

## SYMPOSIUM V

# Low-Vacuum SEM/ESEM in Materials Science: Wet SEM—The Liquid Frontier of Microscopy

November 29, 2000

### Chairs

**Bradley L. Thiel**

Cavendish Lab  
Univ of Cambridge  
Polymers & Colloids Group  
Cambridge, CB3 0HE UK  
44-1223-337272

**Dale Newbury**

Surface & Microanalysis Sci Div  
NIST  
222/A113 Stop 8371  
Gaithersburg, MD 20899-8371  
301-975-3921

**John Mansfield**

N Campus Electron Microbeam Analysis Lab  
Univ of Michigan  
417 Space Research Building  
Ann Arbor, MI 48109-2143  
734-936-3352

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SESSION V1: WET SYSTEMS AND *IN SITU*  
EXPERIMENTS

Chairs: John Mansfield and Bradley L. Thiel  
Wednesday Morning, November 29, 2000  
Room 308 (Hynes)

**8:30 AM \*V1.1**

**LOW VACUUM SCANNING ELECTRON MICROSCOPY: A PERSPECTIVE FROM CONVENTIONAL SEM.** Dale Newbury, National Institute of Standards and Technology, Gaithersburg, MD.

The emergence of the low vacuum scanning electron microscope (LV-SEM, also known as environmental SEM, variable pressure SEM, etc.) has provided an important tool for materials scientists which radically departs from the familiar operational regime of the conventional SEM. The specimen chamber pressure ranges from 1 Pa to 5000 Pa, a factor of 10,000 or more higher than the chamber pressure in the conventional SEM. The most obvious consequence of operating at elevated pressure is the inevitable elastic and inelastic scattering of beam electrons during interaction with the gas atoms prior to reaching the specimen. The user-selected variables of beam energy, chamber gas species, pressure, and path length determine the magnitude of this scattering, expressed as the fraction remaining unscattered in the primary beam. As long as at least 50% of the beam remains unscattered, there is very little practical degradation of the resolution of the SEM image, and even lower unscattered fractions have been used to prepare useful images. The elevated pressure strongly affects the selection of detector strategies, with special gas amplification schemes needed to work with secondary electrons. The passage of the scattered beam electrons, backscattered, and emitted secondary electrons through the gas creates ions and releases low energy electrons. The resulting plasma has profound effects on the state of charging in insulating samples, providing a mechanism to control this phenomenon. The situation for x-ray microanalysis is greatly affected by the remote scattering of beam electrons, requiring the use of special strategies to achieve useful results.

**9:00 AM V1.2**

**ELECTRON MICROSCOPY AT THE LIQUID FRONTIER: APPLICATION OF ENVIRONMENTAL SEM (ESEM) TO THE STUDY OF COMPLEX FLUIDS & SOFT CONDENSED MATTER.** Debbie Stokes, Polymers & Colloids Group, Univ. of Cambridge, Dept. of Physics, Cavendish Lab, Cambridge, UNITED KINGDOM.

Observational studies of complex fluid systems and the physical/chemical reactions in liquids, soft condensed matter & solids have traditionally been restricted by the available experimental techniques. The recent advent of the Environmental SEM (ESEM) enables liquid-containing and/or insulating specimens to be observed directly, without the need for traditional EM preparation techniques such as freezing/drying and metallic coating. This represents a significant advance in the study of complex fluids & soft condensed matter, extending electron microscopic capabilities to the study of such materials as emulsions, gels, colloidal dispersions, biological specimens and biomaterials. Maintaining specimens in a hydrated/liquid state is achieved by choosing appropriate environmental conditions in the specimen chamber. Typically, a water-cooled Peltier stage is employed to keep the specimen at around 3°C, within a chamber environment of water vapour at a pressure in the region of 4.5 torr. In this way, the specimen is held in an atmosphere close to 100% relative humidity and is thus stabilised against moisture loss or gain. During the initial pumpdown of the chamber it is essential to ensure that the specimen's natural moisture is preserved. It is therefore usual to perform a sequential pumpdown such that the air in the chamber is successively replaced with water vapour. One of the major advantages of this technique is that it is possible to carry out real-time *in situ* studies, including the observation of dynamic processes such as changes in the microstructure of emulsions (e.g. droplet coalescence). Further, by controlling the chamber environment to alter the relative humidity (by adjusting temperature or pressure), the hydration/dehydration behaviour of complex fluids & soft condensed matter can be observed. Examples are the formation of polymer films upon dehydration of a polymer latex and phase separation in gels as a result of changes in solvent concentration or temperature.

