JAVAC — The Vacuum Specialists

SCREWLINE — Specifically developed for covering the requirements of industrial and difficult applications, the innovative and modular design of the SCREWLINE vacuum pumps is ideal in all cases where reliable, compact and low maintenance vacuum technology is demanded. They are suited for all applications with high requirements regarding the backing pump, like processes involving particles or in rough everyday production.

The SCREWLINE pumps offer numerous advantages to the user:

- Minimum downtimes, maximum availability, highly rugged
- Low cost of ownership
- Long maintenance intervals and low servicing complexity
- Highly flexible
- High pumping speed at low ultimate pressure
- Excellent suitability for the short cycles of load lock chambers or similar applications.

SCREWLINE — The Dry Vacuum Solution

SOGEVAC Rotary Vane Vacuum Pumps

Many years of experience in vacuum engineering and the latest developments in pump technology combine in the SOGEVAC range the capability to adapt to the requirements of both the industry and the environment. The comprehensive range (pumping speeds ranging from 10 to 1200 m³/h (5.8 to 707 cfm)) allows every customer to select the right pump for their particular needs:

- Continuous operation from atmospheric pressure to ultimate pressure
- Low noise level
- Low vibrations
- Integrated exhaust filter, better than 99.9% efficient
- High water vapour tolerance

Sogevac — World Renowned Industrial Products

... Now A Cost Effective Solution for Every Application

For more information visit www.javac.com.au
or Free Call 1300 786 771

Sogevac SV65B — Compact, Quiet & Robust
SIIS STANTON SCIENTIFIC SIIS
Vacuum Science Products

A & N Vacuum components
meeting all international standard
specifications. CF, ISO, KF, ASA and other
conventions in the broadest of
configurations, Custom Chambers

Aalborg Mass Flow Meters and Controllers

Electron Multipliers and
Channeltron Detectors

ADVANCED ENERGY
Power Supplies RF and DC
for Thin film deposition, also components
and Networks for Plasma loads

Ion sources and Magnetron sources
For Thin Film, Surface Science and sample preparation applications

Ceramaseal
A division of CeramTec

HV and UHV feedthroughs
Ceramaseal as used by major instrumentation companies and world class
research projects alike

Granville Phillips Vacuum Gauges

Thickness Monitors Quartz Crystal monitoring systems
0.1 Angstrom resolution. Piezo electric valves

Mass Spectral data bases N.I.S.T. (USA) and Wiley Mass
Spectral Library

RHK Technology
Imaging the Future of Nanoscience

SIMION Ion Optics Software

PHYSICAL ELECTRONICS

Diener Plasma Systems

Ion Pumps from Gamma Vacuum

Electron Guns and Power
Supplies from TFI Telemark an established
standard in the Field of Vacuum Deposition
Processes

Surface Science Systems
& Components

www.stantonscientific.com    email: bill@stantonscientific.com
Ph. 02 66856902    Fax 02 66856530
AP Instruments Pty Ltd
Andre Peters  33 Hunter Ave  St Ives 2075 NSW
02 91446600         0448 750 885         andrepeters@optusnet.com.au

PREVAC  www.prevac.eu

- Ultra High Vacuum and High Vacuum System
- Manipulators, Goniometers and Mechanical Feedthroughs
- Chambers and Mechanisms
- Sample Holders
- X-Ray, Electron, Ion sources
- Accessories
  - Bakeout equipment, Load locks, Vacuum doors, Mass flow controllers, Water cooling devices, vacuum fittings, Titanium sublimation pumps etc.
- Eelectronics
  - Pressure measurements, Stepping motors controls, Emission regulators, Electron beam evaporator PS, Electron and Ion source PS, Bakeout control units. etc
- Software
  - TOF acquisition applications, Space simulator control appl., Dedicated software for Customer’s systems and devices, Pressure control appl., Thermal desorption Spectroscopy Control, Automatisation of sample transfers, etc.

TOYAMA  www.toyama-jp.com

Synchrotron Radiation (SR) Beam Line and Related Systems
- Total Beam Line Systems
- Branch Beam Shutters
- Absorbers
- Mirror Positioning Systems(3-7 axes,Bent type)
- Monochromators(VUV,Soft X-ray,Photoelectron)
- Analysis Instruments
- Beam Monitors
- Beam Ducts
- Slits
- Pumping Units for Vacuums

Particle Accelerators and Related Devices
- Magnets(Bending,Quadrupole,Multipole,Steering,etc.)
- Monitors(Profile Monitors,Core Monitors,Current Monitors,etc.)
- Ion Sources
- Electron Guns
- Injectors,Deflectors
- Accelerating Electrodes
- Beam Ducts
- Pumping Units for Vacuums
- Analyzers

Other Systems and Components
- Experiment Systems and Instruments for Space Development,
- Condensed Matter Physics and Electrical Engineering

Systems and Instruments for Nuclear Fusion and Nuclear Engineering
- Ion Source Drawing Electrodes
- Calibration Spectroscopes for Plasma
- Measuring Instruments
- High-Frequency Antennas for Plasma Heating
- Beam Dumps
- Fixed/Movable Limiters
- Calorimeters
- Collimators
- Manipulator Tongs

Vacuum Experiment Systems and Instruments
- Vacuum Chambers(Low to Ultra-High Vacuum(LV-UHV) in various configurations for all types of applications)
- Instruments for Plasma Experiments
- Pumping Units for Vacuums

Various Parts & Components for Vacuum Experiments
- Fittings
- Feed Throughs
- Linear/Rotary Motion Drivers,Linear Motion Thimbles
- Magnet Couplings,Manipulators
- Current Conductors,Electrical Isolators;
- Goniometers
Great VG Scienta Discounts
Up to 25% discount on selected vacuum components

VG Scienta are offering up to 25% discount on selected vacuum components for all ThermoFisher customers.

Discounted components include;
• all metal/viton right angle valves
• pumped rotary feedthroughs
• linear drives
• leak valves
• mechanical hands
• magnetic probes
• high power magnetic probes
• rack & pinion drives
• viewports
• wobble sticks
and more!

For full details of this offer and further information on VG Scienta’s range of quality HV & UHV components, please contact ThermoFisher directly or visit www.vgscienta.com.

Thermo Fisher Scientific
Unit 14, 38-46 South Street
Rydalmere, NSW 2116, Australia

Dominic Gomez
Tel: +61 2 8844 9500
Mobile: +61 411 676 007
Fac: +61 2 8844 9599
Email: dominic.gomez@thermofisher.com

Andre Peters
Tel: +61 2 8844 9500
Mobile: +61 448 750 885
Fac: +61 2 8844 9599
Email: andre.peters@thermofisher.com

* selected products until 31st December 2007

VG Scienta brings over 40 years’ experience, innovation and expertise in providing UHV components and high performance instruments for surface science.

Mansell Road, Castleknock Industrial Estate, Hastings, TN38 9AN, UK
Phone: +44 (0) 1424 851 291 Fax: +44 (0) 1424 851 469
E-mail: sales@vgscienta.com Web: www.vgscienta.com
Scitek Australia Pty Ltd was originally called Balzers Australia. We changed our name six years ago after changes to our parent organization. In keeping with our policy for providing quality products and services, we have aligned our organization with the world’s leading names of the industry that is involved in the vacuum industry.

**Scitek is “your partner in Vacuum!”**

### Our Products and Services

**Sales**
- Vacuum pumps
- Vacuum measurements
- Gauges and leak detectors
- Mass spectrometers
- Thin film coatings
- Valves
- HV and UHV components
- Field portable GCMS
- Portable Explosive Detection
- RAC charging/testing equipment
- Fast cycle water vapour cryo pumps

**Service**

*In-house Services:*
- Mass spectrometers (incl. calibration)
- Turbo molecular pumps
- Vacuum gauge heads
- Leak detectors
- Gas analyzers
- Haplotics

*Onsite Services:*
- Trouble shooting on vacuum systems
- Vacuum leak detection with helium
- Onsite training

**Parts**

Parts available on all of our products.

**For more details**

**CALL**

1800 023 467

---

Scitek Australia Pty Ltd
Suite 1B, 10-18 Cliff Street
Milsoms Point
Sydney NSW 2061
PO BOX 355
Milsoms Point
Sydney NSW 1565

Toll Free: 1800 023 467
Phone: 02 9954 1925
Fax: 02 9954 1939
E-mail: contact@scitek.com.au
Web: www.scitek.com.au
Program
Tuesday 20th November 2007

16:30 - 18:30 Registration
17:30 - 19:30 Welcome and light refreshments

Wednesday 21st November 2007

08:15 - 09:15 Registration
09:15 - 09:40 Welcome

Session 1  Environment and Bioscience (1)
Chair: Jeff McCallum

09:40 -10:20 David Paterson, Australian Synchrotron
Microanalysis capabilities of the microspectroscopy beamline at the Australian Synchrotron

10:20 - 10:40 Samuel Marx, University of Queensland
Evidence of enhanced El Niño activity in the mid Holocene inferred from records of Australian dust deposition in New Zealand.

10:40 - 11:00 Dora Pearce, University of Ballarat
Toenails: they know where you’ve been!

11:00 - 11:30 Morning Tea

Session 2  Advanced Materials and Analysis
Chair: Rob Elliman

11:30 - 12:00 Daniel Riley, University of Melbourne
Use of ultra-fast diffraction in the design of novel materials

12:00 - 12:20 Imam Kambali, University of Newcastle
Determination of hydrogen adsorption site on palladium(100) using low energy ion scattering spectroscopy

12:20 - 12:40 Babs Fairchild, University of Melbourne
Fabrication of sub micron layers in single-crystal diamond

12:40 - 13:10 Claudia Schnohr, Australian National University
Comparison of the atomic structure in InP amorphised by electronic or nuclear ion-energy-loss processes

13:10 - 14:30 Lunch

Session 3  Environment, Bioscience (2) and Nanotechnology (1)
Chair: Peter Johnston

14:30 - 15:00 Paul Pigram, Latrobe University
Detecting oligonucleotide immobilization and hybridisation using TOF-SIMS

15:00 - 15:20 Robert Haworth, University of New England
Blending lead-210 and AMS age profiles from estuarine sediment cores to reconstruct Holocene climate change in the Sydney Region

Page 7
<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>15:20 - 15:40</td>
<td>Andreas Markwitz, GNS</td>
<td>Low energy lead implantation into Si for novel group IV nanomaterials</td>
</tr>
<tr>
<td>15:40 - 16:00</td>
<td>Michael Gladys, University of Newcastle</td>
<td>Bridging the gap between the nano-particle and single crystal surface science</td>
</tr>
<tr>
<td>16:00 - 16:30</td>
<td>Paul Munroe, University of NSW</td>
<td>Application of focused ion beam systems to materials analysis</td>
</tr>
<tr>
<td>16:30 – 18:30</td>
<td></td>
<td>Poster Session 1 and Afternoon Tea</td>
</tr>
<tr>
<td>18:00 onwards</td>
<td></td>
<td>BBQ</td>
</tr>
</tbody>
</table>

**Thursday 22nd November 2007**

**Session 4**
**Environment and Bioscience (3)**
**Chair: David Cohen**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:00 - 09:30</td>
<td>James Robertson, AFP</td>
<td>Nuclear science and forensic science - complementary sciences!</td>
</tr>
<tr>
<td>09:30 - 09:50</td>
<td>Serena Abbondante, University of Canberra</td>
<td>Radiologically contaminated evidence: extraction procedures and the effect of radioactive materials on forensic DNA profiling</td>
</tr>
<tr>
<td>09:50 - 10:10</td>
<td>Laura Gladkis, ADFA@UNSW</td>
<td>A new methodology in prosthesis research: radioisotope tracing of knee implant wear</td>
</tr>
<tr>
<td>10:10 - 10:30</td>
<td>Amy Ziebell, University of Wollongong</td>
<td>Cylindrical silicon-on-insulator microdosimeter: charge collection characteristics</td>
</tr>
<tr>
<td>10:30 - 11:00</td>
<td>Julian Adams, Australian Synchrotron</td>
<td>Protein crystallography using the Australian Synchrotron</td>
</tr>
<tr>
<td>11:00 - 11:30</td>
<td></td>
<td>Morning Tea</td>
</tr>
</tbody>
</table>

