corresponding theoretical Chung-Everhart distribution. It demonstrates how, with the right spectrometer design, the SE energy spectral signal obtained in a SEM can closely match its theoretical one, comparable to the kind of SE spectral signals obtained by ultra-high vacuum systems [5].

Figure 2 presents experimental full-range electron energy spectral signals $E.N(E)$ of different metals. It demonstrates how material contrast causes a relative change between SE and BSE peak heights and produces characteristic changes in signal shape. This talk will investigate the possibility of quantifying material contrast in the SEM by detecting and quantifying such changes.

References

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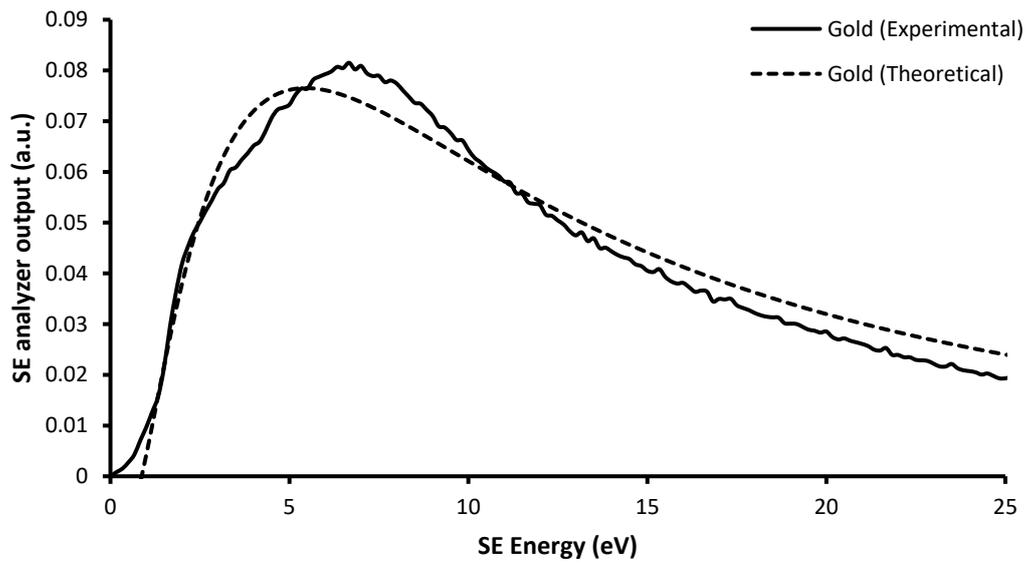


Figure 1: Experimental SE energy spectral signal inside a SEM and fitted theoretical spectrum of gold sample for a primary beam voltage of 2 kV.

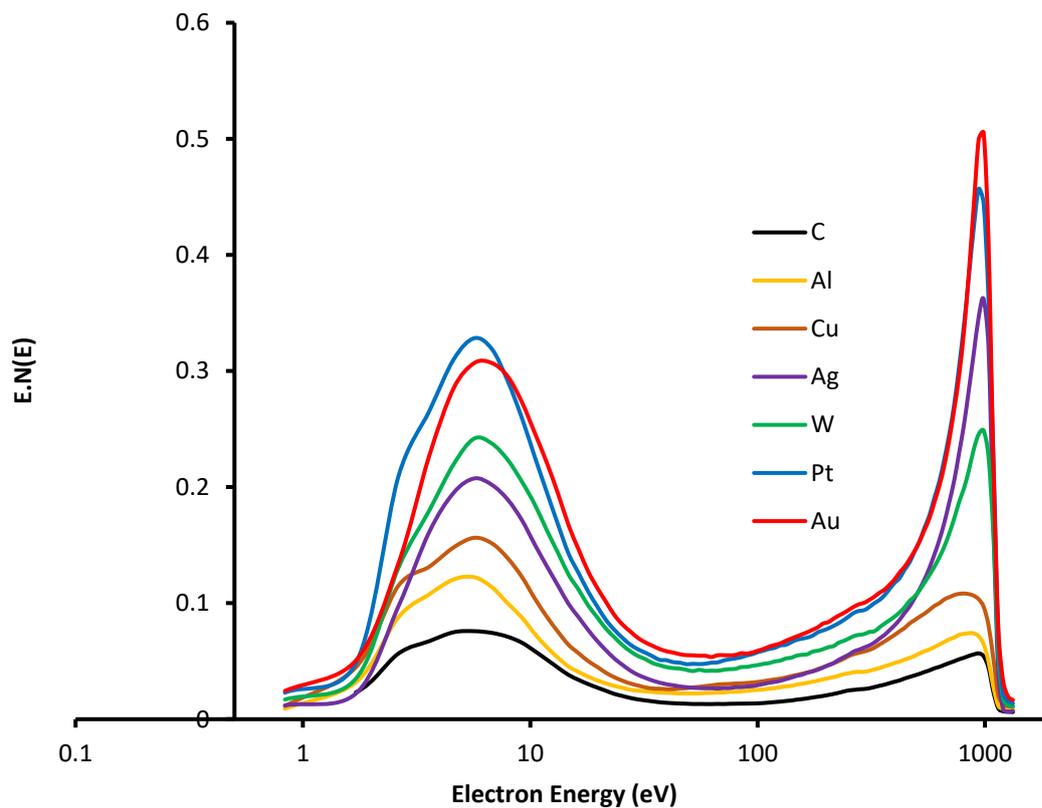


Figure 2: Experimental full-range scattered electron energy spectral signal for different metals with a primary beam voltage of 1 kV inside a SEM.

SECONDARY ELECTRON SPECTROSCOPY FOR IMAGING SEMICONDUCTOR MATERIALS USING A FOUNTAIN DETECTOR

T. Agemura* and T. Sekiguchi**

* Hitachi High-Technologies Cooperation, 882 Ichige, Hitachinaka, Japan 312-8504

e-mail: toshihide.agemura.zh@hitachi-hightech.com

** Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Japan 305-8571

The low energy secondary electrons (SEs) are sensitive for the surface potential in scanning electron microscopy (SEM), and it has been demonstrated to image the surface potential depending on the conductive type, carrier density and/or defects in various semiconductor materials. Thus, if effective low energy SE detector is developed in SEM, the application for imaging the semiconductor materials will be significantly expanded. For such purpose, we have developed a low-pass secondary electron detector (LP-SED), named as "Fountain Detector (FD)" [1], which is composed of a bias grid above and an electron detector below the specimen. A negative filter bias of V_f is applied on a bias grid, so that electrons emitted upward from a specimen with energies lower than eV_f are reflected and travel downward to the detector.

We have devoted much effort to improve the detector characteristics. Such effort includes, (1) sandwiching the bias grid with ground grids, (2) replacing the planar grid with spherical one, (3) increasing the aperture ratio of grids to suppress the SE3s generated by BSE collision on the grids, and (4) adopting a lock-in amplifier to selectively detect pure SEs more. After such developments, the signal intensity and S/N ratio have been significantly improved. [2-3].

A 4H-SiC sample was obliquely fabricated using an ion milling system to enlarge the p-n junction area of interest, then we observed the p-n junction of 4H-SiC using the improved fountain detector. Figure 1 shows the specimen information of prepared 4H-SiC. Figure 2 shows an SEM image with FD as changing V_f from -0.25V to -3.25V in steps of -0.5V. It has been commonly said that the contrast on p-region is brighter than that on n-region [4]; however, we have found that the contrast between p-region and n-region is reversed from -1.25V to -2.25V. This tendency was also observed when energy spectra at each region were acquired using an Auger Electron Microscope as shown in Figure 3. Furthermore, we have also found that the FD can clearly discriminate between the different dopant areas in p-region.

In the presentation, we show the basic FD performance such as the surface potential sensitivity, the energy calibration, and so forth, and results and discussion in detail about the practical applications mentioned above.

References

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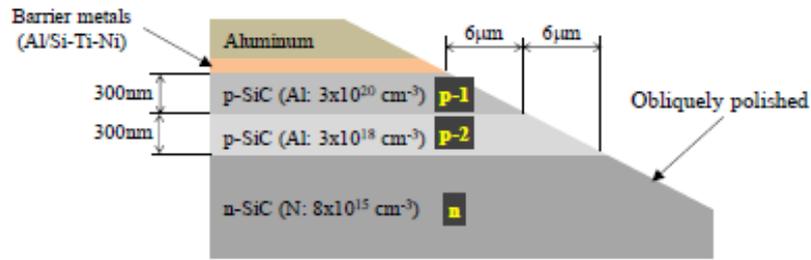


Figure 1: Preparation of 4H-SiC specimen.