**9:15 AM V1.3**

**APPLICATION OF THE ENVIRONMENTAL SCANNING ELECTRON MICROSCOPE TO HIGH RESOLUTION WETTING STUDIES.** John Craven, Brad Thiel, Cavendish Laboratory, University of Cambridge, Cambridge, UNITED KINGDOM.

Wetting of liquids on solids is of fundamental importance in many different areas of surface science. One important parameter involved in such studies is the contact angle that a liquid makes with a solid substrate. Conventional optical techniques limit the size range over which such measurements can be made and provide little ready indication of the exact physical condition of the surface within the

contact area. Scanning electron microscopy combines high magnifications with an increased depth of field allowing such measurements to be made at much smaller length scales. Previous EM studies of contact angle have relied on the material system to include one or more conductive phases and be tolerant to very high vacuums. The ESEM is conventionally operated using 1-5 torr of water vapor as an imaging gas. Ionization of this gas by electron emission removes the need for a conductive sample by providing charge compensation of the specimen due to an influx of positive ions. This allows for this technique to be used in the wetting studies of a much greater variety of material systems. Additionally by using water vapor and provided the specimen is kept cool (around 2°C), it is possible to operate the ESEM around the dew point of water. This has been conventionally exploited to use the microscope for examination of wet biological systems and recently bulk fluids. However it can also be exploited to follow the wetting behavior of water. By very fine adjustments of the environmental conditions it is possible to condense water droplets of a few microns onto a variety of different substrates and follow their evolution whilst maintaining a very good perspective on the physical nature of the substrate.

**9:30 AM V1.4**

**DETERMINATION OF IMPURITY LOCATION IN ICE CORES USING EDS/ESEM.** Daniel Cullen, Ian Baker, Dartmouth College, Thayer School of Engineering, Hanover, NH.

The spatial variation of impurities found in natural polycrystalline ice has been of interest for over a century. There have been only two studies of the microchemistry in glacier ice. In the first, Mulvaney et al. (Nature 331 (1988) 247) showed, performed x-ray microanalysis in a SEM of aluminum-coated ice from Dolleman Island in Antarctica held at 113 K, that the triple junctions contained substantial concentrations of sulfur. In the second study, Fukazawa et al. (Geophysical Research Letters 25 (1998) 2845) used Raman scattering to study ice from two Antarctic sites (Nansen and South Yamato). In the Nansen ice, held at temperatures between 267 K and 238 K, nitrate and hydrogen sulfate ions were found in liquids at the triple junctions. In the South Yamato ice, held at temperatures between 267 K and 253 K, sulfate ions were found in liquids at the triple junctions. Here, we report on the location of impurities in ice from the GISP2 site in central Greenland. Ice core specimens were examined in a JEOL 5310LV low-vacuum SEM, operated at 10 kV, and equipped with a Princeton Gamma Tech. IMIX energy dispersive x-ray microanalysis system utilizing a pure germanium, thin-window detector. The ice was kept at 160 K using a home-built cold stage. Preferential sublimation of the ice occurred and left behind impurities. This enabled us to observe, for the first time, impurities in both the grain boundaries and the grain interiors. After sublimation, filaments consisting chiefly of NaCl were observed in the grain boundaries, small amounts of sulfur and chlorine were found in the grain interiors of the ice, and large concentrations of sulfur were observed in inclusions. This research was supported by grants from the National Science Foundation and the Army Research Office.

**10:15 AM \*V1.5**

**ESEM ANALYSIS AND DAMAGE SIMULATION WITH STONE SAMPLES FROM THE MAYAN CITY OF COPAN, HONDURAS.** Eric Doehne, David Carson, Getty Conservation Institute, Los Angeles, CA.

The carved stone glyphs that make up the Hieroglyphic Stairway at the archaeological site of Copan in western Honduras form the longest Maya text in existence. Unfortunately, the surfaces of many of the glyphs—which date from 746-756 AD—appear to be eroding rapidly due to deterioration phenomena that are not well understood. A collaborative project to analyze the problem was developed in coordination with the Honduran authorities and preliminary documentation and characterization studies using a range of methods are underway. Results using ESEM/EDS analysis show the main stone at Copan is a green, relatively homogeneous rhyolitic to andesitic welded tuff containing a matrix composed of heulandite, quartz and plagioclase with quartz xenocrysts and phenocrysts of biotite and clinopyroxenes, as well as plagioclase and potassium feldspars. Fine crystals of ilmanite are also common. Comparison of microsamples of weathered stone to fresh stone show some differences that help explain the loss of material from the glyphs. Biotite crystals are often altered to chlorite and iron hydroxides (goethite) often with a change in crystal volume. The presence of gypsum at the top of the stairs suggests salt damage as an important mechanism related to the presence of concrete. This damage mechanism has been simulated through dynamic ESEM experiments. The identification of a vein-filling calcium compound (apparently calcite with intermixed calcium oxalate and calcium phosphate) associated with flaking elsewhere on the stairway may be related to damage from sub-surface microbial communities and organic material. Additional ESEM studies are in progress to determine the relative importance of these deterioration mechanisms.