**Session 5**
**Nanotechnology (2)**
**Chair: Andreas Markwitz**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>11:30 - 12:00</td>
<td>Matt Kilburn, University of Western Australia</td>
<td>NanoSIMS: Recent advances and new applications in SIMS</td>
</tr>
<tr>
<td>12:00 - 12:20</td>
<td>Damian Carder, GNS</td>
<td>Ion-beam sputtered germanium thin films – self-assembly of surface nanostructure using post growth annealing</td>
</tr>
<tr>
<td>12:20 - 12:40</td>
<td>Michael Dunn, University of Melbourne</td>
<td>Interface trap density reduction in thin silicon oxides using ion Implantation</td>
</tr>
<tr>
<td>12:40 - 13:00</td>
<td>Dinesh Venkatachal, RMIT</td>
<td>Surface fraction statistics of gold nanoclusters of dissimilar sizes determined by RBS</td>
</tr>
</tbody>
</table>
13:00 - 13:30 Rob Elliman, Australian National University
Photonic nanostructures and their influence on Er luminescence 81

13:30 - 14:30 Lunch

14:30 – 18:30 Conference Tour of Synchrotron

19:00 - 22:30 Conference Dinner at Treetops Restaurant, Melbourne Museum

Friday 23rd November 2007

09:00 Session 6: Advanced Materials, Devices and Analysis
Chair: Chris Ryan

09:00 - 09:30 John Kennedy, GNS
Unravelling the mystery of zinc oxide 85

09:30 - 09:50 Julius Orwa, University of Melbourne
Towards a formula for optimized production of single NV centres in diamond by ion implantation 89

09:50 - 10:10 Kane O’Donnell, University of Newcastle
Neutral atom microscopy: a non-destructive, high-resolution surface analysis technique 89

10:10 - 10:30 Andrew Baloglow, University of Wollongong
Characterization of silicon detectors utilized in an on-line dosimetry system for microbeam radiation therapy 90

10:30 - 10:50 Perry Davy, GNS
Diffusion characteristics of silicon implanted with group IV elements 94

10:50 - 11:20 Rachel Caruso, University of Melbourne
Porous titanium dioxide materials fabricated by using templating techniques 97

11:10 - 11:30 Morning Tea

11:30 -13:00 Poster Session 2

13:00 - 14:00 Lunch

14:00 - 16:30 Session 7: Ion Beam Science and Advances in Analysis
Chair: David Jamieson

14:00 - 14:30 John O’Connor, University of Newcastle
Helium ion microscope – high resolution, high contrast microscopy for nanotechnology 99
Chris Ryan, CSIRO
14:30 - 14:50
Next generation x-ray microspectroscopy: towards full-spectral XANES and high throughput fluorescence imaging using massively parallel detector arrays and realtime spectral deconvolution

Michael Went, Australian National University
14:50 - 15:10
Extended interface analysis using high energy electron scattering

Changyi Yang, University of Melbourne
15:10 - 15:30
Avalanche detector technology for keV single ion detection and implantation for quantum bits construction

David Cohen, ANSTO
15:30 - 15:50
Towards a better understanding and prediction of the bremsstrahlung background in PIXE spectra

Andrew Gleadow, University of Melbourne
15:50 – 16:10
Fully-automated counting of fission tracks in natural minerals for fission track dating and thermochronology

David Belton, CSIRO
16:10 - 16:40
PIXE imaging of a developing corrosion front beneath a protective coating on galvanized steel

16:40 - 17:00 Closing Remarks and Award of Prizes

We Will Keep You Dry
The XDS35i is the only completely dry scroll pump on the market.
- No oil to change or dispose of – environmentally friendly
- Dry scroll technology eliminates the risk of oil backstreaming
- Patented bearing shield isolates all bearings from the vacuum environment
- Significantly reduced maintenance costs and downtime over oil-sealed and conventional scroll pump designs
- Clean, quiet operation well-suited for most laboratory applications
Posters index

N. Biluš Abaffy
Deposition of high quality metal oxide thin films using a filtered cathodic vacuum arc 124

A. Alves
Detection and placement of single ions in the keV and MeV regimes: MeV ion-aperture scattering 127
The effect of annealing temperature on the optical properties of sputter-deposited hafnium oxide thin films 133

K. Belay
The introduction of the k0-method of neutron activation analysis at ANSTO 136

John W. Bennett
Investigation of surface crystallites on C54 titanium silicide thin films using transmission electron microscopy 140

M. Bhaskaran
Structural parameters of wheat starch granules differing in amylose content and functional characteristics studied by small-angle x-ray scattering 143

Jaroslav Blazek
The ANSTO ECR ion source and its application to mass spectrometry 147

D. Button
Design considerations in the development of magnetic nanoparticles for MRI contrast enhancement 152

M. R. J. Carroll
Plasma immersion ion implantation and deposition of titanium nitride onto polymers 153

C. Chaiwong
DLTS study of ion and molecular implantation damage in silicon 157

C. T. Chang
Surface modifications of nanoporous alumina membranes by plasma polymerisation 161

Martin A. Cole
Characterisation of nanostructures for photovoltaics 166

Gavin Conibeer
XANES from ROI vs. DA deconvolution of full spectral SXRF data 175

M. A. Draganski
The refractive index of ion implanted diamond 167

Glenna L. Drisko
Metal oxides produced from sol-gel templating of agarose gel applied to vanadium adsorption 168

Optimisation of Density Functional Theory 170

Daniel W. Drumm
(DFT) parameters for calculating the electronic and optical properties of diamond. 179

Barbara Etschmann
Fabrication of periodic Al2O3 nanomasks 179

Fang Fang
High temperature electronic properties of field-effect transistor based on SiC nanowires 182

V.S. Gill
Age mapping of radioisotopes by daughter trace element analysis 185

M. J. Gladys
Enantioselectivity of chiral molecules on chiral copper surfaces 189

M. J. Gladys
Delineating groundwater flowpaths using 14C dating in the Upper Loddon catchment, central Victoria 195

Sarah K. Hagerty
ANSTO heavy ion ToF for analysis of light elements in thin films 196

M. Ionescu
<table>
<thead>
<tr>
<th>Name</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. C. Johnson</td>
<td>Dopant enhanced hydrogen diffusion in amorphous silicon layers</td>
</tr>
<tr>
<td>M. Hult</td>
<td>On the use of mercury as a means of locating background sources in ultra low background HPGe-detector systems</td>
</tr>
<tr>
<td>L. M. Jong</td>
<td>Identification of ion strike location by precision IBIC</td>
</tr>
<tr>
<td>Anthony G Kachenko</td>
<td>Nuclear microprobe studies of metal(loid)s distribution in hyperaccumulating plants</td>
</tr>
<tr>
<td>Teera Kamvong</td>
<td>PIXE/PIGE microanalysis of trace elements in hydrothermal magnetite and exploration significance: a pilot study</td>
</tr>
<tr>
<td>John V Kennedy</td>
<td>Transmission electron microscopy studies of polycrystalline zinc oxide thin films grown by ion beam sputtering</td>
</tr>
<tr>
<td>Taehyun Kim</td>
<td>The synthesis and structure of silica nanowires SIMS and SNMS analysis of solar wind</td>
</tr>
<tr>
<td>Bruce V. King</td>
<td>implanted silicon from the NASA Genesis Mission</td>
</tr>
<tr>
<td>Bao-ping Li</td>
<td>Differentiation of white-bodied ancient ceramics from north China kilns: the ICP-MS and TIMS techniques and their significance</td>
</tr>
<tr>
<td>Anwaar Malik</td>
<td>Carbon cluster output from SNICS: Impact angle dependence</td>
</tr>
<tr>
<td>Zeya Oo</td>
<td>In-Situ study of the self-recovery property in aluminium titanate</td>
</tr>
<tr>
<td>Manickam Minakshi</td>
<td>Examining Manganese Dioxide as a cathode in aqueous LiOH battery</td>
</tr>
<tr>
<td>Patrick T Moss</td>
<td>Comparative ages of pollen and foraminifera in the ODP 820 marine core</td>
</tr>
<tr>
<td>Anthony Musumeci</td>
<td>Application of radioisotopes for nanotoxicological studies</td>
</tr>
<tr>
<td>Ashley Natt</td>
<td>Preliminary paleolimnological data from a Santiago Island coastal lagoon, Galapagos Archipelago, Ecuador</td>
</tr>
<tr>
<td>Huynh Nguyen</td>
<td>Mechanical properties of cortical bone allografts irradiated at a series of gamma doses from 5 to 25 kGy</td>
</tr>
<tr>
<td>R. Nigam</td>
<td>Superconducting and magnetic properties of RuSr$<em>2$(Eu$</em>{1.5}$Ce$_{0.5}$)Cu$<em>2$O$</em>{10}$</td>
</tr>
<tr>
<td>G. J. Oberman</td>
<td>Drying of a sol gel droplet suspended in a flowing atmosphere</td>
</tr>
<tr>
<td>D. J. O'Connor</td>
<td>Surface structure analysis of Ni/Cu(100), Fe/Cu(100) and Ni/Fe/Cu(100)</td>
</tr>
<tr>
<td>D. J. O'Connor</td>
<td>Helium ion microscope - high resolution, high contrast microscopy for nanotechnology</td>
</tr>
<tr>
<td>W. K. Pang</td>
<td>Depth-profiling of thermal dissociation of Ti$_3$SiC$_2$ in vacuum</td>
</tr>
<tr>
<td>J. G. Partridge</td>
<td>Deposition of high quality metal and metal oxide thin films using a filtered cathodic vacuum arc</td>
</tr>
<tr>
<td>Author</td>
<td>Title</td>
</tr>
<tr>
<td>------------------------</td>
<td>-------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>J.R. Prescott</td>
<td>Thermoluminescence spectra of quartz from single crystals</td>
</tr>
<tr>
<td>Daniel Pyke</td>
<td>Raman measurements of hydrogen ions implanted into silicon</td>
</tr>
<tr>
<td>Daniel Pyke</td>
<td>Hydrogen refinement during solid phase epitaxial crystallisation of buried amorphous silicon layers</td>
</tr>
<tr>
<td>M. Raiber</td>
<td>Application of environmental isotopes to study aquifer interactions and their impact on groundwater salinisation in western Victoria</td>
</tr>
<tr>
<td>A.B. Rosenfeld</td>
<td>Investigation of monolithic Si ΔE-E telescope using IBIC and application for radiobiological efficiency estimation in proton therapy</td>
</tr>
<tr>
<td>Y M Sabri</td>
<td>Gold nano-structures electroplated on au electrodes of quartz crystal microbalance (QCM) for enhanced mercury vapour sensitivity</td>
</tr>
<tr>
<td>R. Siegele</td>
<td>Localisation of trace metals in hyper-accumulating plants using μ-PIXE</td>
</tr>
<tr>
<td>Vijay Sivan</td>
<td>Wafer scale etching of lithium niobate using conventional diffusion process</td>
</tr>
<tr>
<td>Michael Smith</td>
<td>Establishment of efficiency function for the gamma-ray spectrometry system</td>
</tr>
<tr>
<td>Paul Spizzirri</td>
<td>A TEM study of Si-SiO$_2$ interfaces in silicon nanodevices</td>
</tr>
<tr>
<td>Paul Spizzirri</td>
<td>Characterisation of high quality, thermally grown silicon dioxide on silicon</td>
</tr>
<tr>
<td>Paul Spizzirri</td>
<td>An EPR study on the activation of low energy phosphorus ions implanted into silicon</td>
</tr>
<tr>
<td>S. Sriram</td>
<td>Modified unit cell of preferentially oriented strontium-doped lead zirconate titanate thin films on Pt/TiO$_2$/Si</td>
</tr>
<tr>
<td>Alexander M. St John</td>
<td>Separation of uranium using polymer inclusion membranes</td>
</tr>
<tr>
<td>Eduard Stelcer</td>
<td>Ion beam analysis and positive matrix factorisation modeling: tools for exploring aerosol source fingerprints</td>
</tr>
<tr>
<td>Jessica A. van Donkelaar</td>
<td>Single ion implantation using nano-apertures: precision placement for CTAP</td>
</tr>
<tr>
<td>L. Velleman</td>
<td>Template fabricated gold nanotubes membranes: a nucleation and growth study</td>
</tr>
<tr>
<td>Dinesh Kumar Venkatachalam</td>
<td>Surface fraction statistics of gold nanoclusters of dissimilar sizes determined by RBS</td>
</tr>
<tr>
<td>Byron J. Villis</td>
<td>A low energy, angle dependent, defect study of H implanted Si</td>
</tr>
<tr>
<td>Xingdong Wang</td>
<td>Synthesis, characterization and photocatalytic application of porous Au/TiO$_2$ nano-hybrids</td>
</tr>
<tr>
<td>J.L. Wang</td>
<td>Magnetic phase transitions in PrMn$_{2-x}$Fe$_x$Ge$_2$</td>
</tr>
<tr>
<td>Mark Thomas Warne</td>
<td>History of natural environmental events in a pristine estuary: ostracod proxies and $^{210}$Pb chronology from Wingan Inlet, Victoria</td>
</tr>
<tr>
<td>A-M. M. Williams</td>
<td>Iron deposition in archaeological teeth</td>
</tr>
<tr>
<td>Name</td>
<td>Title</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Myint Zaw</td>
<td>Oxidation profiles of arsenic, iron, manganese and uranium in tailings dam samples using x-ray absorption near-edge structure spectroscopy</td>
</tr>
<tr>
<td>Waven Zhang</td>
<td>Reduction of titanium dioxide: comparison of analysis by Raman spectroscopy and XRD</td>
</tr>
<tr>
<td>B. Zorko</td>
<td>Measurement of actinides by the unfocused beam AMS</td>
</tr>
</tbody>
</table>
Posters
Deposition of high quality metal oxide thin films using a filtered cathodic vacuum arc