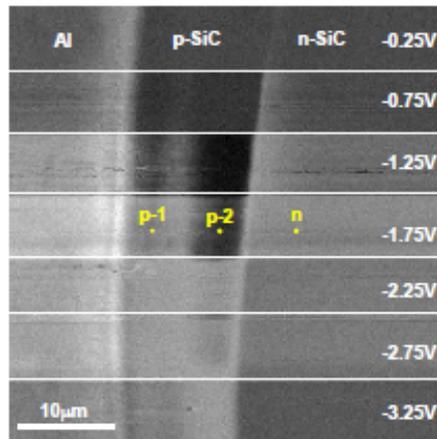


Figure 2: FD images at each $-V_f$ condition. Dots and labels are where SE spectra were obtained using both FD and Auger Electron Microscope (AEM).

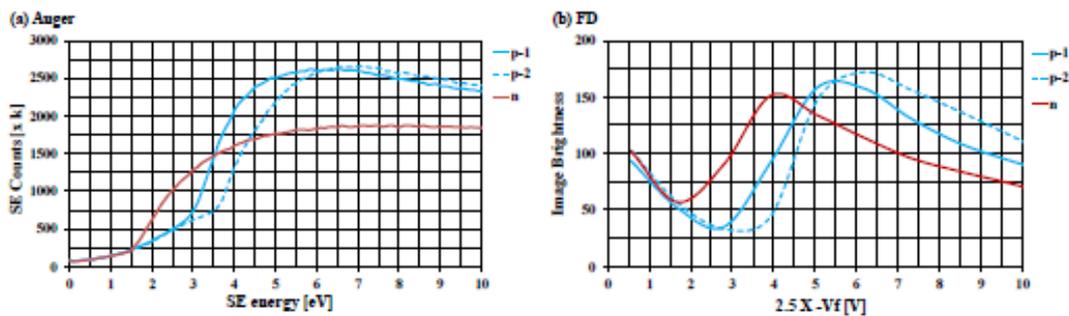


Figure 3: SE spectra obtained using (a) AEM and (b) FD. In AEM, SE can be directly counted at each energy using the cylindrical energy analyzer mounted on AEM. Image brightness on vertical axis in FD was derived from averaging the grey level around each point in Fig. 2. The horizontal axis of $-V_f$ was multiplied by 2.5 time based on the calibration between $-V_f$ and emitted SE energy.

CONFIRMED APPLICATIONS AND LIMITATION OF SE SPECTROSCOPY IN MATERIAL SCIENCE

C. Rodenburg*, K.J. Abrams

Department Materials Science & Engineering, University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK

*e-mail: c.rodenburg@sheffield.ac.uk

First works in Secondary electron spectroscopy (SES) were published since 1925, well before the first SEM with a highly sensitive SE detector was proposed in 1938 [1]. Many of the questions to be discussed in this workshop were already asked in 1940 [2]. For example, Kollath compared SE spectra obtained by two different spectrometer types and compared the SE spectra of a number of materials that were of technological interest in 1936-1940. This comprised of a number of metals, metal alloys and layered alkali based photo sensitive materials. The latter two showed very clear differences in spectra, but for metal alloys these only became apparent after high temperature treatments under vacuum. Kollath concluded that the similarity of many of the base metal spectra prior to high temperature exposure is due to contaminants entrapped in the bulk materials and speculates that clear differences must exist based on the discrete peaks in the electron energy loss spectra (EELS) [3].

In spite of very clear material- specific EELS peaks demonstrated in 1941 [3], it was only around 2011 that EELS became main stream in Materials Science [4]. EELS only achieved this status thanks to successive generations of commercially available EELS devices that could combine spectroscopy and imaging (spectrum-imaging) [4]. Likewise, as described above SES goes back many decades but for its real analytical power to be recognised as mainstream in Materials Science & Engineering, SES has to be combined with spectrum-imaging with resolution that are similar or better than that obtainable by state-of-the-art SEMs. To avoid confusion with the term spectrum-imaging, normally associated with EELS we call secondary electron image series that deliver SE spectra or SE images that are collected from a defined SE energy range only- Secondary Electron Hyperspectral Imaging (SEHI).

One considerable strength of SEHI is that it allows control of both resolution and information depth to some extent, because SEs of different energies have different inelastic mean free paths. A great demonstration of improved resolution obtained this way can be found in [5], where sub-nanometre resolution could be obtained by limiting the energy range of the SE for image formation. This can be done in empirical manor and does not rely on an intricate knowledge of the origin of any SES peaks. In a similar way, SEHI has the capability to suppress topographical contrast and reveal chemical differences [6]. SEHI can also be used to select scan strategies for beam sensitive materials that ensure that the images represent undamaged materials, as the degradation in SES peaks can be used to judge sample damage [7] or contamination built up. When used with care, SES and SEHI has been shown to be of value to Materials Science & Engineering by revealing differences in doping in semiconductors, molecular order in polymers and protein structures, chemical differences in organic/inorganic hybrid materials as well as structural difference in carbon allotropes [8], organic-inorganic perovskite solar cells active layers [9] and to understand the initial stages of the formation thin films [10]. Therefore, SES and SEHI is of interest for the engineering of solar cells, battery components such as carbon electrodes and separators and the reverse engineering of many natural materials including (spider) silk [11,12]. Importantly, these are

all areas where elemental analysis, well established in SEM is of limited use as it is insensitive to subtle change in bonding. In contrast, SES or SEHI carried out with primary beam energies ~ 1 keV do carry such information and results in SE yields close to 1 - thus a best case scenario if small doses are needed for the analysis of beam sensitive materials.

Potentially SES can be used for finger print analysis of [13] if a sufficiently large and reliable data base was available. The reliability is likely to be one reason why SES and SEHI have not yet reached main stream Materials Science. There are three reasons why SES are usually thought of as unreliable: (1) different spectrometer designs cause differences in spectra shape, (2) contamination build up caused by the sample or residual vacuum in the SEM chamber (see Fig 1) and (3) the absence of a suitable reference material to test both (1) and (2) on a routine basis prior to any SES or SEHI data collection.

This talk will give further examples of the use of SEHI requirements to be of value to Materials Scientist and Engineers and describe strategies as to how overcome some of these current limitations.

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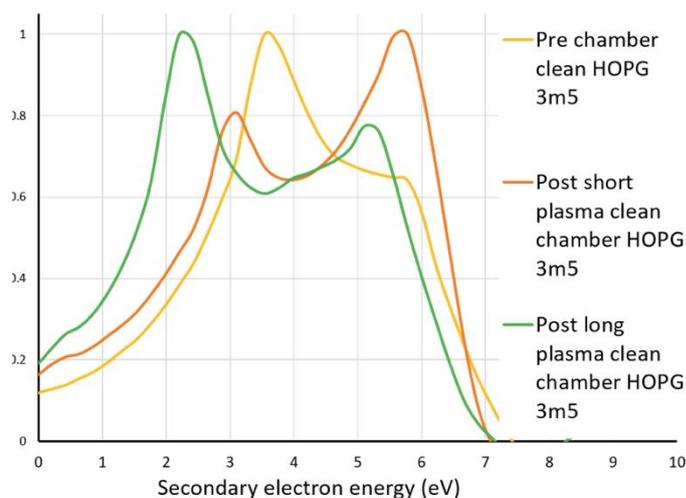


Figure 1 Effects of chamber contamination on SES of HOPG.

ENERGY SELECTIVE ELECTRON DETECTION AND ANALYSIS IN SEM FOR DETERMINATION OF DOPANT CONCENTRATION

F. Mika¹, Z. Pokorná¹, L. Dupak¹, H. Weiding² and A. Khursheed²

¹Institute of Scientific Instruments of the CAS, Královopolská 147, Brno, Czech Republic

²Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117583

e-mail: fumici@isibrno.cz

Energy selective electron detection for the determination of dopant concentration was done many times in standard SEM [1]. Before in-column detection was available at the Institute of Scientific Instruments (ISI), so called cathode lens was used - an electrostatic field applied between the sample holder and the angular YAG detector above it. Cathode lens acts as a low-pass energy filter, choosing only signal electrons under a certain threshold. This is sufficient to discern between differently doped areas of the semiconductor [2].