**10:45 AM V1.6**

PROGRESSIVE CALCIFICATION OF BIOPROSTHETIC HEART VALVE TISSUE. TECHNIQUES FOR ASSESSING DIFFERENT MORPHOLOGIES AND COMPOSITION OF CALCIUM PHOSPHATE DEPOSITS UNDER HYDRATED CONDITIONS USING ENVIRONMENTAL SCANNING ELECTRON MICROSCOPY (ESEM). Stephen M. Habesch, Christophe Delogne, Materials Research Institute, Sheffield Hallam University, Sheffield, UNITED KINGDOM; Vikki A. Carolan, School of Science and Mathematics, Sheffield Hallam University, Sheffield, UNITED KINGDOM; Patricia V. Lawford, Medical Physics and Clinical Engineering, University of Sheffield, Sheffield, UNITED KINGDOM.

Progressive calcification of bioprosthetic heart valve tissue is a major clinical problem. The precise mechanism of di-calcium phosphate dihydrate deposit accumulation is unclear, but is related to interaction with aqueous body fluids or chemical treatment during manufacture. In extreme cases it leads to clinical failure through tissue rupture and dystrophic calcification. This study presents initial environmental scanning electron microscopy (ESEM) results, combined with X-Ray elemental mapping, of different stages of in vivo calcification using explanted porcine and pericardium heart valve tissue. ESEM analysis was carried out under low temperature (5 degrees C), high Water vapour chamber pressures (5 Torr) allowing sample assessment in a completely hydrated state. Sample preparation is minimal (with no need for fixation, drying or conductive coating), preventing structural artefacts within the delicate collagen structures. ESEM therefore represents a major advance over conventional SEM for determining the distribution, form, morphology and surface composition of calcification deposits. ESEM has shown that calcification has evolved through multiple growth stages. In embryonic form, the deposits consist of individual crystal aggregates (5 microns in size) attached to fine internal collagen fibril bundles within the tissue. More evolved forms consist of 50 to 100 micron aggregates on the upper tissue surfaces, showing some evidence of collagen displacement and distortion. Finally in advanced stages, the deposits consist of successive, discrete sheets which replace and coat the surface tissue. Complex internal layering structures are evident. These multiple growth stages could reflect either different mechanisms of formation or a progressive time-dependant 'build-up' through a single process. Elemental X-Ray mapping and spot analysis of the different deposit morphologies identifies major element contents of Ca, P and O with traces of Si, Mg and S. Similar elemental signatures are recorded in each of the different growth forms, which supports a simple mechanism of progressive deposition with time.

**11:00 AM V1.7**

STUDY OF INORGANIC MATERIAL IN ASPHALTENES AND PREASPHALTENES. G.A. Camacho-Bragado, Instituto Nacional de Investigaciones Nucleares, MEXICO; J. Murgich, Centro de Quimica IVic, VENEZUELA; M. Jose-Yacamán, Instituto Nacional de Investigaciones Nucleares, MEXICO.

Heavy fractions of petroleum such as asphaltene usually carry clay particles and other inorganics from the producing reservoir. Vacuum residues also contain other particles produced in the refining process. The elemental composition, size and distribution of these particles have not been studied previously. Particles of colloidal size may play an important role in the asphaltene aggregation and precipitation during the crude oil production and refining. In order to obtain information about the particles, a study using LV SEM and microprobe was undertaken. The asphaltenic, preasphaltenic and maltenic fractions were extracted, using n-hexane as a precipitating agent, from a vacuum residue of oil obtained in Tula, Hidalgo, Mexico. The n-hexane insoluble fraction, (asphaltenes and pre-asphaltenes) was washed by means of the Soxhlet method. This fraction was later dissolved in toluene to separate the asphaltenes (solubles) from the (insoluble) preasphaltenes. The solid preasphaltenes were extracted from the solution while the dissolved asphaltenes were precipitated with n-hexane. A JEOL jsm5900-LV microscope with an Oxford microprobe was employed in the observation of three fractions: toluene-insoluble preasphaltenes, washed asphaltenes (mixed asphaltenes and preasphaltenes) and pure asphaltenes. In the preasphaltenes were found distinct inorganic particles of irregular shape with sizes ranging from 3 to 7 microns. Fe, Ti, Cr and lighter elements such as Si and Al were the main component of these particles. Washed asphaltenes contained smaller particles (1 to 4 microns). Some of them contained mostly Na and Cl while others had Ca and Al as the majority components. The inorganic materials found in the pure asphaltene fraction included not only particles rich in Na, Cl and Ca but also some with significant amounts of Fe, Cr, Ni, and Zn in them. These results show the power of LV SEM and the microprobe methods in the characterisation of inorganic particles found in vacuum residues.