N. Biluš Abaffy, M. Field, J. G. Partridge, J. Du Plessis and D. G. McCulloch
Applied Physics, RMIT University, 124 LaTrobe Street, Melbourne, Australia

Email: jim.partridge@rmit.edu.au

A Filtered Cathodic Vacuum Arc (FCVA) system has been used to produce high quality metal oxide thin films. The FCVA deposition conditions have been tuned by varying the Ar and O₂ gas flows, substrate bias, arc current and process pressures in order to produce the desired composition of each metal oxide. X-ray photoelectron spectroscopy, atomic force microscopy and ellipsometry have been used to characterise aluminium oxide, titanium oxide, tin oxide, and hafnium oxide layers deposited using the FCVA system. The capability of the FCVA system to produce high quality optical coatings is demonstrated in a tri-layer antireflection coating supported on silicon.

1 Introduction

The proposal that a vacuum arc plasma could be used to deposit thin-films was first put forward over a century ago [1]. Recent refinements have made this technique a desirable alternative to other thin-film deposition methods. In particular, the incorporation of a magnetic filter in a method known as Filtered Cathodic Vacuum Arc (FCVA) has been used to produce films that are macroparticle free and hence smoother than those deposited by electron beam evaporation or magnetron sputtering [2]. Furthermore, because neutral atoms are also filtered out of the plasma beam, a substrate bias can be used to vary the energy of the incident ions which can affect the microstructure of the resultant film. Potential applications of FCVA metal oxide films include gas sensing, anti-reflection coatings, heat mirrors, electrochromics and high-k dielectric coatings for metal oxide semiconductor field effect transistors (MOSFETs). In this work, several oxides including Al₂O₃, TiO₂, SnO₂ and HfO₂ have been fabricated using FCVA deposition and their physical, optical and electrical properties have been measured. In order to highlight the benefits of FCVA deposition for optical coatings, we fabricated a tri-layer antireflection coating on silicon. We have used theory to predict the optimum design for a tri-layer anti-reflection coating and then replicated this experimentally.

2 Experimental methods

All the thin film depositions reported here were performed using a nanofilm [3] custom made FCVA system, shown schematically in Fig. 1. The main components of the system are the cathode, double-bend filter and the deposition chamber. The source features a water-cooled rotating M60 threaded copper base which accepts a high purity 70mm diameter metal cathode. The cathode is struck by a grounded mechanical striker to initiate the plasma. The system has a double-bend magnetic filter [4] to prevent deposition of macroparticles onto the sample. The deposition chamber features a retractable shutter on which a Faraday cup is mounted. This Faraday cup provides a current signal which is used to assess the stability of the plasma before and during sample depositions. The sample is mounted on a holder which slides onto an electrically isolated arm inside the chamber. A bias voltage may be applied via a high-voltage feed-through located close to the arm. Using mass-flow controllers, oxygen was bled into the chamber in the vicinity of the substrate while argon gas was released next to the cathode source to promote plasma stability and decrease cathode poisoning.
effects which result from oxidation of both the cathode itself and the metal deposited on the chamber surrounding the cathode.

3 Results and Discussion

Fig. 2 shows the refractive index of a series of aluminium oxide films deposited using various argon and oxygen flow rates. The most stoichiometric film, with an Al content of 42%, was produced using Ar and O₂ flow rates of 20 and 10 mL/min respectively. This film was found to have optical constants of n = 1.76 and k = -0.026, which agree with values reported in the literature [5].

Table 1 shows the optimised conditions (cathode current, process pressures and substrate bias) under which the metal oxides have been deposited. Also shown are the stoichiometries of the films deposited under the listed conditions which were measured using X-ray Photoelectron Spectroscopy (XPS). Auger depth profiling was also performed and showed that the films were homogeneous. AFM has shown that RMS roughness for the deposited oxides is less than 1% of the total film thickness for all the oxides investigated.

Table 1 The experimental conditions under which the various metal oxides have been deposited

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>Cathode current (A)</th>
<th>Gas flow (mL/min)</th>
<th>Process Pressure (mT)</th>
<th>Substrate Bias (V)</th>
<th>XPS stoichiometry metal%</th>
<th>oxygen%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>110</td>
<td>20 Ar, 10 O₂</td>
<td>1.3</td>
<td>-200</td>
<td>42</td>
<td>58</td>
</tr>
<tr>
<td>TiO₂</td>
<td>120</td>
<td>10 Ar, 20 O₂</td>
<td>1.2</td>
<td>-50</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>SnO₂</td>
<td>65</td>
<td>10 Ar, 20 O₂</td>
<td>1.2</td>
<td>0</td>
<td>33</td>
<td>67</td>
</tr>
<tr>
<td>HfO₂</td>
<td>195</td>
<td>40 Ar, 5 O₂</td>
<td>1.8</td>
<td>-100</td>
<td>33</td>
<td>67</td>
</tr>
</tbody>
</table>
In order to demonstrate the capabilities of the FCVA system, a tri-layer anti-reflecting optical coating was fabricated. The FilmStar software package [6] was initially used to calculate the optimum layer thicknesses for a tri-layer Al$_2$O$_3$/Al/Al$_2$O$_3$ coating. These simulations showed that the aluminium layer thickness was critical in minimising the reflectance of this tri-layer system. The final optimised design is shown in Fig. 3(a) with the resulting theoretical reflectance shown in Fig. 3(b).

A tri-layer coating was constructed by first depositing a 120 ± 5nm Al$_2$O$_3$ film onto a silicon substrate. After inspection, the sample was coated with 6nm of Al. This Al thickness was chosen to account for an estimated 1-3nm thick native oxide [7] layer which was expected to grow on the freshly deposited Al surface. Finally, the sample was coated with a 65 ± 5nm thick Al$_2$O$_3$ layer. The reflectance of the sample was then measured and is shown in Fig.3(b). There is good agreement between the response of this sample and the simulation.

![Diagram of tri-layer anti-reflection coating](image)

**Fig. 3** The tri-layer anti-reflection coating (a) designed using FilmStar with layer thicknesses (T) as shown and (b) the reflectance of this theoretical design and the fabricated tri-layer optical system.

### 4 Conclusion

The FCVA was found to produce homogenous and stoichiometric metal oxide films with low surface roughness. Further investigations will be carried out to characterise the microstructure of the coatings using electron microscopy, with the aim of understanding the relationship between deposition parameters and their electrical/optical properties.

### Acknowledgments

The authors would like to thank the Defence Science and Technology Organisation (DSTO) for making this research possible through their funding.

### References


Detection and placement of single ions in the keV and MeV regimes: MeV ion-aperture scattering

A. Alves 1, J. van Donkelaar 1, C. Yang 1, D. N. Jamieson 1, M. Taylor 2, P. N. Johnston 2

1 Centre for Quantum Computer Technology, Microanalytical Research Centre, School of Physics, University of Melbourne, Australia
2 Physics, School of Applied Sciences, RMIT University, Australia

Abstract

Emerging quantum technologies rely on the placement of single ions with precision in the order of 10nm. Ion beams in the keV and MeV regimes, developed as tools in nuclear analysis, offer fabrication of novel solid state devices at the ultimate resolution limit of an implanted single ion (for doping) or a single ion track (for lithography). Examples include solid state quantum computers and photonic band gap materials. There are two criteria that must be met in order to use single ions; (1) single ion detection and (2) placement of single ions with location accuracy. This paper summarises the methods used for detection and placement of single ions in the two energy regimes.

Introduction

keV regime

An ion with energy in the order of 1keV per nucleon has a nanoscale ion range and straggling and therefore a well defined final resting location with respect to the position it entered the target. For example a 14keV P ion in a Si substrate has an ion range of 28nm and straggling FWHM of 26nm [1]. Implantation in this regime has previously been executed using a single 14keV P ion using a poly(methylmethacrylate) PMMA mask to define the ion’s location in the Si detector substrate[2]. This technique has been used to demonstrate charge qubits [3] in the Kane quantum computer scheme, an array of 31P atoms embedded in 28Si substrate with nanometre accuracy [4]. There is, however, no capacity to use this method for scaling up the production of qubits. When using an immovable PMMA mask the yield of devices in which one ion enters each aperture (for a multi-aperture mask) is unacceptably small, since we cannot tell which of the apertures the detected ion has passed through. To place multiple, individually detected, ions with nanometre precision a separate, movable mask is considered here. The first application of this technology will be a line of precisely placed single atoms. This will be used to realise an experimental demonstration of the coherent transfer by adiabatic passage (CTAP) principle [5] for the transfer of quantum information in a solid state quantum computer.

MeV regime

An ion with energy in the order of 1MeV per nucleon has long range in a resist and a well defined latent damage track. For example a 1.5MeV He ion in the resist (PMMA) has a range of ~10µm and track core radius of ~2nm [6-7]. By etching the latent damage track into a void high aspect ratio, nanoscale structures is fabricated. Ion beam lithography (IBL) in this regime has been executed using multiple low linear energy transfer (LET) ions with a focused beam [8] or using a mask [9]. Also tracks in PMMA have been etched from single ion impacts of high mass, high LET ions [10]. A standard text in the lithography field by S.M. Sze [11], points out the significant advantages of the IBL technique. As a direct write technique IBL must be viewed as a
serial process not capable of high throughput and at present the high resolution/direct write technique of electron beam lithography EBL is central in fulfilling the roles of rapid prototyping, mask making for optical, UV and X-ray lithography and fabrication of stamps for nano-imprint lithography. It is comprehensible that IBL will fulfil the similar rolls of prototyping, mask and stamp making, but in cases where a high aspect ratio structure is required.