Our aim at the ISI is to resolve the detected signal electrons by energy with a high resolution. The first experiments with secondary electron filtering were conducted using a through-the-lens detector (TLD), located inside the SEM column and detecting low-energy signal electrons that re-enter the column through the narrow nozzle of the last lens. TLD filtering, however, is rather crude in that it allows setting the width of the bandpass filter with a step of 1 eV. Ultra-High Resolution SEM Magellan 400L from FEI was used to conduct our first proof-of-concept experiments (Fig. 1, 3). The sample was a custom-made silicon wafer with areas of differing, incremental dopant concentration. Electron optical calculations determined the appropriate voltage biases of the TLD electrodes and the sample [3].

Especially for semiconductor applications the energy window should be very narrow, set in steps of 0.1 eV. This is why we decided to incorporate a standalone Second-Order Toroidal Analyzer into the chamber of our UHR SEM. It is based on the design of A. Khursheed, A.Srinivasan and Weiding Han, National University of Singapore (NUS) [4]. It has a 0.5 mm entrance slit, 0.02% energy resolution for input angles $\pm 6^\circ$, good S/N ratio, and allows taking spectra both in the point mode and imaging mode. The energy window is just 0.1 eV wide around the preset value. An example of proof of concept data taken with this spectrometer in NUS is shown in Fig. 2.

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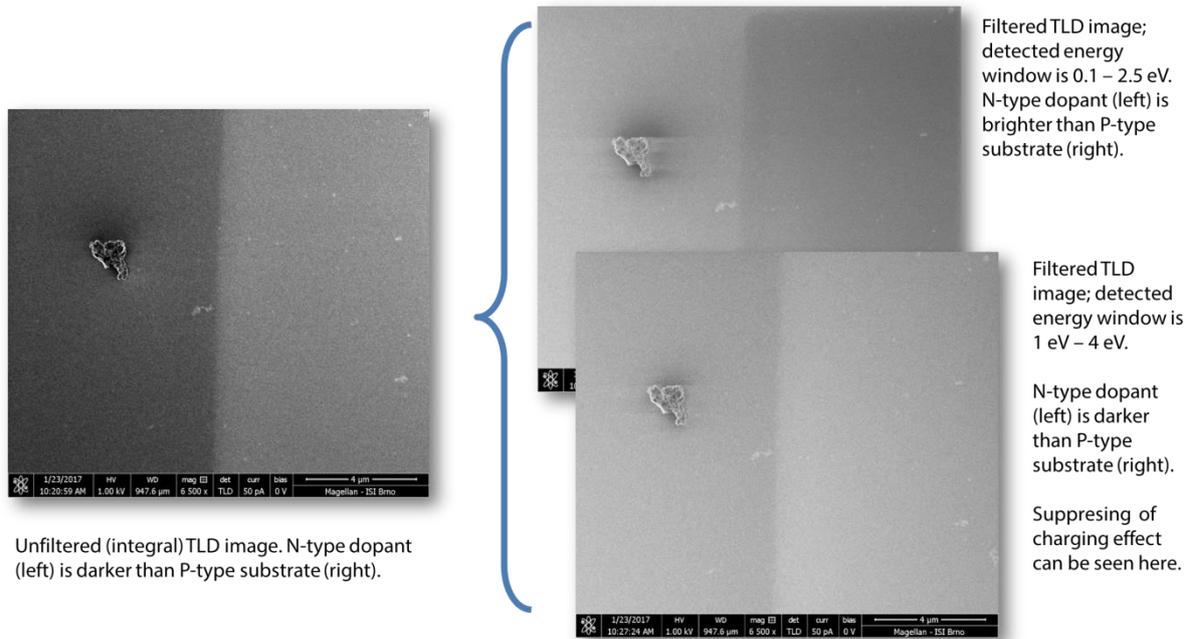


Figure 1: n-type doped patterns of the dopant concentration $1 \times 10^{19} \text{ cm}^{-3}$, made on a p-type Si substrate (dopant concentration $1 \times 10^{15} \text{ cm}^{-3}$)

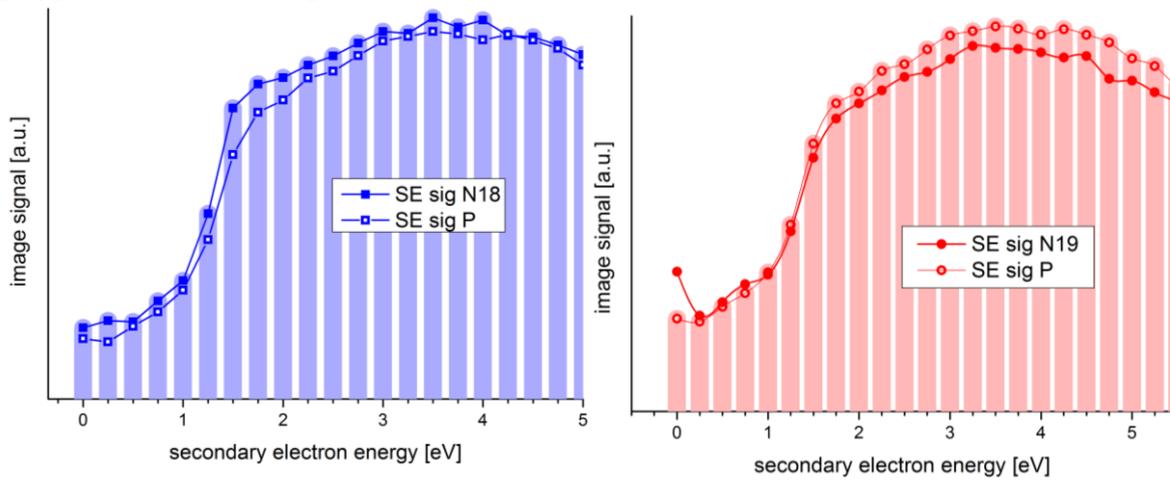


Figure 2: Data on a Si structure with two different dopant concentrations, $1 \times 10^{18} \text{ cm}^{-3}$ (left) and $1 \times 10^{19} \text{ cm}^{-3}$ (right). The Si substrate was doped to $1 \times 10^{15} \text{ cm}^{-3}$

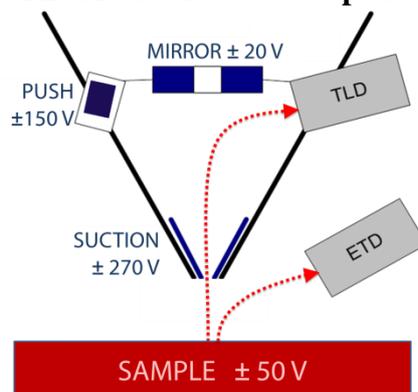


Figure 3: Schematic SEM Magellan 400 chamber arrangement

SECONDARY ELECTRON ENERGY FILTERED IMAGING IN A FE-SEM FOR SEMICONDUCTORS

Y. Yamazawa*, Y. Hashimoto**

* Analysis System Design 1st Dept., Hitachi High-Technologies Corporation, 882, Ichige, Hitachinaka, Ibaraki, 312-8504, Japan

** Application Development Dept., Hitachi High-Technologies Corporation, 3-2-1 Takatsu, Kawasaki, Kanagawa, 213-0012, Japan