**11:15 AM V1.8**

Abstract Withdrawn.

**11:30 AM V1.9**

SPECIMEN MODIFICATION IN AN ENVIRONMENTAL SCANNING ELECTRON MICROSCOPE. Marion A. Stevens Kalceff, Faculty of Science, University of Technology, Sydney, NSW, AUSTRALIA.

In a variable pressure or environmental scanning electron microscope (ESEM), excess charge on the surface of uncoated poorly conducting specimens irradiated with an electron beam can be balanced by environmental gas ionized by secondary electrons in the vicinity of the specimen surface. Grounded conductive coatings in conventional high vacuum mode and ionized gas in environmental mode minimize charging at the specimen surface, however significant charge trapping may still occur in the implanted sub-surface regions of materials which are poor conductors of electrons. A small fraction ( $<10^{-6}$ ) of the incident electrons are trapped at irradiation induced or pre-existing defects within the irradiated micro-volume of specimen. The trapped charge induces a highly localized electric field which may result in the electro-migration and micro-segregation of charged mobile defect species within the irradiated volume of specimen. In an ESEM the presence of the positively charged ion atmosphere in the vicinity of the surface enhances the local irradiation induced electric field. In particular, the influence of electron beam irradiation on silicon dioxide polymorphs has been investigated. Silicon dioxide is a technologically important material with many diverse applications. Electron irradiation induced modifications of poorly conducting specimens in an ESEM are shown to be associated with *electric fields* associated with the localised trapped electrons, the environmental ions and the bias applied to the electron detector. In addition *bulk and surface chemical modification* is shown to result from the interaction of the specimen with the environmental ions and the incident and trapped electrons. The enhanced desorption and the electromigration of mobile charged defect species resulting in structural and chemical modifications may provide the opportunity for electron beam micro-modification and maskless fabrication of non-planar devices.

**11:45 AM V1.10**

AN IN-SITU ESEM INVESTIGATION INTO THE MECHANICAL PROPERTIES OF RUBBER. Sarah V. Hainsworth, Department of Engineering, University of Leicester, Leicester, UNITED KINGDOM; Pete R. Lewis, Department of Materials Engineering, The Open University, Walton Hall, Milton Keynes, UNITED KINGDOM.

A previous forensic investigation into the failure of rubber revealed that examination of the material on two separate occasions in a low pressure scanning electron microscope revealed two differing densities of ozone cracks on the failure surface. The density of ozone cracks was low in the initial investigation and higher in the second examination. This was attributed to enhanced beam damage from the low pressure water vapour environment. The aim of the work reported here is therefore to investigate the effect of imaging in low pressure environments on the density of ozone cracks. Further, the effect of the imaging conditions on the mechanical properties of rubber are investigated. Thus rubber samples have been subjected to tensile testing and cyclic load testing using a Deben Micro tensile tester in a Philips XL30 ESEM and stress-strain curves have been recorded. Various environments such as saturated water vapour and nitrogen have been used to provide the necessary charge neutralisation. A range of differing accelerating voltages have also been used. Finally, strategies for the future analysis of such materials whilst minimising degradation from imaging artefacts are proposed.

SESSION V2: SURFACES AND SEMICONDUCTOR  
DEVICE CHARACTERIZATION

Chairs: Dale E. Newbury and Bradley L. Thiel  
Wednesday Afternoon, November 29, 2000  
Room 308 (Hynes)

**1:30 PM \*V2.1**

A MICRO-GAS DELIVERY SYSTEM FOR IN SITU CVD IN THE ESEM. Scott Wight, Surface and Microanalysis Division, National Institute of Standards and Technology, Gaithersburg, MD.