A key area of interest for the application of IBL is photonic band gap materials. A photonic band gap occurs in a material where periodic changes in refractive index prevent light of certain wavelengths from propagating inside the medium. This phenomenon is analogous to an electronic band gap where many of the properties of an electron in a semiconductor can apply to a photon in a photonic band gap. The positioning of voids in a material with dimensions less than the desired band gap wavelength leads to the ability to fabricate an operational photonic crystal and is an ideal application for the high aspect ratio structuring of IBL. Such materials promise a revolution in computing and communication with uses such as optical waveguides that can perform a right angle turn, optical switches, filters or couplers to be made utilising the photonic band gap. The book by Joannopoulos et al. gives a good overview and theoretical analysis of photonic crystals [12]. These materials draw their inspiration from photonic structures in biology that produce iridescent colours and have already been studied extensively [13-14]. Many applications and previous work were reviewed in the August 2001 MRS Bulletin [15].

A separate, movable mask is also considered here for the placement of MeV ions in IBL using the common resist, PMMA and can realistically be used to fabricate 2D and 3D structures with resolution in the range from 10-1000nm. The photonic band gap fabricated would operate at near infrared and optical wavelengths, such as the 1550nm used in telecommunications applications.

**Detection of single ions is summarised**

For precise placement of single ions to occur the arrival of the ion in the substrate, or through the resist must be detected. Without this capacity a beam of ions might be accurately placed, but not a single ion. Single keV ion detection using P ions from a Colutron source has been developed for use with an immovable PMMA mask [2] and requires advanced detector design and cooling with liquid nitrogen to overcome the electronic noise threshold. A single keV ion only produces a minute electronic signal (average ionisation energy of 3.6keV) following an ion impact. However single MeV ion detection is easy to achieve through use of a commercial Hamamatsu\textsuperscript{TM} S1223-01 Si PIN photodiode. The pulse height is sufficiently higher than the noise floor and no cooling or advanced electronic design is needed.

**Placement of single ions is summarised**

There are two methods of placement of an ion beam, focusing and masking. The focused beam is moved relative to the target via an electromagnetic field that bends the stream of charged ions. This technique is already widely used in the keV regime to perform focused ion beam (FIB) milling with high precision [16], and in the MeV regime applied to IBL [17]. In both energy regimes the ion optical components must be completely controlled over the entire ion accelerator and there are limitations to the ion species that can be selected. The presence of vibrations and stray fields will also affect the beam resolution.
The aim of this paper is to consider retrofitting a nanoscale mask in close proximity to the target surface in an already existing ion accelerator, in both the keV and MeV regimes. The masked beam is moved relative to the target via a scanning stage, using piezoelectric drive. An MeV ion beam system is given priority due to the ease with which MeV ions are detected and therefore experimental results only exist in that regime, however the intention is to apply the technology in both energy regimes.

**Mask fabrication and characterisation**

The fabrication of nano-apertures has been accomplished elsewhere by milling Si with a keV Ga focused ion beam (FIB). Such apertures have been used to mask low energy ions for implantation into a Si substrate [18-20] and to carry out metallic evaporation (nano-stencilling) onto a Si substrate through the aperture [21-23]. The smallest apertures have a width less than 10nm [24]. FIB milling has been attempted locally using 8µm thick Si cantilevers [25]. Slotted apertures have been created for application to the confinement of both MeV and keV ion beams. A slot will confine the beam of ions in one dimension, therefore may only be applied with high resolution in that dimension. In the CTAP application only a 1D line of atoms is required, therefore a slot can be used. Forming the beam limiting aperture from crossed slots is proposed so that alignment in the non-critical dimension is relaxed. One slot is patterned by EBL in a PMMA mask on the substrate and the other in the movable, FIB milled, cantilever. SEM images of FIB milled slots are shown in figure 1.

![Figure 1](image.png)

Figure 1. (a) A series of slots milled through an 8µm thick cantilever. (b) An 8µm thick cantilever is first thinned, then the slot milled.

The Si thickness must be greater than the ion range. The ion range of 1.5MeV He in Si is 5.5µm so the apertures are milled directly into the 8µm Si. Using a beam current of 7.0nA a series of slots were milled and are shown in figure 1(a). The slot width on the top milling surface was found to be approximately 0.5µm for slot number two. For the milling of slots for keV ion placement the Si thickness can be reduced. For 14keV P in Si the ion range is 28nm. To achieve high resolution the slot is milled through a thin section of Si. Figure 1 (b) shows an 8µm thick Si cantilever that has first been thinned in two areas using a high beam current of 7nA. For the final slot a beam current of 1pA was used and the final slot width was approximately 0.1µm.
Experimental verses simulation

Experimental transmission spectra have been collected for analysis using a focused 1.5MeV He beam. Slot number two (see figure 1 (a)) was mounted above a Hamamatsu PIN photodiode detector and a pulse height spectrum acquired. Previously a determination of the damage rate of the photodiode detector was made [26] using slot number three (with a slot width of approximately 0.8µm). It was found that a 1% peak shift was observed due to damage in the detector after $26 \times 10^3$ ion impacts. The experimental spectrum acquired from slot number two had 2307 ion impacts recorded and can therefore be compared with simulation results without a significant damage induced peak shift.

The resolution that can be achieved when using an aperture to confine a beam of ions depends on the level of ion scattering within the aperture material. In an attempt to fully characterise the ion-aperture scattering the experimental spectrum has been compared with a simulation. Simulations of the ion scattering within a cylindrical Si aperture have been carried out in the work of Taylor et al. [27] using a range of ion species. The results indicate that the masking is effective with the percentage of ions transmitted without scatter ranging from 82-93% over the range of geometries reported, with the aperture thickness approximately equal to twice the ion range. This simulation was developed from the TRIM code of Zeigler [28]. This package was implemented here to match the experimental results and simulation. The input was configured with $10^5$ 1.5MeV He ions incident upon a cylindrical Si aperture, 0.5µm wide and 8µm thick. It was not possible to use this code to simulate a slotted aperture. The simulation outputted the energy and direction cosine of each ion that had emerged

![Figure 2. Experimental vs Simulated spectra](image)
from the back side of the aperture. The data was binned so that the full energy peak from the simulation was in the same position as the centre of the experimental full energy peak. The peak areas of the simulated and experimental full energy peaks were normalised and a comparison of the two spectra is shown in figure 2.

In the experimental result 40% of the total counts in the spectrum do not have full energy, therefore, have been scattered from the aperture. In the simulation 15% of the ions have reduced energy, calculated excluding simulated counts below the lower level discriminator of the experimental spectrum. The discrepancy between results is expected due to the known discrepancy between the simulated and experimental aperture geometries. The main difference being that the width of the FIB milled aperture is not uniform. With additional geometries incorporated into the simulation a match to experimental data will reveal the actual internal aperture shape and be a valuable tool in aperture characterisation.

**Conclusion**

A strategy for the detection and placement of single ions in the keV and MeV regimes has been conceived. The experimental work towards this goal has begun with aperture fabrication using FIB milling and aperture characterisation using ion transmission spectra.

**Acknowledgements**

The work is funded by the Australian Research Council, the Australian Government and US Army Research Office under Contract No. W911NF-04-1-0290.

**References**

[26] A. Alves APPC, to be published
The effect of annealing temperature on the optical properties of sputter-deposited hafnium oxide thin films
K. Belay, N.S. Muhammad and R.G. Elliman
Electronic Materials Engineering Department, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia.

Abstract
Hafnium oxide films are of interest as replacement for silicon dioxide in future microelectronic devices due to their high dielectric constant (high-k) and are used as dielectric coatings or dielectric mirrors in many optical applications due to their high refractive index (n > 2) and low optical loss. These properties make hafnium oxide a potential candidate for the fabrication of integrated planar waveguide devices or structures that combine electronic and photonic functionality on a single chip. In this study we examine the effect of deposition and processing conditions on the refractive index of hafnium oxide.

Introduction
Hafnium dioxide (HfO₂) films have potential applications in microelectronic where they are of the interest as a replacement for silicon dioxide (SiO₂), which has been a predominant material in the metal insulator semiconductor field effect transistors (MISFET) for several decades. This is largely a consequence of the high dielectric constant of this material [1,2,3]. Significantly, the high dielectric constant of HfO₂ means that it has a high refractive index, and as a consequence is used extensively in optical devices such as dielectric mirrors.

One potential limitation of HfO₂ is the fact that it crystallizes at relatively low temperatures, ~300-400°C. This can result in increased leakage currents in device applications due to grain boundary conduction. It is also expected to affect the refractive index of films. A comprehensive understanding of the effects of crystallisation on the optical properties of these materials is essential for their effective application.

In this report, the refractive index of HfO₂ films is examined as a function of annealing temperature.

Experimental
Thin films of HfO₂ were deposited onto p-type (100) Si substrates with an ATC 2400-V Sputtering system. The system was pumped to a base pressure of 2e10⁻⁷ Torr before backfilling with Ar or N₂ to an operating pressure of 4e10⁻³ Torr. Sputter deposition was achieved with an RF sputter source using HfO₂ as a target. The deposition rate was calibrated for different RF power settings using a quartz crystal oscillator as a mass sensor. The crystal detector was set at the centre of the chamber and at the working distance from the target. Films of 100 and 500nm thickness were then deposited onto 3” Si substrates at the rate of 4.5nm/min at room temperature using either Ar or N₂ ambients. The substrate was rotated at 2 rpm during deposition to ensure uniformity of the deposited film.

Samples of 5x5mm were cleaved from the HfO₂ coated Si wafer. Rutherford Backscattering Spectroscopy (RBS) using 2MeV He⁺ ions was employed to confirm the thickness and composition of deposited films. Samples were then annealed at temperatures in the range from 200 to 1000 °C using a quartz-tube furnace and an Ar ambient. The refractive indices of the annealed samples were then calculated from
wavelength-dependent reflectivity measurements undertaken with a Film Tek™
system. Selected samples were analysed by transmission electron microscopy (TEM)
to assess their physical structure.

Results and Discussion

Fig. 1 shows an RBS spectrum of an as-grown 100nm HfO₂ film, together with a
simulation of the spectrum using RUMP. The analysis shows that the film has a
thickness of 108nm and that it has a stoichiometry of HfO₂ within experimental
uncertainty.

![RBS spectrum of an as-grown 100nm HfO₂ film](image)

As reported elsewhere [4], HfO₂ thin films crystallise at temperatures in the range
200-400°C. Figs. 2 shows the calculated refractive index as a function of wavelength
for 500nm films annealed in Ar at temperatures in the range 200-1000°C. These
preliminary results show that the refractive index decreases monotonically with
wavelength over the wavelength range 400-1800nm, and that it decreases with
increasing annealing temperature in the range 200-800°C. After annealing at 1000°C
the refractive index appears to increase to a value close to that of films annealed at
400°C. This suggests that there is an optimum annealing temperature between 800 and
1000°C for which the refractive index of the film reaches a minimum value.
Fig. 2: Refractive indices (n) vs. wavelength (λ) for HfO₂ films annealed at temperatures in the range 200-1000°C.

TEM analysis confirmed that films crystallised in the temperature range between 200°C and 400°C. Thus the initial reduction in refractive index for temperatures in the range up to 800°C is correlated with crystallisation of the films. The subsequent increase in refractive index for films annealed at 1000°C is counter to this trend and may result from densification of the film due to elasto-plastic flow. In future work, nanoindentation measurements will be performed to test this assertion.

Acknowledgements

The author acknowledge partial financial support from the Australian Research Council and technical assistance from Mr David Llewellyn.

References

The introduction of the k0-method of neutron activation analysis at ANSTO

John W. Bennett
Australian Nuclear Science and Technology Organisation,
PMB 1, Menai, NSW 2234, Australia
john.bennett@ansto.gov.au phone (02) 9717 3743

Abstract
The introduction of the k0-method of neutron activation analysis (k0-NAA) at ANSTO will provide the Australian research community with a versatile, user-friendly and reliable tool for multi-elemental analysis. The method has wide applicability in geoscience, mineral processing, archaeological, health and environmental research.