*e-mail: yu.yamazawa.wj@hitachi-hightech.com

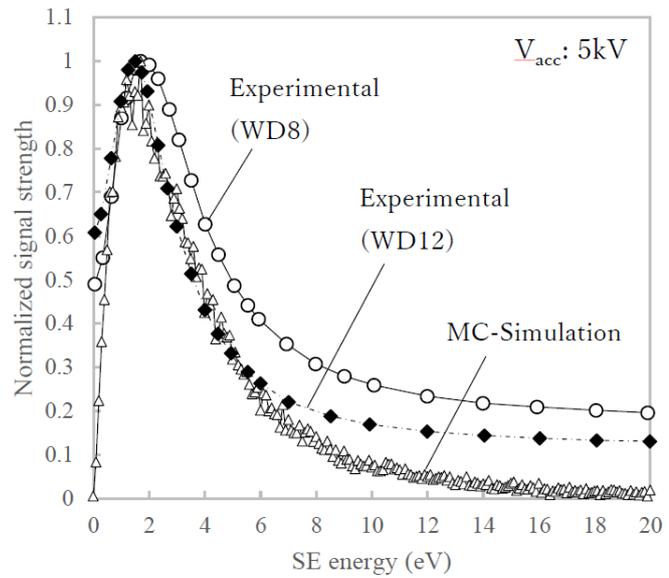
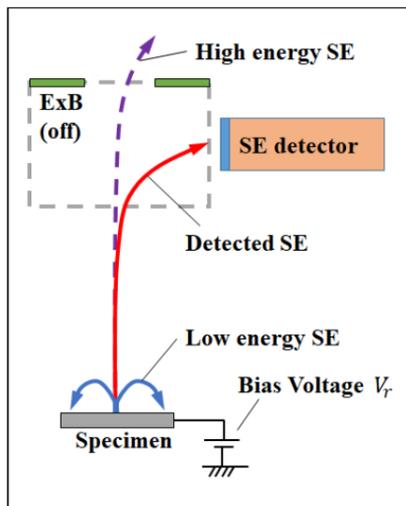
Voltage contrast (VC) imaging with a secondary electron (SE) signal in a scanning electron microscope (SEM) is essential to visualize the surface potential differences of dedicated areas on the specimen. VC imaging has achieved to visualize the dopant distribution and realized that the observed contrast is not only depending on the type of dopant but also sensitive to the dopant concentration levels. To enhance the contrast of dopant distribution, it is important to select the energy of detected SE. Thus, various SE energy filtering methods have been studied [1][2].

We have developed a new Band Pass Filter (BPF) detection technique using a commercial SEM. Figure 1(a) shows a schematic illustration of signal detection system using a BPF detection technique. The BPF consists of three main components: a E x B filter, a signal control electrode and a voltage power supply to specimen. The BPF detection technique is that the positive bias voltage, which is electrically connected to the stage for trapping the low energy SEs, applies to the specimen stage while E x B system is switched off to let the high energy SEs escape. Thus, V_r corresponds to the lowest energy in the detected energy range and the detected energy range is controllable by changing V_r . In addition, the signal intensities variation of BPF against specimen bias voltage can be considered as SE spectrum. Figure 1 (b) shows the experimental and the Monte Carlo (MC) simulation results of SE spectra for copper. The original software (MCAM_ver4.1) developed by Hitachi was used for the MC Simulation. The spectrum at working distance (WD) 12 was coincident with the MC simulation result below around 6 eV, but was higher than the MC result above 6 eV. Another spectrum at WD 8 was higher than that above 2 eV, which suggests that the percentage of the back scatter electron (BSE) was bigger than WD 12.

Figure2 shows the experimental results using Hitachi FE-SEM SU8030 with the BPF. Figure2 (b) and (c) show secondary electron images with different energies using the BPF technique. A clear image at $V_r=2$ V in all dopant densities was obtained, and the contrast derived from the equation, which was $(I_p - I_n)/(I_p + I_n)$, was confirmed to be proportional to the dopant density as shown in Figure2 (e).

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(a)

(b)

Figure 1: (a) Schematic illustration of SE signal detection system using a BPF detection technique, (b) Experimental and Simulation results of SE energy spectrum for copper.

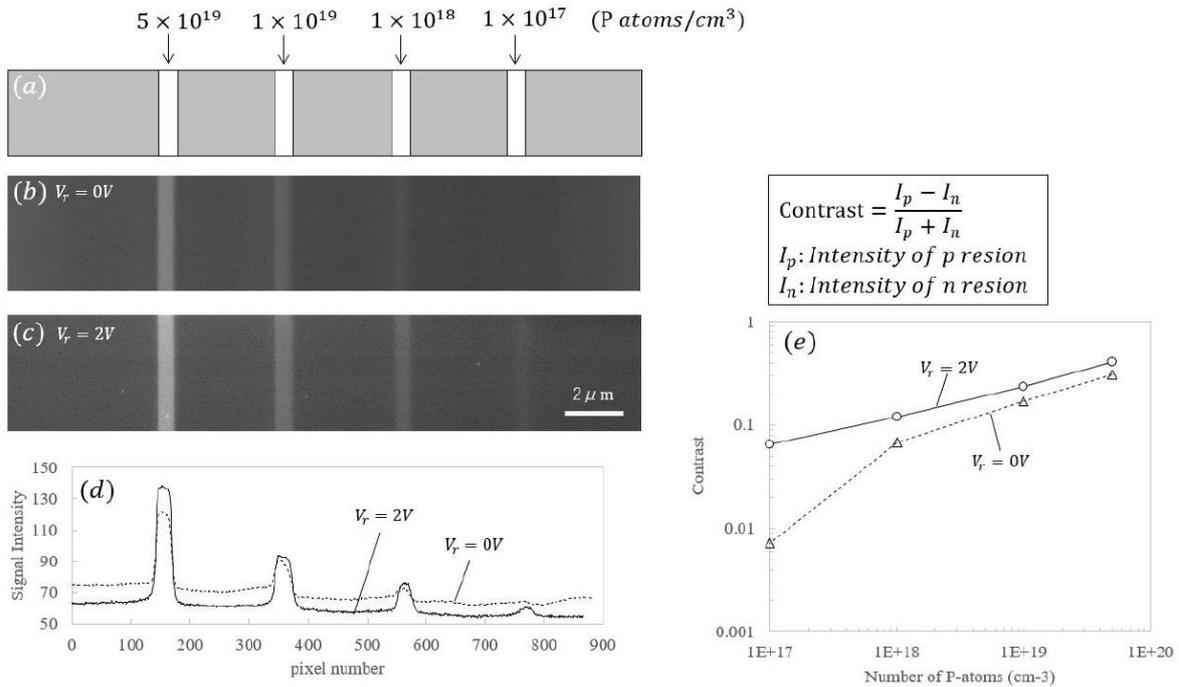


Figure 2: (a) Schematic illustration of a specimen, (b)(c) SEM images taken by BPF detection technique ($V_{acc}:0.8kV$, $WD:12mm$), (d) intensity profile extracted from the SE images, and (e) the contrast calculated from the intensity profiles.

Secondary Electron Spectroscopy with an ELSTAR Column: Current Challenges and Future Potential

N. Stehling*, K. J. Abrams, C. Holland and C. Rodenburg

Department of Materials Science and Engineering, University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield, S1 3JD

*e-mail: nastehling1@sheffield.ac.uk

Parallel to the exciting progress in purpose-built secondary electron analyzers, efforts are under way to communicate the potential of secondary electron (SE) spectroscopy using currently available filter set-ups in commercial through-lens detection systems in SEMs. However, as the exact mode of action of these systems is often kept as proprietary knowledge, some systematic evaluation and validation work from the materials science community is needed to maximize these capabilities and discover their potential and limitations.

Here we present our experiences using an FEI ELSTAR column for SE energy analysis. The FEI ELSTAR column, in our case, is part of a Helios NanoLab G3 UC and is a very high specification electron column featuring a monochromator. Its SE spectroscopy capability arises from the presence of a mirror electrode which influences the energy ranges which are collected by the through-lens detector. Incrementing the mirror voltage within an image series leads to a 'stack' of hyperspectral images with a cumulative collection of SEs of different energies, which can be differentiated to yield spatially resolved SE spectra.

In these through-lens systems a suction tube voltage is commonly applied to increase the angular collection efficiency of SEs and thus reduce the effect of topography of the sample on the SE signal. We have previously observed that this suppression of topography is further enhanced through imaging within certain energy windows^{1,2}, which is a major advantage of hyperspectral imaging over regular SE imaging. However, in the ELSTAR column the angular effects also include a 'detector shadowing' effect which has not been previously characterized (see Fig. 1a and b).