One of the advantages of the environmental scanning electron microscope (ESEM), model 2020, is the capability to introduce different gasses to the specimen chamber. However, when the gas is expensive, toxic or corrosive it may be desirable not to fill the entire chamber but to deliver a locally high concentration of the gas directed at the specimen. This is especially true for a reactant gas that is consumed by a chemical or physical reaction that has to rely on diffusive mixing from the chamber to replenish the consumed gas molecules. A micro-gas delivery system has been developed and an

application is described. The micro-injector attachment is reversibly modified to deliver gas from outside the microscope directly to the specimen. The micro-gas delivery system was employed to deliver tetra-methyl tin vapor to a micro-hotplate chemical vapor deposition experiment in the ESEM. Micro-machined heating elements (100 micrometers square) were resistively heated to 500°C. The precursor gas was delivered to the hotplate via the modified micro-injector. When the precursor gas contacted the hotplate surface it decomposed depositing a reactive tin metal coating that in the presence of oxygen formed tin oxide coating on the hotplate surface. Nucleation and growth of films was observed in real time in the ESEM. Film growth was manipulated by controlling the hotplate temperature, gas composition, surface treatment and gas concentration. Progression of the film growth was monitored by four point conductivity measurements. These metal oxide coated hotplates have applications as gas sensors. Application of the micro-gas delivery system has been successfully demonstrated. The modifications are simple enough to be duplicated by anyone desiring to deliver small amount of a gas directly to the specimen and observe the process in situ in the ESEM chamber.

#### **2:00 PM V2.2**

**ELECTRON BACK SCATTERING IN THE ENVIRONMENTAL SCANNING ELECTRON MICROSCOPE - THE PRESSURE LIMIT.** John F. Mansfield, North Campus Electron Microbeam Analysis Laboratory, University of Michigan, Ann Arbor, MI.

The large specimen chambers found on environmental scanning electron microscopes ensure that it is usually easy to attach electron back-scattering diffraction systems. However, in a typical environmental SEM it is possible to operate at pressures in excess of 1500 Pa of a residual gas (usually water vapor). Although chamber pressures in excess of 750 Pa have been shown to severely degrade the quality of electron back-scattering patterns (or EBSPs), the naked eye and human brain combination can easily detect the patterns (Thaveprungsriporn et al, 1994). To date, however, there has been no quantitative determination of the pressure above which it is not possible to index and analyze the patterns. Most computer analysis of EBSPs relies upon Hough transforms, which allow the indexing of very noisy patterns. Early studies of patterns recorded at a range of operating pressures indicate that, while the patterns maybe barely visible above 900 Pa, careful Hough-based pattern analysis can result in reliable indexing up to 1200 Pa.

"Development of an Economical Electron Backscattering Diffraction System for an Environmental Scanning Electron Microscope." V. Thaveprungsriporn, J.F. Mansfield, D.C. Crawford & G.S. Was, J. Mat. Res 9 (1994) p1887-1894.

#### **2:15 PM V2.3**

**EBSI IN THE LOW VACUUM SEM.** Patrick Camus, David Rohde, NORAN Instruments Inc., Middleton, WI.

While LVSEM is one of the fastest growing segments of the SEM market, EBSI is one of the fastest growing segment of analysis techniques. Their combination is extremely powerful for the characterization of crystalline solids. The use of LVSEM benefits an EBSI analysis by reducing the sample charging during the analysis without the use of conductive surface coatings. This permits the routine analysis of insulating samples (monolithic ceramics and metallurgically-mounted metals) at high beam currents and short collection times. However, the gaseous atmosphere can contribute to degradation of the diffraction pattern quality if the pressure is raised to too high of a level. Analyses of phase identification and crystal orientation mapping performed at low vacuum will be presented. Quantification of the effect of the LV pressure on diffraction pattern quality will be presented and discussed.

#### **3:00 PM \*V2.4**

**THE ESEM AND VPSEM IN SEMICONDUCTOR TECHNOLOGY.** David Joy, EM Facility University of Tennessee, Knoxville, TN and Oak Ridge National Laboratory, Oak Ridge, TN.