Introduction
Australia’s new 20 MW research reactor, OPAL, was officially opened in April 2007. It was designed specifically for radioisotope production, silicon ingot doping for the semiconductor industry, scientific research and neutron activation analysis. Facilities for instrumental neutron activation analysis (INAA) and delayed neutron activation analysis (DNAA) provide true thermal neutron fluxes from 3.4×10^{12} to 1.3×10^{14} cm^{-2}.s^{-1}.

The OPAL reactor core design is very compact in order to maximise the neutron flux. It is located under 13 metres of demineralised light water, near the bottom of the main open pool. The core is surrounded by an enclosed reflector vessel containing heavy water. This acts as a neutron reflector and ensures the availability of high neutron fluxes over a large volume. The facilities for the irradiation of materials are within the reflector vessel. A particular advantage for INAA is that the neutron spectrum is highly thermalised at the outer measurement locations.

Method of INAA
INAA is a method of quantitative elemental analysis based on the nuclear activation of the chemical elements present in an analysed sample. Elements are activated by placing the sample in the neutron flux of the reactor, producing radioactive nuclides by means of nuclear reactions. The rate of activation of a given element is proportional to the incident neutron flux, the number of target nuclei and the neutron cross-section of those nuclei. The induced activity also depends on the duration of the irradiation and the half-life of the formed radionuclide. The specific activity of each radionuclide may be determined by measuring the characteristic gamma radiation emitted from the sample after it is removed from the reactor. The energy and intensity of the gamma-rays are measured using an ultra-high purity germanium (HPGe) detector.

Whereas INAA can in principle be carried out ‘absolutely’, using nuclear data and measured neutron flux parameters, much greater accuracy can be achieved by using ‘comparator’ methods of standardisation. The two different methods of standardisation that will be implemented for INAA in OPAL are described below.
Strengths of INAA

In the decades after it became available in the mid-1940s, neutron activation analysis was considered to be the pre-eminent analytical method because few, if any, alternative techniques could match its high sensitivity (ppm or ppb) and accuracy. Even now that inductively coupled plasma mass spectrometry (ICP-MS) is available, NAA has the potential for superior accuracy because ICP-MS is more subject to matrix effects and interferences, at least for trace analysis.

The particular advantages of INAA are that:

- the method is non-destructive, allowing full recovery of samples;
- measurements are made of the bulk composition so samples do not need to be dissolved;
- around 62 elements can be determined (although not lead or light elements such as hydrogen, carbon, nitrogen or oxygen);
- multi-elemental determination can be made in one measurement;
- the method is traceable to the SI system of units and qualifies as a primary ratio method as defined by the Consultative Committee for Amount of Substance (CCQM);
- measurement uncertainties of less than 3.5 per cent may be routinely achievable; and
- high reproducibility between laboratories and over time has been demonstrated.

In many applications INAA may be the best and only analytical technique required. In others it may comprise one of a suite of analytical methods or may serve as a primary calibration or reference method.

Methods of Standardisation

Relative (comparator) method

The relative (comparator) method of standardisation has been used successfully at ANSTO for more than three decades. This method has the advantages of being obvious, simple, accurate and traceable.

In this method a sample is co-irradiated with a standard reference material that has an accurately known, certified composition. The ratio of the intensity of the characteristic gamma-ray energy peaks for a particular activated element that appears in both the sample and the comparator can be used to determine the amount of that element in the unknown sample. This relative method eliminates errors due to uncertainties in nuclear and reactor parameters, detector efficiencies etc.

Whilst the method can produce the most accurate results, this can only be achieved if it is used with great care. It is not always easy to ensure that for both the sample and standard: the measurement geometry is matched; the matrix composition is matched; the full energy gamma-ray detection efficiency of the HPGe detector is identical; and the neutron self-shielding factors are identical. The method is also not well-suited to multi-element analysis due to the need for the preparation or acquisition of appropriate standards. There is also the potential loss of quantitative information.
when elements are found to be present in the sample that are not certified in the standard.

ANSTO will continue to use the method in applications for which it is best suited.

$k_0$-method

In order to overcome some of the practical shortcomings of the relative method, the $k_0$-method of standardisation was developed more than 25 years ago in Europe and is now used in many NAA laboratories around the world. The $k_0$-method of standardisation is widely used for multi-element NAA because it allows flexibility with respect to changes in the neutron spectrum and gamma-ray counting geometry while eliminating the task of repeatedly preparing numerous standards. As well as eliminating the need for standard reference materials, the $k_0$-method is traceable and the measurement error can be typically reduced to around 3.5 per cent. The method is currently being introduced to expand the versatility of INAA at ANSTO.

The $k_0$-method can be considered to be an absolute standardisation that uses one single composite nuclear constant for each chemical element, the $k_0$-factor. All required $k_0$-factors have been experimentally determined and tabulated for the case where gold is used as the co-irradiated monitor of neutron flux. It is also necessary to have characterised the neutron flux at the irradiation position in the reactor with respect to: (a) the ratio of the thermal to epithermal neutron flux; and (b) the functional relationship between the epithermal neutron flux and neutron energy.

In practice a sample is co-irradiated with a gold monitor in the form of a wire or foil. Following irradiation, the sample and monitor are each measured using a HPGe detector for which the detection efficiency with respect to gamma-ray energy and geometry has been accurately determined. Readily available software that incorporates $k_0$-factors, gamma-ray spectrometry data and reactor characterisation data is used to calculate the elemental composition of the sample.

Hardware and Software

For relative INAA at ANSTO there are three ORTEC HPGe co-axial p-type detectors in use, each having a relative efficiency of around 20 per cent at 1.33MeV. Two of these detectors have automatic sample changers, for measuring samples that contain longer-lived radioisotopes.

In order to make optimum use of the $k_0$-method, two new gamma-spectrometry systems have been purchased. For samples irradiated in the short residence time facility, there is an ORTEC model GEM25P-PLUS p-type HPGe co-axial detector, 32.2 per cent relative efficiency at 1.33MeV, with ultra-high count rate preamplifier. For samples irradiated in long residence time facilities, there is an ORTEC model GEM25P4 p-type HPGe co-axial detector, 27.7 per cent relative efficiency. Both systems employ an ORTEC model DSPEC-Pro digital spectrometer that incorporates the MAESTRO-32 multi-channel analyser emulation software for Microsoft Windows. This spectrometer allows for ‘loss free’ or ‘zero dead time’ accumulation.

An additional automatic sample changer is being acquired (Changer Labs, Oak Ridge). The unit can hold up to 100 samples and has features that are particularly suited to INAA.

The package HyperLab 2005 (HyperLabs Software, Budapest) has been chosen for the analysis of gamma ray spectra. This deconvolution software is able to handle the ‘loss free’ spectra that may be accumulated by the spectrometer.
The two most widely used software packages for $k_0$ analysis, Kayzero for Windows ($k_0$-ware, Delft) and $k_0$-IAEA (IAEA, Vienna), have been installed at ANSTO.

**Quality**

The quality management system operating in ANSTO’s ATLAS analytical laboratories has ISO 9001:2000 accreditation. Consideration will be given to seeking ISO 17025 accreditation for INAA measurements.

Once the complete suite of activation analysis techniques has been commissioned, ANSTO will be keen to participate in inter-laboratory comparison programs, benchmarking exercises and to be involved in international NAA networks.

**Conclusions**

The installation of state-of-the-art systems and methods for neutron activation analysis using the new OPAL research reactor will provide exciting research opportunities. Beneficial outcomes can be expected across a broad range of disciplines including geoscience, mineral processing, archaeology, health and the environment.

**References**


Investigation of surface crystallites on C54 titanium silicide thin films using transmission electron microscopy

M. Bhaskaran a *, S. Sriram a, D. R. G. Mitchell b, K. T. Short b, and A. S. Holland a

a Microelectronics and Materials Technology Centre, School of Electrical and Computer Engineering, RMIT University, GPO Box 2476V, Melbourne, Victoria 3001, Australia
b Institute of Materials Engineering, Australian Nuclear Science and Technology Organisation (ANSTO), PMB 1, Menai, New South Wales 2234, Australia

* Contact author – E-mail: madhu.rock@gmail.com, Tel.: +61-403596934

Abstract

The C54 phase of titanium silicide (TiSi2) is the desirable low resistivity phase for use in ohmic contacts. This article discusses the occurrence of crystallites on the surface of titanium silicide thin films formed by vacuum annealing, which will influence the estimation of contact resistance in multi-layer ohmic contacts. Cross-sectional transmission electron microscopy analysis of these samples indicates the existence of a uniform thin film with crystallites on the surface at regular intervals. The presence of these crystallites results in enhanced surface roughness of the titanium silicide thin films, the presence of which has also been verified by atomic force microscopy surface scans. Jump ratio maps and dark field imaging with hollow cone illumination have been used to study the composition and crystallographic orientation of these crystallites. Results have shown that the crystallites have the same composition and orientation of the underlying grain, with each grain being about a micron in size.

Keywords thin films, titanium silicide, C54 phase, TEM, AFM

1. Introduction

Titanium silicide (TiSi2) of the C54 phase is highly suitable for use as local interconnects and in ohmic contacts. Titanium silicide exists in two phases – C49 and C54. The desired phase of TiSi2 is C54, as it exhibits low resistivity and has better stability.1

In this article, the occurrence of crystallites on the surface of C54 TiSi2 thin films has been extensively studied using transmission electron microscopy (TEM) and atomic force microscopy (AFM). These crystallites are of interest, as the occurrence of such surface crystallites (previously unreported) play a crucial role in contact resistance estimation in multi-layer ohmic contacts. In modelling or calculating the contact resistance, a fixed contact area cannot be assumed, due to accentuated surface roughness.

2. Experimental Details

Thin films of titanium (100nm) were deposited on n-type silicon (100) wafers (resistivity of 1-10 Ωcm) by electron beam evaporation. The native oxide on the silicon wafers was removed by a buffered hydrofluoric acid dip, prior to titanium deposition. The samples were then annealed in vacuum (1 x 10⁻⁵ Torr) at 800 ºC for 60 minutes to form approximately 250nm of TiSi2 thin films. In order to minimize oxygen contamination during annealing, a HF dipped silicon wafer was placed polished side down on the nickel coated samples.1

Mechanical polishing was used to create wedge-shaped XTEM specimens. These were subsequently thinned to electron transparency by argon ion milling. The XTEM analysis was carried out at an accelerating voltage of 200 kV on a JEOL 2010F TEM with a Gatan Imaging Filter (GIF2001) and an EmiSpec E Vision energy dispersive...
X-ray analysis (EDX) system. The surface morphology of the silicide thin films was studied using an AFM. AFM scans were performed in contact mode using a Digital Instruments Dimension 3100 scanning probe microscope with a Nanoscope IIIa controller. The composition of the titanium silicide thin films was analysed using Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) depth profiles. These depth profiles show a very uniform composition for titanium and silicon, and an ideal 1:2 ratio of titanium to silicon. The presence of a thin layer of surface oxide (as a result of the ‘snowplough’ effect) is also evident.

3. Results and Discussion

3.1. Surface morphology analysis

XTEM analysis of these samples indicates a uniform thin film with crystallites on the surface at regular intervals. The thickness of the titanium silicide thin film was determined to be 244±10nm. Figure 1(a) shows 100-150nm sized crystallites on the large titanium silicide grains (flat plate-like grains approximately 1μm in diameter). The AFM surface scan in Fig. 1(b) shows the presence of crystallites at regular intervals on the thin film surface. The presence of these crystallites results in enhanced average surface roughness (Ra = 26nm) of the titanium silicide thin films.

3.2. Crystallographic orientation analysis

Dark field imaging with hollow cone illumination was carried out to study the crystallographic orientation of these crystallites at a grain boundary in the titanium disilicide. This indicates that the crystallites have the same orientation as the underlying titanium silicide grain. This is shown in Fig. 2.
3.3. Composition analysis

Jump ratio maps (Fig. 3) have shown that the crystallites have the same composition as the thin film. The ratio maps for titanium, silicon, oxygen, and carbon were obtained for the region corresponding to the bright field image shown in Fig. 3(a). These maps show the presence of titanium and silicon only in the thin film and the crystallites [Figs. 3(b, c)]. The titanium map [Fig. 3(b)] shows a high titanium signal at the outer surface of the silicide, which is also rich in oxygen [Fig. 3(d)]. Figure 3(e) indicates presence of carbon in the hydrocarbon-based epoxy used for TEM specimen preparation.