This detector shadowing is a complication for chemical mapping, but may simultaneously be an opportunity for the imaging of 3D structured samples, such as multiscale structural materials: if the influence of angle on the detection efficiency for each SE energy is well characterized, the material and angular contributions could be deconvoluted, as demonstrated simplistically in Fig. 1c and d respectively. In that case, a single SE spectral series has the potential to yield a separate topography and a chemical map of the same field of view. Our work shows that the nanoscale chemical contrast is sensitive to key material properties such as crystallinity, order and orientation of technology enabling materials²⁻⁵, and eliminating topography would lead to higher quality chemical mapping using SE electron energies.

With the vast potential of surface chemical analysis a further hurdle, not only for the ELSTAR column but for any surface analysis in the SEM, is the presence of contaminants in the vacuum which can originate from the sample itself or vacuum chamber walls. Contamination can accumulate easily on the sample surface but through our work we can

recognize its presence by its characteristic SE spectrum. By knowing contamination signatures, we have also been able to show through SE spectroscopy that the in-built sample plasma cleaner in the Helios Nanolab instrument can be effective at removing a carbon layer adsorbed in the atmosphere. Thus, we recommend a further specification for the ideal SE spectrometer: the set-up would either be in ultra-high vacuum, or would allow for the elimination of carbon contamination through thermal desorption or through plasma treatment for thermally sensitive samples as was required in our case.

In conclusion, we report our experiences of using an ELSTAR column for SE analysis and present the vast potential for additional insight which lies in overcoming current challenges. We believe our experience of using commercial systems which are not yet optimized for SE spectroscopy and hyperspectral imaging can serve as input for engineers to design efficient and powerful tools for SE spectroscopy. Thus in conclusion, we assert that a better understanding of the systems and their easy and efficient operation will ultimately lead to a broader uptake of the method in the materials science community.

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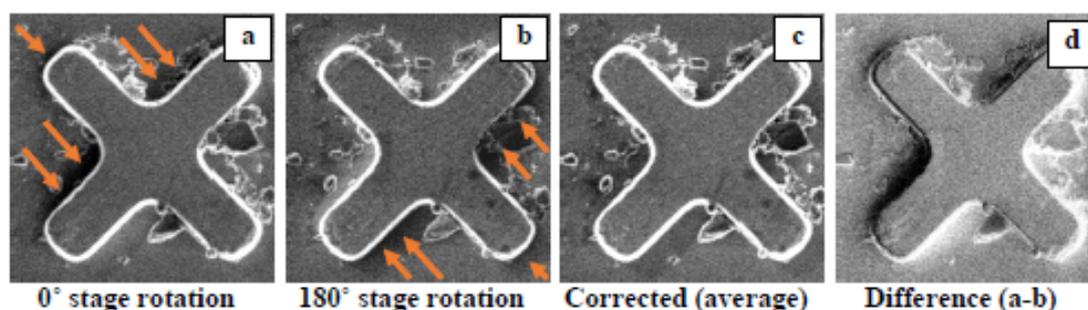


Figure 1: Helios SEM micrographs showing detector shadowing (orange arrows) on a 5x5 μm Si cross using through-lens detection at a mirror voltage of 10.2 MV (collection of 0-1.47 eV electrons) at a) 0° stage rotation and b) 180° stage rotation - image rotated back 180° for direct comparison with a; c) Angular corrected images by taking the average of a and b; d) depiction of the difference (a-b) between a and b isolating the shadowing effect of the detector.

SIMS based Correlative Microscopy for Materials Science Applications

Hung Quang Hoang, Jean-Nicolas Audinot, Santhana Eswara, Tom Wirtz
Advanced Instrumentation for Ion Nano-Analytics (AINA), MRT Department, Luxembourg
Institute of Science and Technology (LIST), 41 rue du Brill, 4422 Belvaux, Luxembourg

Nano-analytical techniques and instruments providing both excellent spatial resolution and high-sensitivity chemical information are of extreme importance in materials science for investigations at the nanoscale. New characterisation tools need to anticipate these research trends, but as more and more techniques approach their fundamental limits it is only by combining multiple techniques that disruptive advances may be made.

While techniques such as Electron Microscopy, Helium Ion Microscopy are commonly used for high-resolution imaging, they provide no or only limited analytical information. In particular, both Energy-Dispersive X-Ray Spectroscopy (EDX) and Electron Energy Loss Spectroscopy (EELS) that are routinely used in electron microscopy have limited sensitivity, neither can distinguish isotopes and both have difficulty with light elements. In contrast, Secondary Ion Mass Spectrometry (SIMS) offers extremely high chemical sensitivity, but it typically suffers from poorer lateral resolution. However, by combining SIMS with one of these high resolution microscopy techniques, these intrinsic drawbacks may be overcome [1].

Therefore, in order to get chemical information with a highest sensitivity and highest lateral resolution, we developed integrated instruments combining SIMS with the Transmission Electron Microscope (TEM) [2], Helium Ion Microscope (HIM) [3-5] and Dual-beam instrument (FIB-SEM) and developed associated correlative methodologies and workflows. An example of the integration of our SIMS system on a HIM instrument is shown in Figure 1. The developed workflows allow TEM, SE images of exactly the same zone analysed with SIMS to be acquired easily and rapidly, followed by a fusion between the SE and SIMS data sets [6]. These correlative microscopy techniques are well suited for elemental and isotopic ratio mapping at nanoscale from a wide range of applications in material sciences. Figure 2 shown an example of SE and SIMS images of a copper indium gallium selenide (CIGS) solar cell after applying a rubidium fluoride (RbF) post-deposition treatment. The Rubidium is found to accumulate along the grain boundary.

In this talk, we will present the concepts, describe the instruments and discuss their performance characteristics. We will then present a number of examples showing the powerful correlative microscopy possibilities enabled by these new in-situ methods in applying to the field of materials science.

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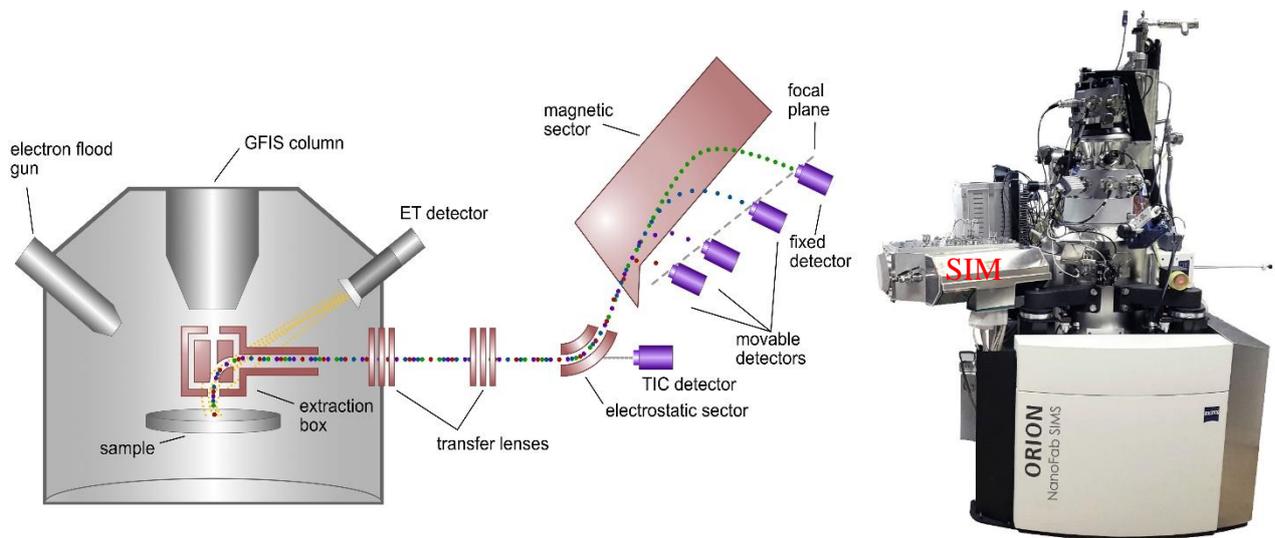


Figure 1. Schematic diagram and photo of the HIM-SIMS combination.