The environmental scanning electron microscopes (ESEM) and the variable pressure SEM (VPSEM) are most usually thought of as best suited for the study of biological materials, or for samples that are otherwise dirty, hard to pump, moist, or even wet. However, the ESEM and VPSEM have very important roles to play in the field of semiconductor device technology and failure analysis. These instruments can make contributions in at least three different areas: (a) The ability of the ESEM or VPSEM to guarantee charge neutrality at any chosen beam energy by adjustment of the ambient gas environment makes it possible to produce stable images of even the most difficult combinations of materials combinations. The unique gas mediated imaging capability of the ESEM/VPSEM is beneficial when examining structures of high aspect ratio such as deep trenches or vias because 'black holes' caused by positive charging are absent, and because the gas amplification resulting from the additional path length enhances the brightness of the floor of the trench relative to

the top surface. (b) Devices covered with a glass or ceramic passivation can readily be examined without the need to remove the over layer. By making a suitable choice of the beam energy high resolution backscatter and EBIC images of the encapsulated chip can be obtained. (c) Failure analysis of packaged devices is difficult to carry out in a conventional SEM because of the mixture of materials that must be imaged simultaneously (i.e. metals, semiconductors, plastics, ceramics). In the ESME/VPSEM such problems are absent and because charge control can be achieved at any beam energy X-ray microanalysis can also readily be carried out. These instruments are therefore ideally suited for quality control and failure analysis.

#### **3:30 PM V2.5**

**ESEM OF ORGANIC SEMICONDUCTOR DEVICES.** D. Stephen Thomas, Ian C. Bache, Henning Siringhaus, Richard H. Friend, Cavendish Laboratory, University of Cambridge, Cambridge, UNITED KINGDOM.

We present the results of the use of ESEM in the imaging of organic semiconductor devices. Conventional SEM has been an invaluable tool in the development of the inorganic semiconductor industry, its high resolution and depth of focus being of paramount importance in the imaging of VLSI circuitry and other mesoscopic architectures. Organic semiconductors, in particular conjugated polymers, are a relatively new but rapidly developing class of electronic device materials whose potential in optoelectronic, and large-scale integrated devices has already been demonstrated. Conventional SEM of organic devices usually requires that the samples be coated in gold to avoid charging under the electron beam. This layer prevents the imaging of all but the topographical information from the sample and does not allow for any contrast mechanism between the various device components. The low vacuum environment of ESEM gives rise to the production of positive ions which neutralize charge at the sample surface, thus eliminating the need for a conducting coating and allowing the bare materials to be examined. Variations in density, atomic number and electronic structure of component materials give rise to contrast mechanisms which allow the imaging of heterojunctions between dissimilar materials. Careful choice of primary beam energy allows the user to select which features come into contrast, a technique which is of particular use in the imaging of multilayer structures. The availability of in-situ energy dispersive x-ray microanalysis (EDX) allows these contrast mechanisms to be correlated with the elemental compositions of component features. In this paper we demonstrate the application of these techniques to the imaging of basic organic device structures and demonstrate its potential in the imaging of the microstructures of multicomponent organic systems.

#### **3:45 PM \*V2.6**

**ESEM MICROCHARACTERIZATION OF SEMICONDUCTOR MATERIALS AND DEVICES.** Matthew R. Phillips and Scott Morgan, Microstructural Analysis Unit, University of Technology, Sydney, AUSTRALIA; Milos Toth, Polymer & Colloids Group, The Cavendish Laboratory, University of Cambridge, UNITED KINGDOM.

The environmental scanning electron microscope (ESEM) has great potential in the electronics industry as a highly versatile analytical tool for materials microcharacterization, failure analysis and quality evaluation of semiconductor materials and devices. With the ESEM, electronic materials and powered devices can be observed and analyzed in situ using voltage contrast and charge collection techniques without a conductive coating under controlled gaseous conditions at elevated temperatures. In addition, the ESEM imaging parameters can be adjusted to maximize the sensitivity of the gaseous secondary electron detector (GSED) to localized electric fields within the specimen. In this mode of operation (unique to the ESEM), regions of charge flow and accumulation due to p-n junctions, band bending effects, device contacts and interfaces in metal oxide semiconductor (MOS) devices can be observed under ESEM conditions. The effect of condensed water on device performance can be assessed dynamically when water vapor is used as the imaging gas in the ESEM. Using a hot stage and wet mode imaging, moisture-induced damage processes such as lead/contact corrosion, device encapsulation swelling and electrical short-circuiting can be observed in situ under accelerated conditions. Dielectric breakdown and electrostatic discharge phenomena in insulators can be studied by simply injecting minority carriers at selected areas and depths at high pressure then decreasing the pressure to initiate the charge-induced damage processes. All time dependent experiments can be recorded on video tape and digitized using a video capture system for careful examination. Spatially resolved elemental microanalysis can be carried out in the ESEM using an energy dispersive X-ray detector, but the presence of the imaging gas must be considered in the analysis.