![Figure 3: (a) Reference bright field XTEM image for jump ratio maps. (b-e) Jump ratio maps for titanium, silicon, oxygen, and carbon, respectively.](image)

4. Conclusions

In summary, cross-sectional TEM analysis results of titanium silicide thin films are discussed in this article. The presence of crystallites on the surface of the titanium silicide thin films is of particular interest and is discussed. XTEM analysis of these specimens indicates a uniform thin film with crystallites on the surface at regular intervals. AFM scans also show the presence of the crystallites. Dark field imaging with hollow cone illumination has shown that the crystallites have the same orientation as the underlying micron-sized grains. Jump ratio maps have shown that the crystallites and the film are of the same composition.

Acknowledgements

The authors acknowledge support for this project from the Australian Institute of Nuclear Science and Engineering (Award numbers AINGRA07071).

References

Introduction

Semicrystalline native starch granules display a hierarchical structural periodicity. Starch granules have a typical layered organization with alternating amorphous and semicrystalline growth rings of 120 to 400nm radial thickness. At a finer level of structural detail, the amorphous rings consist of amylose and amylopectin in a disordered conformation, whereas the semicrystalline rings contain lamellae with a repeat distance of 9-10nm that, in turn, contain alternating crystalline and amorphous regions (Cameron & Donald, 1992). The crystalline regions are mainly formed by double helices of amylopectin A chains packed laterally into a crystalline lattice, whereas amorphous regions contain amylose plus the amylopectin branching points. Small-angle X-ray scattering (SAXS) has been shown to be useful for studying the arrangement of crystalline and amorphous regions in semi-crystalline starch granules (Waigh, Jenkins & Donald, 1996). SAXS patterns from hydrated native starches show a broad scattering peak, from which the average thickness of the lamellar repeat unit (i.e. the thickness of the crystalline plus amorphous region) can be calculated. The position of the SAXS peak is related to the characteristic repeat length in granular starches, whereas peak width and intensity are mainly dependent on the regularity of the arrangement of lamellae and the electron density differences between the amorphous and crystalline regions of the lamellar structure.

Recent studies using SAXS and high-sensitivity differential scanning calorimetry (DSC) have increased our understanding of the influence of amylose located within amylopectin clusters in native starch granules. Starches with increased amylose content produced by genetic backcrossing of wheat cultivars grown in Australia have been studied by Blazek & Copeland (2007) and Hung et al. (2007a). These starches have been shown to possess characteristic pasting, swelling and viscoelastic properties related to amylose content, which indicates that they have differences in the structural organization that may be related to the lamellar architecture. In this study, SAXS together with several complementary techniques, such as DSC and X-ray diffraction (XRD), were employed to further examine structural features that provide starches, within a narrow range of amylose content, a wide range of functional properties.

Materials and Methods

Materials

Twelve wheat (Triticum aestivum L.) varieties selected from the set of samples described by Blazek & Copeland (2007) were used in the study. Amylose content was determined colorimetrically by iodine binding. Amylopectin chain length distribution was determined by fluorophore-assisted carbohydrate electrophoresis using the Beckman P/ACE System 5010.
Small Angle X-Ray Scattering

SAXS measurements were obtained with a Bruker Nanostar SAXS camera (available at ANSTO, Lucas Heights). Starch samples were presented in 2mm sealed glass capillaries as starch suspensions containing excess water above the settled starch granules. SAXS curves were plotted as a function of relative intensity $I$ versus $q$. Parameters of the SAXS curves were determined by fitting the experimental curves with peak-fitting models. SAXS peaks were characterized by the following set of parameters: intensity at peak maximum $I_{\text{max}}$, position of the peak $q_{\text{max}}$ and width of the peak $\Delta q$. The Bragg spacing $d$, representing the interlamellar distance, was calculated according to the Bragg equation.

XRD and DSC analysis

XRD measurements of starch samples were made with a Difftech Mini Materials Analyser X-ray diffractometer (GBC Scientific Equipment Pty. Ltd.). XRD diffractograms were acquired at room temperature (20±1°C) over the 2θ range of 5 – 35 at a rate of 0.50 degrees 2θ per minute and a step size of 0.05 degrees 2θ. DSC measurements were made using a Modulated Differential Scanning Calorimeter MDSC 2920 instrument (TA Instruments Inc., New Castle, DE). Starch with distilled water (starch to water ratio of 1:2) was heated from 30 to 140°C at a rate of 10°C/min in hermetically sealed aluminium pans.

Results and Discussion

Composition and pasting properties of wheat starches

Amylose content varied between 35 and 43%. A waxy wheat variety included in the study had 4% amylose content. The relative amounts of amyllopectin chains were classified into four fractions according to chain length. These were very short chains with degree of polymerization (DP) 6 to 12, medium length chains with DP 13 to 24, long chains with DP 25 to 36, and very long chains with DP greater than 36. The waxy wheat variety displayed more clearly defined peaks characteristic of A type crystallinity, whereas starch from commercial wheat displayed less well defined peaks compared to the remaining varieties. The XRD patterns of the 10 varieties from the other wheat samples were very similar. Starch melting temperature as measured by DSC varied among the varieties from 61.5 to 65.4°C, whereas the waxy variety displayed a melting temperature of 66.8°C. The Bragg spacing $d$, representing the lamellar distance calculated according to the Bragg equation, ranged from 10.7 to 11.2nm, whereas the lamellar distance of the waxy starch was 10.4nm. Width of the peak $\Delta q$ for the waxy wheat was 0.0242 compared to the average value of 0.0355 for the other samples and intensity at peak maximum $I_{\text{max}}$ was higher than for the remaining starches.

Effect of amylose content on the structural parameters of starch granules

Native starches extracted from different plants usually display a continuously decreasing trend in the intensity of the scattering maximum as the amylose content of the starches increases (Jenkins & Donald, 1995). This observation is accounted for by a decrease in the electron density difference between the crystalline and amorphous regions of the lamellae with increasing amylose content. Kozlov et al. (2007) suggested that an increase in amylose content is accompanied by accumulation of both amylose tie-chains, forming defects in crystalline structure, and amylose chains oriented transversely to the ordered stacks within amorphous regions. Disordered ends
of amylopectin double helices and/or pre-existing double helices not participating in
the formation of crystals are also contributing factors adding to the defects of the
crystalline arrangement and hence greater disorder in the packing of the lamellar
structure (Kozlov et al., 2007).

When the waxy wheat variety was compared with the other varieties used in this
study, the following trends were observed: the waxy variety had better defined XRD
peaks, higher melting temperature, smaller repeat lamellar distance, higher intensity
of the SAXS peak and lower variation in lamellar repeat distance. In the set of 11
other starch samples with normal and increased amylose content (waxy wheat
excluded), lamellar repeat distance increased, intensity of SAXS scattering peak
increased and variation in lamellar distance increased with increasing amylose
content. Additionally, within this amylose content (35 - 43%), higher proportion of
amylopectin chains with medium chain length (DP 13-24) was linked with increased
melting temperature, while higher proportion of short amylopectin chains (DP 6-12)
correlated negatively with melting temperature. It is also interesting to note that
melting temperature did not seem to be affected by amylose content and lamellar
arrangements as studied by SAXS.

Based on combined results acquired by SAXS, DSC and XRD analyses, we conclude
the differences between the waxy variety and the other samples used in this study are
due to amylose inducing defects in the crystalline regions and also accumulating in
the amorphous regions of the lamellar structure. Increased defects in amylopectin
crystallites in the amylose-rich starches compared to waxy starch is consistent with
observed lower melting temperature, less well defined XRD peaks and lower intensity
of SAXS peak, whereas more amylose in the amorphous regions was evident from the
greater repeat distance. We propose that the variation in the amount of crystalline
defects caused by amylose tie-chains is not significant within the range of amylose
content of the set of amylose-rich samples studied. This is consistent with invariance
in XRD patterns and lack of correlation between melting temperature and amylose
content. The observed increasing intensity of the SAXS peak with increasing amylose
content can be explained by assuming that thicker lamellae in starches with increased
amylose content provides higher mobility in the hydrated form, allowing better
plasticization and transformation of the nematic phase into a smectic phase due to
alignment of the double helices into register. We also assume there may be an
additional protective effect of amylose on the crystallites. It is possible that higher
amylose content provides a more intricate network, which helps to stabilize the
crystalline structure, consistent with increased lamellar thicknesses and higher peak
maximum $I_{\text{max}}$. Variations in the melting temperature and amylopectin chain length
distribution indicates that rather than crystalline defects or accumulating amylose in
amorphous regions, it is the amylopectin chain length distribution that prevails in
determining thermodynamic behaviour of studied starches within a narrow range of
amylose content. This is consistent with observed significant correlations between
melting temperature and amylose chain length and lack of correlation between
melting temperature and SAXS characteristics, including a lack of correlation
between SAXS characteristics and amylopectin chain length distribution.

Our results indicate that, for the samples analysed within a narrow range of amylose
contents, increased amylose content was not accompanied by the accumulation of
crystal defects as described in the literature (Kozlov et al., 2007). Nevertheless, when
structural characteristics of amylose-rich starches were compared with waxy wheat
starch, the general trends described by Kozlov et al. (2007) were confirmed. In
summary, over a wide range of amylose content, there are three main factors that exert influence on the structural parameters of native starch granules at a nano-scale: (1) amylose defects (both as amylose ‘tie-chains’ and amylose-lipid complexes) located in the crystalline lamellae, (2) population of amylose accumulated within the amorphous lamellae, and (3) chain length distribution of amyllopectin chains.

Several breeding approaches aiming at obtaining wheat starches with increased amylose content have been reported in the literature. Some of the breeding programs are based on the genetic manipulation of the enzymes involved in starch synthesis (Morell & Myers, 2005; Kozlov et al., 2006). However, selecting wheat varieties of desired functional characteristics has also been reported to lead towards increasing amylose content (Blazek & Copeland, 2007). Different breeding approaches can result in starches with increased amylose and variations in their functional, structural and thermodynamic characteristics. For instance, Hung et al. (2007b) described starches with increased amylose content that retained most of the crystallinity as compared to the starches with normal amylose content, whereas Hung et al. (2007a) described wheat varieties, in which increased amylose content was linked with the loss of crystallinity. Therefore, genetic background of wheat cultivars with increased amylose seems to be the determining factor in the molecular structure of starches.

Conclusions

Analysis of the thermodynamic and structural properties of a set of wheat starches consisting of a waxy variety and a set of amylose-rich varieties enabled us to distinguish between multiple factors affecting lamellar architecture of native starch granules. While our results are in general consistent with the link between increasing amylose content and the accumulation of defects within crystalline lamellae, this study shows the value of studying wheat varieties of diverse genetic background in order to fully understand the level of variation in the structural arrangements of molecular starch components over micro and nano-scales.

References


The ANSTO ECR ion source and its application to mass spectrometry

D. Button, D. Buckley, T. Esat, M.A.C. Hotchkis

Abstract

At ANSTO we have built an Electron Cyclotron Resonance (ECR) ion source to investigate new concepts for mass spectrometers [1,2] designed to measure isotopic ratios in small samples.

ECR ion sources are capable of producing beams of multiply-charged atomic ions with high efficiency and are widely used as heavy ion injectors for accelerators. To meet the requirements of mass spectrometry, we have needed to adapt ECR ion source techniques to our purpose. In this presentation, these and other recent developments of our ECR ion source will be discussed.

Introduction

Isotopic Ratio Mass Spectrometry (IRMS) techniques are applied to a range of elements to investigate naturally-occurring isotopic ratio variations. Current IRMS systems utilise ionization methods such as Electron Impact to generate ion beams for analysis by a mass spectrometer. This ionization method typically achieves 0.1% ionisation efficiency, dominantly of a 1+ charge state and with little break up of molecules.