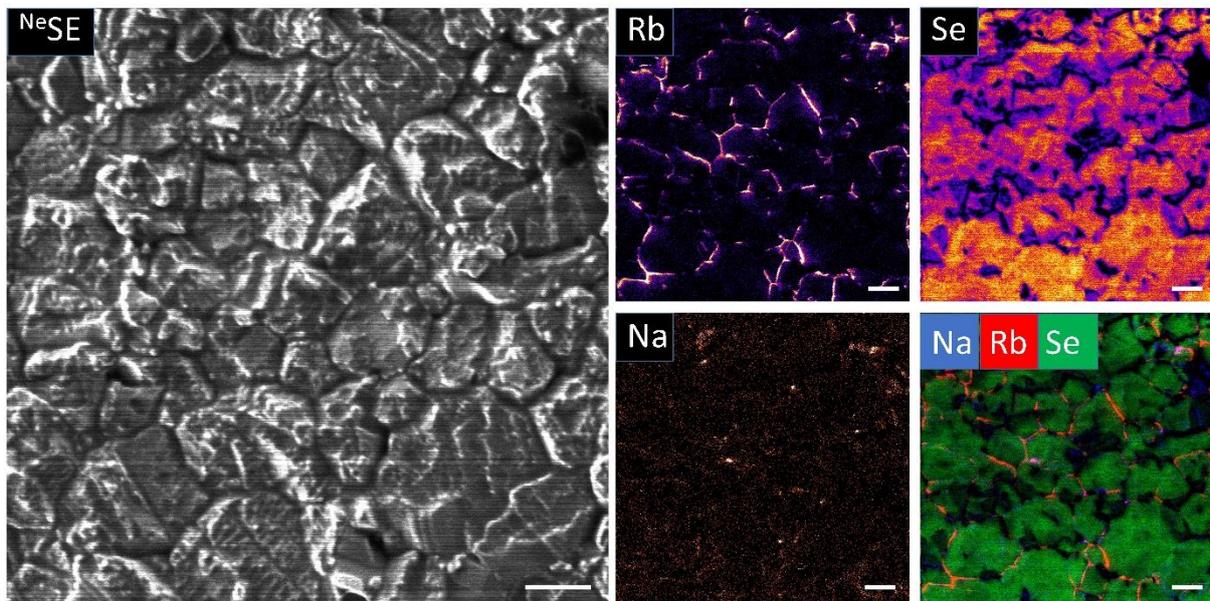


Figure 2. SE and SIMS images of a copper indium gallium selenide (CIGS) solar cell after applying a rubidium fluoride (RbF) postdeposition treatment. Secondary electron image (SE) is obtained with Ne⁺ beam at 20 keV and 1 pA. SIMS images of Sodium, Rubidium and Selenium (512 × 512 pixels, dwell time per pixel of 5 ms) are generated with Ne⁺ beam at 20 keV and 3 pA. The bar-scale is 2 μm

A HIGH RESOLVING MASS SPECTROGRAPH FOR AN INVESTIGATION OF SECONDARY IONS FORMED AT THE TARGET OF AN ELECTRON MICROSCOPE

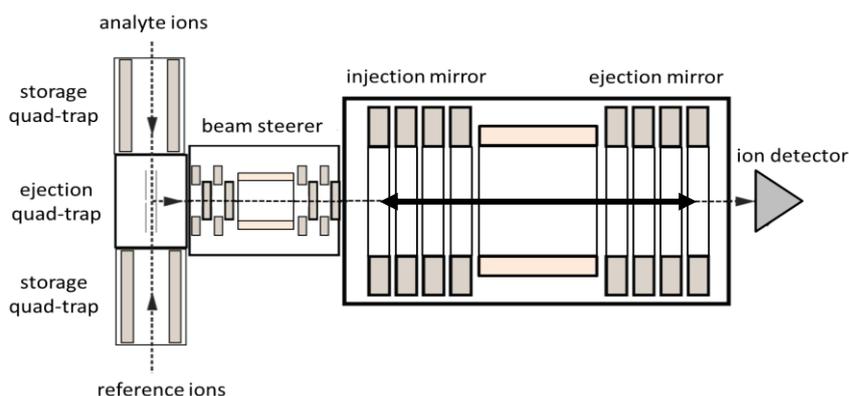
H.Wollnik¹, M.Wada², P.Schury²

1. New Mexico Stat University, Las Cruces 88003, NM, USA

2. High Energy Accelerator Research Organization (KEK), Wako City, Saitama, Japan

To identify atoms or molecules in the surface of a sample it is possible to monitor the energy distribution of secondary electrons. This can be done by using inhomogeneous electric or magnetic sector fields. A more rigorous identification, however, would be to alternatively investigate secondary ions.

In principle the same inhomogeneous electric or magnetic sector fields could be used to obtain a lateral dispersion of such secondary ions. A better method that achieves higher mass resolving powers, would be to use a longitudinally dispersive time-of-flight analysis of these secondary ions. Such time-of-flight mass analyzers¹⁾ can easily achieve mass resolving powers $m/\Delta m$ of a few 1000. Here we want to suggest to use much higher performing MRTOF-MS, i.e. multi-pass time-of-flight mass spectrographs²⁾ as have been used so far mainly for the mass analysis of short-lived nuclear physics investigations. In order to achieve very high mass resolving powers extremely stable power supplies are necessary except if in close sequence the masses of analyte- and of reference-ions are investigated, as has been done by the sketched system.



In order to do this for secondary ions in the proposed system these ions must first be introduced into an RF ion trap, from which they are extracted after they have been accumulated for some time and are cooled by collisions with rest gas atoms, so that the extracted ion beam occupies only a small phase-space volume.

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TIME RESOLVED SEM CHARACTERIZATION OF PHOTOINDUCED SURFACE VOLTAGES BY SECONDARY ELECTRON CONTRAST

A. Tagliaferri^{1,2*}, M. Battaglia¹, G. Irde^{1,2}, V. Sala^{1,2}, S. M. Pietralunga^{2,3}, M. Zani¹, G. Cerullo^{1,3}, G. Lanzani^{1,2},

1. Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci, 32 - 20133 Milano, Italy
 2. CNST@PoliMi, Istituto Italiano di Tecnologia (IIT), Via Giovanni Pascoli 70/3, Milano, Italy
 3. Istituto di Fotonica e Nanotecnologie (IFN), CNR, Piazza Leonardo da Vinci 32, Milano, Italy
- * e-mail: alberto.tagliaferri@polimi.it

Time-resolved Scanning Electron Microscopy (TR-SEM) stems from the interest in non-invasive nanoscale characterization of advanced microelectronics materials and devices. Since the development of the early SEMs, the capability of image acquisition down to the ms timescale, in real-time mode, and to the microsecond timescale in pump-probe mode together with the sensitivity of Secondary Electrons (SE) to surface potentials gave rise to experimental effort to access dynamics information [1]. Electron Beam Probers were commercially available since the second half of the '80s, providing real time capabilities, while prototypes of pulsed electron beams aimed to the investigation of fast and ultrafast repeatable phenomena were developed since the early '90s. Based on beam slicing approaches, these former apparatuses attained sub- μ s temporal resolutions [2]. The sub ps timescale was achieved in the early years of this millennium, by means of laser triggered ultrafast pulsed electron beams [3,4].

While the morphological sensitivity of SE is rather well established and understood, the insight on the material's electronic structure and charge dynamics by the SE probe is still matter of research and debate [5,6], mostly due to the interplay between the SE spectral and angular emission distributions, and the energy and angular filtering operated by the detector. Understanding and controlling these phenomena is crucial to extract the photo-induced dynamical properties in time resolved SEM images, where the photo-exciting beam profile and/or the specimen's spatial structure determine the formation of field gradients at the specimen surface. These fields affect the SE electron trajectories, as they travel in vacuum between specimen and detector, in dependence on the SE energy and emission direction, and contribute to the final signal intensity and mapping. Thus information on the surface fields, potentials and charge dynamics can be accessed by SE imaging, both in real time and in pump-probe mode.

The talk will cover SE imaging in TR-SEM for slowly evolving phenomena over timescales from seconds to days (real time approach), and over ultrafast timescales in the ns and ps regime (pump-probe mode). We will address the experimental procedure and data treatment, devised to extract the information regarding charge dynamics at prototypical specimens. Examples will be proposed on the investigation of ion migration in hybrid semiconductors (Figure 1) [7], of color center dynamics at insulator surfaces (Figure 2) [8] and of carrier and surface state dynamics at inorganic semiconductor surfaces. Finally, we will discuss the potential of trajectory and energy filtering specifically designed for TR-SEM.