#### **4:15 PM V2.7**

**MICROCHARACTERIZATION OF ION BEAM IRRADIATED GaN USING ENVIRONMENTAL SCANNING ELECTRON**

**MICROSCOPY.** M. Toth, M.R. Phillips, Microstructural Analysis Unit, University of Technology, Sydney, Broadway, AUSTRALIA; S.O. Kucheyev, J.S. Williams, C. Jagadish, Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, AUSTRALIA; G. Li, LED Expert Corporation, Kaohsiung County, Taiwan, PR CHINA.

We discuss the utility of the environmental scanning electron microscope (ESEM) for characterization of damage produced in GaN by (*ex-situ*) selective area ion implantation. The ESEM allows for electron imaging at elevated specimen chamber pressures. Ionized gas molecules in the specimen chamber can effectively neutralize insulating surfaces. Control over the ionization rate (and hence the mean ion concentration) provides control over the extent of charging exhibited by insulating specimens, thus facilitating imaging of charge trap distributions in semiconductors and insulators. Unintentionally n-doped,  $\sim 2 \mu\text{m}$  thick GaN epilayers grown on c-plane sapphire substrates were bombarded with 6.6 MeV C and 1.8 MeV He ions to a number of doses. Nonradiative recombination centers and charge traps produced by ion implantation were detected by cathodoluminescence spectroscopy and energy dispersive x-ray spectrometry (EDS). The lateral extents of regions subjected to ion bombardment were imaged using the ESEM. The contrast observed in ESEM images is attributed to electron emission enhancement (in the implanted regions) caused by an electric field produced by electrons trapped at defects during imaging. Conditions under which such field-assisted contrast is observed and distinguishing dependencies on gas pressure and temperature were identified. Implantation of GaN by low energy ions (10 keV H, 40 keV C, 150 keV C and 100 keV Au) also produced regions visible in ESEM images. However, these specimens did not exhibit charging detectable by EDS, and the contrast observed in ESEM images did not exhibit the pressure and temperature dependencies characteristic of the above mentioned field-assisted contrast. Unlike bombardment by 6.6 MeV C and 1.8 MeV He ions, low energy ion implantation only produced damage in the near-surface region of the investigated epilayers. The presented technique allows for the detection of resistive regions that extend throughout the entire thickness of semiconductor films on insulating substrates.

#### 4:30 PM \*V2.8

**CONTACTLESS IMAGING AND LOW VOLTAGE MICRO-ANALYSIS OF CONTAMINANTS, DEFECTS AND DOPANTS IN AND ON SILICON WAFER, SILICON NITRIDE FILMS ON GALLIUM ARSENIDE AND MERCURY CADMIUM TELLURIDE DEVICES BY ESEM.** Brendan Griffin, James Browne, Travis Baroni, Univ of Western Australia, Centre for Microscopy and Microanalysis, Perth, AUSTRALIA; Dominique Drouin, Sherbrooke Univ, Dept of Mechanical Engineering, Sherbrooke, Quebec, CANADA; Stephen Hinckley, Edith Cowan Univ, Dept of Applied Physics, Perth, AUSTRALIA.

Solvent residues to less than 10 nm and crystallographic defects in silicon wafer have been imaged using the recently developed charge contrast imaging (CCI) technique in the environmental scanning electron microscope (ESEM). The contrast observed in these CCI in the ESEM has also been quantitatively calibrated against the amount of dopant (B and P) implanted into silicon wafer. The dopant distribution in mercury cadmium telluride (MCT) devices is also clearly visible in CCI and both mask defects and substrate influences have been imaged in recent studies. The chemical nature of a 350nm thick silicon nitride film deposited on gallium nitride has also been investigated. By employing a 3 kV electron beam energy the analysis depth was found both from modelling and in practice to be contained within the film. Gas-induced electron scatter was minimised by use of a long aperture assembly in the ESEM. Argon, rather than the standard water vapour, was used to avoid spurious x-ray generation from gas-electron interaction as oxygen contents in the film were of interest. The observed x-ray spectra matched modelled spectra and lacked the limiting carbon contamination observed in spectra recorded using conventional SEM. The gas-electron interactions within the ESEM act as a plasma cleaner and importantly preclude the conventional contamination problems. Use of helium as the chamber gas, in conjunction with a forward projection aperture to limit the high pressure gas path length, minimises beam scatter. This combination has been found to provide an analytical resolution of better than 30  $\mu\text{m}$  at very low electron beam energies (3 kV). In summary, the ESEM has been found to be a unique platform for the rapid characterisation of a range of features present in microelectronics-related samples.