Elements for investigation in an IRMS instrument may naturally exist in an atomic state such as noble gases like Argon and Neon, but more commonly as a constituent of a molecule such as oxygen in water. Oxygen isotopes in water cannot be analysed directly due to interferences at the mass values of the rare isotopes $^{17}\text{O}$ and $^{18}\text{O}$. Interferences are generated by 1+ ions of H$_2$O and OH, which cannot easily be separated from the rare isotopes. The problem is overcome, in part, by processing of water samples to convert the oxygen component into carbon dioxide gas (CO$_2$). The $^{18}\text{O}/^{16}\text{O}$ ratio can be derived from the ratios of molecular ions at measured at masses 46 and 44. However, $^{17}\text{O}$ cannot be determined in this way, due to the higher abundance of $^{13}\text{C}$ which means that the mass 45 ions are dominated by $^{13}\text{CO}_2^+$ ions.

We are using an ECR ion source as an alternative to electron impact ionisation for mass spectrometry. Figure 1 shows the conceptual layout of the ECR based IRMS instrument. Our ECR ion source has been proven to be effective at generating ion beams of multiple-charge state from a range of sample types. This has two major benefits on the IRMS sample process.

First, the process of ionising a molecule to a charge state grater than 1 will lead to most molecules breaking apart, with only very few molecules able to maintain a 2+ charge state. The implication of the molecular break up means that molecules cannot
be ionised to high charge states whereas atoms can. Secondly, producing atoms of charge states greater than 1 changes their m/q value. This means that the mass spectrometer is able to effectively separate the multiple charge state atoms free of the parent molecule which can only maintain a single charge state.

In our investigation oxygen, nitrogen, carbon, and argon have been tested in our ECR ion source which has been coupled with an analysing magnet and Faraday cup system to measure mass to charge ratios (m/q) of beams in the range 0 – 120 at a beam extraction energy of 15kV. The efficiency of our enclosed ECR ion source achieves greater than 10%, giving two orders of magnitude improvement on Electron Impact techniques. The removal of sample pre-processing also cuts down of the original sample size required, adding to the overall efficiency of the system.

This investigation of the sample gases has yielded promising results, but has also exposed an issue of sample retention within the ion source as a problem requiring further investigation to reduce the impact of possible memory effects.

ANSTO is working towards constructing a viable IRMS++ instrument for isotopic ratio measurements [2], and further developing a variation on the instrument to allow the measurement of $^{14}C/^{12}C$ ratios free from $^{14}N$, $^{12}CH_2$, and $^{13}CH$ interferences [1].

**Experimental Arrangement**

The ECR ion source, shown in Figure 2, is a variation on other ECR source designs. Featuring a single ended plasma bottle, and miniaturised magnet arrangement so as to reduce the plasma bottle volume. This was done to maximise the efficiency of the source, as the only paths for gas to be removed from the plasma bottle is via beam extraction as an ion, or by pumping which is restricted by the low conductance of the extraction aperture.

Sample gases are introduced to the ions source via the gas inlet indicated in figure 2. This is fed by 2 capillary lines of 25µm internal diameter. One line delivers the sample gas/vapour, and the other delivers a support gas (if required -- typically helium).

Static pressures of sample and support gas are placed on the inlet side of the capillaries typically in the order of hundreds of Torr, so that the transition between lamina and molecular flow can occur within the capillary preventing fractionation effects.
Molecular Interference with Water

When water vapour is introduced to the system via a capillary line, the H$_2$O molecule is first ionised to the 1+ charge state within the ECR region of the source. Further bombardment of the molecule by energetic electrons results in the molecule breaking up as it cannot maintain a 2+ charge state. This results in the generation of a free hydrogen atom, and an OH molecule. Following a similar process the OH will be broken into its single constituent, a hydrogen and oxygen atom.

The oxygen free of the parent water molecule can continue to be stripped to higher charge states by further electron bombardment in the ECR region. When extracted the oxygen atom maybe at a charge state ranging from 1+ to 8+. The extracted beam can then be analysed for example in the 2+ charge state meaning that the $^{16}$O$^{2+}$, $^{17}$O$^{2+}$, and $^{18}$O$^{2+}$ will now appear at the m/q values 8, 8.5, and 9. As the H$_2$O and OH molecule can’t maintain a 2+ charge state these values are free of molecular interference.

Figure 3 shows an example water vapour scan. The 2+ charge state has been shifted and expanded to line up with the 1+ charge states of the oxygen isotopes at mass 16, 17, and 18 to show the removal of molecular interference at the 2+ charge state.

Working with High Charge States

The developed ECR ion source is effective at generating a range of charge state ions. This can be scene in Figure 4, which is the mass scan of argon. The scan also indicates the presence of background hydrogen, oxygen, nitrogen and carbon within the scan, due to residual gases in the vacuum system. Many of the low intensity peaks with m/q 24 and greater can be attributed to various molecular species formed from H, C, N and O, such as hydrocarbons, CO, NO, O$_2$, N$_2$, etc.

Although the production of higher charge states is useful for the generation of alternative charge states free of molecular interference, it does introduce the occurrence of other form of interferences. There are 2 main forms of interference that can be observed in our results of the current experimental IRMS instrument.

Firstly, similar or identical m/q values can result from different charge states of atomic ions formed from a number of elements and their isotopes. The most apparent point where this occurs is at m/q of 4 which can contain contributors such as $^{12}$C$^{3+}$, $^{16}$O$^{4+}$, $^{40}$Ar$^{10+}$, $^{36}$Ar$^{9+}$, $^{20}$Ne$^{5+}$ and $^{3}$He$^+$. This can be seen in Figure 4 at m/q value of 4, and another such interference at m/q of 18 where H$_2$O$^+$ coincides with $^{36}$Ar$^{5+}$.
Secondly, charge changing events can occur. This is where a higher charge state ion can recapture 1 or more electrons after extraction. The resulting peak does not appear at the correct m/q value, but takes on an apparent value higher up the spectrum due to the additional energy. The apparent value can be calculated as using Equation 1.

Figure 4 shows 2 peaks labelled A and B which are the result of charge changing. Peak A corresponds with $^{40}\text{Ar}^{2+}$ changing to $^{40}\text{Ar}^{+}$. Thus the resulting ion has an energy of 30keV due to the 15kV extraction voltage when in the ion.

**Equation 1:**

$$\frac{m}{q_{\text{apparent}}} = \frac{mq_i}{q_f}$$

Where:
- \(m\) = Mass
- \(q_i\) = Initial Charge
- \(q_f\) = Final Charge

Figure 4: The above are a mass spectrum of Argon gas spit into three sections.
was extracted at the 2+ charge state, shifting the apparent m/q value to 80. Peak B, is the result of $^{40}$Ar$^{3+}$ changing to $^{40}$Ar$^{1+}$ giving it an apparent m/q value of 120. The peak at m/q = 30 is a further example, due to the $^{40}$Ar$^{3+}$ to $^{40}$Ar$^{2+}$ charge change. These peaks show a distorted peak shape as the charge change may occur very close to or within the extraction region.

Potential interferences from charge changing events can be overcome by the addition of an Electro-Static Analyser (ESA) to eliminate ions of incorrect energy to charge ratios.

References


Design considerations in the development of magnetic nanoparticles for MRI contrast enhancement


1 School of Physics, The University of Western Australia, Perth, Western Australia.
2 School of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg Virginia USA.

Since the development of magnetic resonance imaging (MRI) in the mid 1970s, it has become one of the most widely used advanced diagnostic tools. Magnetic nanoparticle contrast agents provide the opportunity to extend the versatility of MRI by enhancing the contrast between different tissue types. A series of potential MRI contrast agents based on surfactant coated iron oxide nanoparticles have been studied. These nanoparticles have been characterised by transmission electron microscopy, SQuID magnetometry, elemental analysis, small angle x-ray and neutron scattering as well as proton relaxometry to assess their potential as MRI contrast agents and to elucidate the mechanisms of proton relaxation enhancement.
Plasma immersion ion implantation and deposition of titanium nitride onto polymers

C. Chaiwong, D.R. McKenzie, M.M.M. Bilek
School of Physics, The University of Sydney, NSW 2006, Australia

Abstract
Deposition of hard coatings onto polymers requires knowledge of the phenomena occurring when materials of different elastic properties are brought into contact. Buckling and delamination are undesirable effects that may occur and are frequently linked to the stress induced in the film. The use of energetic deposition by ion implantation has been shown to be an effective surface modification technique that can solve the problem of delamination. In this work, titanium nitride films were prepared on polycarbonate substrates by cathodic arc deposition combined with plasma immersion ion implantation (PIII). The stress in the film could be remarkably reduced by using 3 kV bias with plasma immersion ion implantation. Excellent adhesion strength for films produced under these conditions was demonstrated using tensile testing. Cross sectional transmission electron microscopy revealed an intermixed layer between the film and the substrate that was believed to enhance the adhesion strength.

1. Introduction
Polymers have widespread use as composite materials for many application areas. Examples of existing applications include materials for consumer products, structural materials for automotive and aeronautical industries and packaging for the food and medical industries. However, their use is sometimes limited by the undesired properties of the surface, as opposed to the useful characteristics of the bulk, such as light weight, high strength. Polycarbonate is known to be one of the toughest among the engineering polymers. However, polycarbonate surface is easily scratched and somewhat limited chemical resistance. The performance of polycarbonate can be enhanced by surface modification, thus the potential for its application can be significantly increased. Titanium nitride has a wide range of applications due to a unique combination of properties such as high hardness, good chemical inertness, and excellent wear resistance. It may also be a suitable protective layer for the surface of polymeric materials. In this work, we investigated the adhesion of TiN films grown on polycarbonate using a combination of filtered cathodic vacuum arc and plasma immersion ion implantation and deposition (PIII&D). The stress in the film was studied. The adhesion strength between the film and the substrate was evaluated.

2. Experimental details
The substrate material was 1-mm thick polycarbonate (Lexan®) sheet. The sheet was used in the as-received state. Filtered cathodic vacuum arc with titanium cathode was employed for deposition of the titanium nitride (TiN) films. The details of the filtered cathodic arc and the parameters were explained elsewhere [1]. The substrate holder was mounted on a high-voltage, insulating feed-through and connected to the pulser unit. The deposition rate was kept low (2nm/min) to minimize substrate heating. Film thickness was measured after deposition with a Tencor™ surface profilometer. The stress of the film was deduced by measuring the radius of curvature of a 20mm x 20mm x 0.5mm sheet before and after deposition and by applying Stoney’s equation [2]. For adhesion test, polycarbonate sheet was cut into a tensile sample with a parallel gauge section of length 12mm and width 3mm. The tensile test was
performed by a small tensile device positioned under an optical microscope was used. The displacement and load during straining at a crosshead speed of 3µm/s were measured and images of the surface were captured every 2 seconds. Post-analysis of the sample was done by a scanning electron microscopy (SEM), Phillips XL30. The cross-sectional specimen for transmission electron microscopy (TEM) was obtained by ultramicrotomy (Reichert Ultracut S). Bright-field image of the cross-sectional specimen was taken with a TEM (Phillips CM12).

3. Results and discussion

Residual stress in titanium nitride films

It is known that thin films deposited with PVD processes suffer high level of compressive residual stress. A high level of stress in combination with insufficient adhesion at the interface can be adequate to initiate spontaneous buckling [3]. In this work, the stress in the TiN films deposited without high voltage substrate bias was measured. The residual stress state in the film was found to be compressive. The film thickness was 105 ± 8nm. Using Young’s modulus and Poisson’s ratio of polycarbonate as 2.21GPa and 0.37, respectively, the residual stress is 1.6 ± 0.4GPa. SEM micrograph (Figure 1) of the sample shows that randomly directed wrinkles have formed on the film surface. Film delamination is also observed.