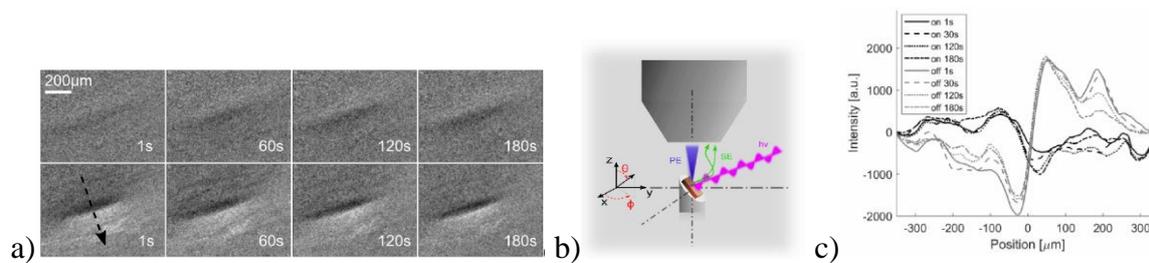


Figure 1: Real-time evolution of the SE contrast [Error! Bookmark not defined.]. a) Differential SE images during laser illumination (top row) and in dark condition after illumination (bottom row); b) Experimental layout; c) Intensity line profiles along the dashed line in a), showing the asymmetry reversal of the contrast between the laser illumination condition (black lines) and in dark condition (grey lines), related to the gradient of the photoinduced surface field and the symmetry breaking by the detection direction.

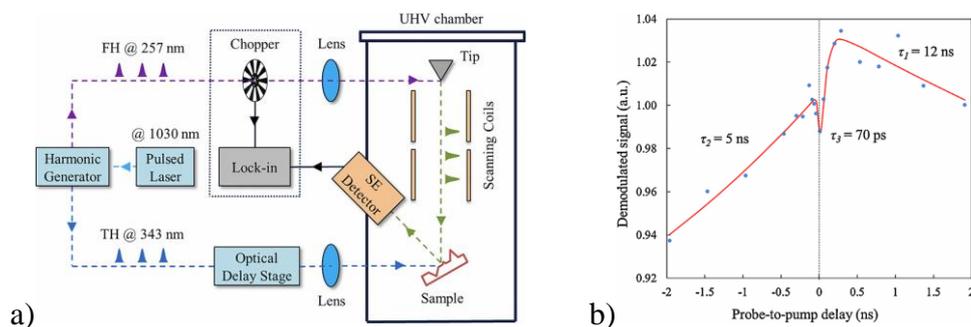


Figure 2: a) Ultrafast pump-probe setup; b) Lock-in SE time series showing the growth of the photoinduced signal while the time delay between photon and electron pulses is decreased (the delay time is positive for photon pulses arriving at sample surface before the electron pulses, negative in the opposite case). Slopes in the negative delay quadrant is related to the lifetime of the particular color center (F^+ , $\tau_2 = 5$ ns) excited by the electron pulse and probed by the photon pulse; and in the positive quadrant, the photon pulse excites F color centers ($\tau_1 = 12$ ns) that are then probed by the electron pulses. The 70 ps dip close to zero delay time is attributed to the sample surface polarization or charging by the photon pulse, that creates a potential barrier opposing SE emission. From Ref. Error! Bookmark not defined..

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THE DESIGN OF PRE-RETARDATION COLUMN OPTICS TO IMPROVE THE ENERGY RESOLUTION OF ENERGY ANALYSERS

Theo J.M. Zouros¹, Matthew Chew² and Anjam Khursheed²

¹Department of Physics, University of Crete, Heraklion Crete, GR70013, Greece

²Department of Electrical and Computer Engineering, National University of Singapore,
4 Engineering Drive 3, Singapore 117583

High resolution electron spectroscopy is a technique utilized in many different fields of physics, material science, chemistry, and even medicine [1]. One of the most popular spectrometers in use is the hemispherical deflector analyser (HDA) [2] also available commercially from many different high tech companies. Currently, modern HDAs are equipped with state-of-the-art multi-element zoom lens and position sensitive detector (PSD) and therefore enjoy a very large collection efficiency. The zoom lens focuses the source electrons into the HDA entry, thus increasing the overall collection solid angle. Of outmost importance is also the overall energy resolution of the spectrometer which can be further improved by pre-retardation. The same input lens, can also decelerate the electrons from an initial source energy E_0 down to a much lower energy E just prior to HDA entry, improving the energy resolution by a factor of $F=E_0/E$ within the constraints imposed by the Helmholtz–Lagrange law [3]. An example of direct ray tracing through such an HDA is shown in Fig. 1 for pre-retardation with $F=10$ [4].

This paper will present a pre-retardation conical electrode design for the second-order focusing 270° deflection toroidal energy analyser for use in scanning electron microscopes (SEM) as an add-on attachment [5]. An example of direct ray tracing through such a design is shown in Figs. 2a and 2b, where 2 keV backscattered electrons emitted with $\pm 2^\circ$ around a 45° polar angle are retarded to a pass energy of 10 eV through the analyser. These simulations predict that the analyser has second-order focusing optics, and that a 200 μm wide exit slit will capture a 1° emission polar angular spread with an energy width of 0.3 eV, corresponding to an energy resolution of around 0.015%.

The paper will discuss how pre-retardation might be used to significantly increase the energy resolution for SEM applications where high energy resolution is required, such as detecting bulk plasmon peaks on the trailing edge of the backscattered energy spectrum. Comparisons of the energy resolutions attainable in simulations of comparable toroidal and HDA analysers will be presented.

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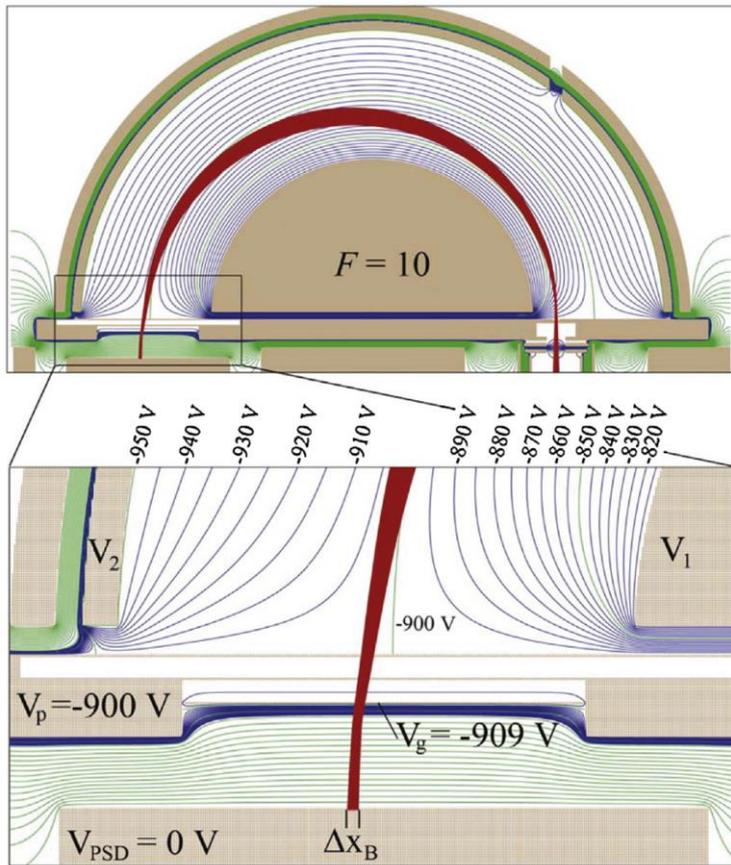
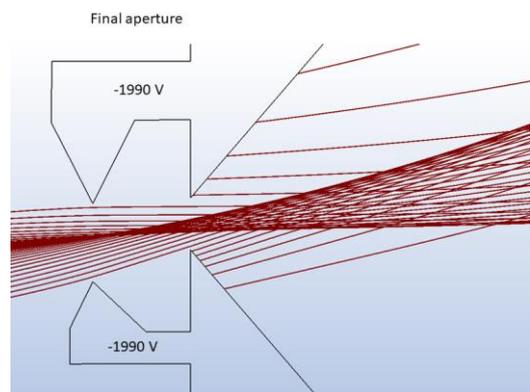
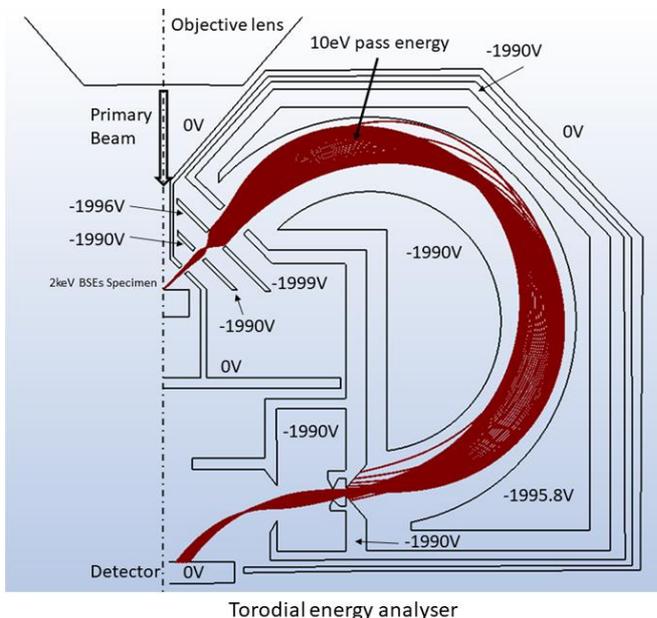