#### V3.1

**A COMBINED STUDY OF TRACE METAL CATION CONCENTRATION AND SURFACE MORPHOLOGICAL CHARACTERISTICS ON SEAWEED SURFACES UNDER HYDRATED CONDITIONS USING ENVIRONMENTAL SCANNING ELECTRON MICROSCOPY (ESEM). IMPLICATIONS FOR EFFLUENT TREATMENT MODELLING.** Stephen M. Habesch, Maria Romero, Materials Research Institute, Sheffield Hallam University, Sheffield, UNITED KINGDOM.

The use of de-alginate seaweed biomasses in effluent filtration processes is gaining increased importance for commercial treatment operations. One of the major technical problems is the behaviour of different toxic metal cations in aqueous 'carrier' solutions and the mechanism for absorption on the biomass structures. As part of a laboratory-scale modelling study to investigate the 'take-up' of different metal species by the seaweed, a programme of environmental scanning electron microscopy (ESEM) techniques, combined with elemental X-Ray analysis, have been developed to assess metal distribution on a microscopic scale on the seaweed surfaces. The advantages of ESEM over conventional SEM for this application include the minimal amounts of sample preparation (and surface artefacts), no need for conductive coatings and the ability to look at surfaces under fully hydrated conditions at high resolution. Selected seaweed samples, treated in concentrated solutions with Pb, Au, Ag, Cu and Al were examined to establish; 1. The quantitative distribution of metal species on seaweed surfaces. 2. Any heterogeneity in metal concentration in different cellular structures. 3. The different mechanisms for 'take-up' on the sea weed surfaces. Seaweed surfaces were examined under both fully hydrated chamber conditions and at intermediate relative humidity conditions, using a Peltier stage at 5 degrees C. In each case, elemental X-Ray mapping and spot analysis identified metal concentrations on the seaweed surface, quantified at up to 5 percent. In the case of Au, direct particulate precipitation was recorded in large concentrations, with particle size range of 1 to 20 microns. In all cases, metal species distribution was homogeneous on the seaweed surface, with no form of concentration on specific cell parts. These experimental results demonstrate the potential for metal cation filtration using seaweed in effluent treatment processes.

#### V3.2

**OBSERVATION OF MICRODROPS OF WATER FORMED ON FLAT, ROUGH AND MICROPATTERNED WATER-REPELLENT SURFACES BY ENVIRONMENTAL SCANNING ELECTRON MICROSCOPY.** Atsushi Hozumi, Ceramics Technology Department, National Industrial Research Institute of Nagoya, Nagoya, JAPAN; Hiroyuki Sugimura, Osamu Takai, Department of Materials Processing Engineering, Graduate School of Engineering, Nagoya University, Nagoya, JAPAN.

Water repellency is an attractive phenomenon because of its applications in a wide variety of engineering fields. Although extensive researches on water-repellent coatings have been done, microdrops of water formed on water-repellent surfaces have been studied a little. Environmental scanning electron microscopy (ESEM) is one of the powerful tools to investigate phenomena of adsorption and desorption of micro drops of water on surfaces. Here we report on the observed results of microdrops of water formed on the water-repellent coatings on Si substrates by ESEM. We studied the effects of morphologies of coated surfaces on the shapes of the microdrops. The following three types of water-repellent surfaces were used in this study. (1) A flat surface prepared by chemical vapor surface modification method. This surface showed a high contact angle of about  $112^\circ$  and was terminated completely with  $\text{CF}_3$  groups. (2) A rough surface prepared by microwave plasma-enhanced chemical vapor deposition. This surface showed ultra water-repellency and a ultrahigh contact angle of about  $160^\circ$ . (3) A micropatterned surface prepared by photolithography. This surface was composed of hydrophobic and hydrophilic regions with  $2\sim 20 \mu\text{m}$  in width. The shapes of microdrops of water formed on the high and ultra water-repellent surfaces in the water-vapor atmosphere of 500 Pa were confirmed by ESEM to be similar to those of water drops of 2 mm in diameter formed at the atmospheric pressure. The shapes of the drops are independent of the sizes of the drops on the same water-repellent surfaces. On the other hand, the shapes of the microdrops formed on the micropatterned surfaces were influenced largely by the pattern width and the drop size. When the water-vapor pressure increased, the drops on the hydrophobic regions were pulled to right and left hydrophilic regions and distorted consequently.

SESSION V3: POSTER SESSION

Chair: Bradley L. Thiel

Wednesday Evening, November 29, 2000

8:00 PM

Exhibition Hall D (Hynes)