Figure 1. SIMION schematic of HDA electrodes, equipotentials and trajectories in the symmetry plane showing the position sensitive detection (PSD) region (zoom insert) at the exit of the HDA. Electrons with energy $E_0=1$ keV enter from the right, where a zoom lens (only partly shown) focuses and retards them down to a central pass energy of $E=100$ eV (pre-retardation factor $F = 10$). The source half angular spread is 0.397° . The distance h between the HDA exit plane and PSD is adjusted for optimal beam spot size Δx_B . The trajectories spread out in the dispersion plane resulting in an improved energy resolution proportional to $1/F$. A grid biased to $V_g=-909$ V is used just in front of the PSD to eliminate any spurious electron back-ground (adapted from Ref. [4]).



Torodial energy analyser

(a)

(b)

Figure 2: Direct ray tracing simulations through a second-order toroidal SE energy spectrometer with pre-retardation optics inside a SEM. 2 keV backscattered electrons emitted with $\pm 2^\circ$ around a 45° polar angle are retarded down to a pass energy of 10 eV through the analyser for $F=200$.

Transmission EELS spectrometer attachments for SEMs

T Luo and A Khursheed

Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117583 *e-mail: eleka@nus.edu.sg

Transmission electron energy loss spectrometer (EELS) designs start with the application for material elemental identification. As the EELS spectrometer becomes more precise and accurate, it is able to provide detailed and unambiguous analysis of chemical and physical composition of most materials. In order to achieve this goal, we need to achieve detailed distribution data in the core energy loss spectrum. Only transmitted electrons, which experience a single-inelastic-scattering event with an inner core electron carry such core energy loss data, so single scattering events is the focus in development of EELS designs. EELS with single scattering dominance requires high energy incident electrons, ultra-thin specimen thickness, low contamination in ultra-high vacuum levels, and small energy dispersion relative to primary energy levels. Since high energy transmitted electrons up to a few hundreds of keV are used, a magnetic spectrometer is a much more practical approach (in terms of low noise and ease of voltage insulation) compared to voltage dispersion. Because core energies loss are usually small (about a few tens of eV to a few keV) compared to primary electron energies of the order of 100 keV, the aberrations of the magnetic spectrometer must be corrected in order to achieve fine detail of the core loss data. There are multiple ways of aberration correction of magnetic EELS spectrometers. The very first aberration corrected EELS attachment was developed by A Crewe [1], shown in Fig. 1a, and the most widely used commercial approach was developed by Gatan Inc for transmission electron microscopes (TEM) or scanning transmission electron microscopes (STEM) [2]. These are static methods, which correct the aberration by a finding a unique shape of the magnetic prism predicted by simulations, as shown in Fig. 1b [3]. For the application of EELS attachments in SEMs, major challenges are to miniaturize the spectrometer with aberration correction, vacuum contamination, and the relatively low energy of the primary electron beam. EELS attachments for SEMs was first proposed by Luo and Khursheed [4]. An example of their permanent magnet sector design is shown in Fig. 2.

This talk will firstly review the development of different EELS spectrometers, and will discuss EELS attachment designs for SEMs.

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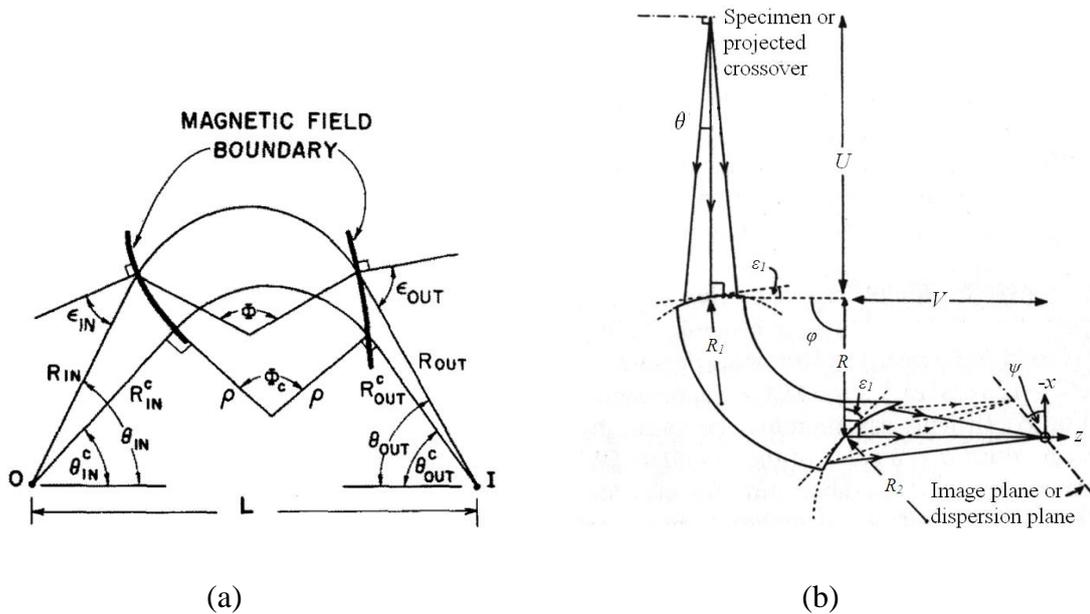


Figure 1: Conventional aberration corrected magnetic spectrometer designs

- (a) The pioneering design reported by Albert Crewe in 1971 [1]
- (b) The widely used curved magnetic prism design used in commercial transmission electron microscopes [3]

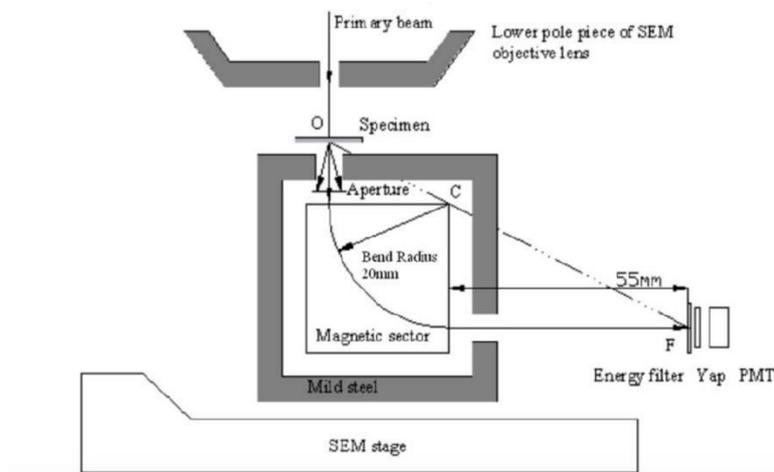


Figure 2: Example of a magnetic sector EELS attachment inside a SEM by Luo and Khursheed [4]