Figure 1 SEM micrograph of the surface of the TiN film deposited without high voltage substrate bias. The film thickness is 105 ± 8nm.

Figure 2 A graph of TiN film stress as a function of high voltage pulse frequency.
The effect of the pulse voltages and the pulse frequencies on the stress of TiN films on polycarbonate substrates was investigated. The relation between the residual stress and the high voltage pulse frequency is shown in Figure 2. A remarkable stress relief can be obtained at the voltages 2 and 3kV. However, the pulse frequency does not show significant effect on the stress relief. Optical microscopy of the film surface show smooth film without of cracking. The stress relief in the film can be explained by the concept of thermal spike during energetic ion bombardment [4].

**Adhesion measurement**

Figure 3 shows the typical stress-strain curve of the test. The test was performed on the film deposited with 3 kV substrate bias. The film thickness is 80nm. The strain at which the film started to crack (fracture strain) is about 2 % and the crack saturation occurred at about 4% strain. The SEM micrograph of the sample after the tensile test reveals that there is no evidence of severe delamination or buckling. The ultimate shear strength of the interface was calculated from the relationship of the fracture strain and the crack spacing [1, 5]. The ultimate shear strength of the interface is 0.6 GPa. This excellent adhesion observed is due to the interface mixing and the stress relaxation induced by energetic ion bombardment [6, 7]. The cross-sectional TEM (Figure 4) shows the interface mixing between the film and the substrate. The film appears to be dense and the columnar structure was suppressed.

![Figure 3 Stress-strain curve of the sample during the tensile test. The film thickness was 80nm.](image)

![Figure 4 Cross-sectional TEM micrograph of TiN/polycarbonate interface.](image)

**4. Conclusion**

The stress in the film deposited with PIII&D was found to be remarkably reduced compared to that of the film deposited without PIII&D. The adhesion of the film to the substrate was studied by means of a tensile test. Adhesion strength comparable to that found for TiN films on steel substrates was achieved. The good adhesion is attributed to the reduction of stress and interface mixing induced by using PIII&D during deposition.
References


DLTS study of ion and molecular implantation damage in silicon

C. T. Chang, J. C. McCallum

School of Physics, University of Melbourne, Victoria, 3010 Australia
Email: echang3@physics.unimelb.edu.au

Abstract
In this paper we present preliminary DLTS results of H implanted silicon. These results will form the basis of further studies of the defects produced with ion and molecular implantation. Here, implantations were performed to various fluences with 70keV H. The ion beam flux was also varied. Three kinds of defects were identified with a VP, or V2 related defect having the greatest concentration.

Introduction
The use of implantation in the semiconductor industry results in defects being formed in the silicon substrate. These defects must to a large extent be removed, usually by post-implantation thermal processing, for active devices to be obtained. As microchip sizes continue to decrease more detailed information is required about the nature and quantities of the defects formed during the implantation process so that the thermal budgets required to remove the defects can be reduced. Deep-Level Transient Spectroscopy (DLTS) allows the study of these defects through the determination of their energy levels in the band-gap and the depth at which the defects are located within the substrate.

Results presented here form the basis of a comparative study between the defect profiles created by ion and molecular implantation.

Experimental
In the present study, 70keV H was implanted into phosphorus doped Czochralski grown silicon to various concentrations and fluences using the 150 kV ion implanter at the Australian National University. Three different measurements were performed on the SULA Technologies DLTS system at the University of Melbourne. These were capacitance-voltage (CV), capacitance-temperature (CT) and standard DLTS measurements. The CV measurement enabled the determination of the active donor concentration, depletion width, the built-in voltage of the diode and barrier height. The steady state capacitance value under the full reverse bias was determined with CT measurements. Finally, ion implantation induced deep-level defects were classified by their energy level and capture cross section using DLTS. This was achieved by using four separate correlator signals. By combining these techniques it was possible to determine the defect concentration as a function of depth [1]. For all measurements the voltage pulse was set to –2 V, which was found, to be adequate for measuring the 70keV implant.

Sample sets were divided into four groups, 1-4, determined by their H concentrations 1×10⁹, 2×10⁹, 2×10¹⁰ and 1×10¹¹ H/cm³. A fluence dependence study of the defects created during ion implantation was performed with group 1 samples (1×10⁹ H/cm³) using an ion beam flux of either 1 nA or 0.5 nA.
Results and discussion

Figure 1 shows the DLTS signal as a function of temperature for samples having a H concentration of $2 \times 10^{16} \text{H/cm}^3$ (group 3). Each correlator had respective delay times of delay times of 5, 2, 0.5 and 0.2 ms. The noise levels in the DLTS spectra from groups 1 and 2 samples (not shown) were significantly greater because of the relatively lower trap concentrations. This made it difficult to distinguish between these two groups. Likewise, there were indistinguishable differences between the two different fluences of group 1. Three distinct peaks can be seen in each correlator signal in Figure 1. Each peak corresponds to a different trap energy determined with the Arrhenius plot shown in Figure 2.

![Figure 1](image-url)

Figure 1. Typical DLTS spectra for Si implanted with 70keV H to a concentration of $2 \times 10^{16} \text{H/cm}^3$. Four correlators where used with respective delay times of 5, 2, 0.5 and 0.2 ms.

The gradients determined in Figure 2 allowed us to classify three traps by their energy levels and capture cross section [2]. This was achieved through a comparative analysis with previous studies [3, 4, 5]. The trap with an energy of 0.44eV could be associated with a $V_P$ (Vacancy-Phosphorus complex) or a $V_2^-$ (divacancy complex). The trap with an energy of 0.33eV is assigned to a VO-H (Vacancy Oxygen-Hydrogen complex) or a H-related defect. Finally, a VO defect is responsible for the signal resulting in a trap energy of 0.18eV. The capture cross-section for these three traps are $\sigma_c = 2.6 \times 10^{-15}$, $1.6 \times 10^{-15}$, and $7 \times 10^{-15} \text{cm}^2$, respectively.
Figure 2. An Arrhenius plot for the DLTS spectra presented in Figure 1.

Figure 3 shows a CV measurement from a 70keV H implanted Si sample. From the line of best fit the active donor concentration was approximated to be $n_d = 7.65 \times 10^{15}$ P/cm$^3$ and the build-in voltage was $V_{bi} = 1.326 eV$. These results will enable the further analysis of the donor concentration as a function of the depletion width. When pulsing $-2$ V into the sample the depletion width reaches a maximum of $7.30 \times 10^{-5}$ cm.

Figure 3. C-V plot with a line of best fit for Si implanted with 70keV H to a concentration of $2 \times 10^{10}$ H/cm$^3$. 
Conclusion

The preliminary results here show the analysis of the damage caused by hydrogen ion implantation. The classification of the defects through the determination of their trap energies and capture cross-sections tells us that the majority of defects are VP$_s$ or V$_2$ related.

Currently a comparative study between the damage created after H ion implantation and H$_2$ molecular implantation is being pursued. The molecular implant will be implanted at twice the ion energy presented here. This is to ensure the depth profile of both H and H$_2$ implants are similar. Other investigations will include lithium and phosphorus. Interest in the Li and Li$_2$ implant has been sparked by the fact that lithium is electrically active after implantation [6]. The phosphorus implants are of particular interest to the CQCT (Centre of Quantum Computing Technology) group for investigating P-P interactions.

References

Surface modifications of nanoporous alumina membranes by plasma polymerisation

Martin A. Cole, Björn Dollmann, Krasimir Vasilev, Hans J. Griesser and Dusan Losic

University of South Australia, Ian Wark Research Institute, Mawson Lakes Campus, Mawson Lakes, Adelaide, SA 5095, Australia

Summary
Nanoporous alumina membranes (PA) have a variety of applications in bioseparation, biosensors and targeting delivery. This work describes the surface modification of these membranes using of plasma polymerisation in order to improve their morphological and chemical properties. Commercial porous alumina membranes (with pore sizes from 20 to 200nm) were used and modified by plasma deposition of ultra-thin polymer films. Monomer n-heptylamine was employed to achieve chemically reactive polymer surface on PA terminated with amino groups. The purpose of these amino groups is to provide functionality and ideal surface properties for building more complex architectures in the pores and in order to improves selectivity and separation properties of the membranes. The effect of processing parameters during plasma deposition on the morphological and chemical properties of plasma modified porous alumina membranes was studied using field emission scanning electron microscopy (FESEM) atomic force microscopy (AFM) and X-ray electron spectroscopy (XPS).

Introduction
Nanoporous inorganic membranes regarding their unique thermal, mechanical, structural, optical and chemical properties, have attracted intensive research interest in the last decade for applications in various fields such as separation, adsorption, catalysis, sensors, energy storage, and drug delivery. A range of nanoporous materials based on zeolites, siliceous materials, inorganic oxides, carbon nanotubes, metal and metallo-organic composites have been explored. Among them porous alumina (PA) membranes fabricated by electrochemical anodisation are one of most popular nanoporous materials due to simple and low cost fabrication, chemical and thermal stability, remarkable hardness, uniform pore size and high pore density. PA membranes with controlled pore dimensions can be fabricated by well established procedures based on electrochemical anodisation of aluminum foil using selected acids, applied voltage and temperature. The fabricated PA membranes possess uniform, dense and hexagonally packed pores (nanochannels) with a high aspect ratio running in the direction perpendicular to the membrane surface with diameters ranging between 20 and 300nm and thickness from 1 to 100 µm. These properties are of particular interest for membrane applications and recently PA membranes called “Anodisc” or “Anopore” membranes with limited pore sizes (20nm, 100nm and 200nm) are commercially available. One limitation on the application of these membranes as membranes for separation of smaller molecules is their relatively larger minimum pore diameter (20nm). Therefore it is important to find a simple and reliable approach to reduce the pore size of existing PA membranes in a controlled way into a dimension that will enhance their nanoseparation and molecular sieving properties. In addition, to introduce other separation strategies based on chemical or interfacial properties of molecules rather than their size, it is necessary to perform chemical modification and functionalisation of PA membranes.
Several modification approaches for pore size reduction and surface functionalisation have been explored in recent years to improve the selectivity and separation properties of PA membranes. These methods to enhance membrane application and performance include atomic layer deposition (ALD), chemical vapor deposition (CVD), thermal vapor metal deposition, electroless deposition, sol-gel and layer by layer deposition. Plasma-based methods initially developed for microelectronics in the fifties, present clean, simple and extremely flexible fabrication technology to perform surface modifications (cross-linking, grafting, and etching), and allow tuning of surface properties (morphological, interfacial and chemical). Based on these advantages and the preparation of ultrathin polymer films plasma polymerization has received great attention for surface modification of various devices including membranes. This work focuses on exploring the application of plasma polymerization for membrane modification with particular goals to achieve controlled reduction of pore size and introduction of reactive surface groups amenable for the covalent immobilization of biologically active molecules. Morphological, topographical and chemical properties of plasma polymer coating were investigated using field emission scanning electron microscopy (FSEM), atomic force microscopy (AFM) and X-ray electron spectroscopy (XPS).

**Experimental**

The PA membranes ("Anodisc") with pore sizes of 20nm, 100nm and 200nm were obtained from commercial sources (Whatman, UK). Prior to the plasma deposition, PA membranes were repeatedly washed in ethanol followed by Milli Q water and drying with a nitrogen jet. Plasma polymerization was carried out in a custom built plasma reactor described elsewhere powered by a commercial 13.56 MHz radio-frequency generator. The scheme of reactor is shown in Figure 2. A monomer vapor of n-heptylamine (98%, supplied from Fluka) was used. The deposition was carried at a pressure of 0.2 Torr using a power of 40 W. To obtain films with thicknesses in the range from 20nm to 200nm the deposition time was varied from 20 s to 200 s. Polymerisation was repeated a minimum of three times for each deposition time using a series of PA with different pore sizes. Silicon wafer is used for each experiment as a control to confirm thickness of deposited films.

FESEM characterisation of prepared PA membranes was performed using the Philips XL 30. The samples were cut into small pieces, mounted into a holder with double sided conductive tape and coated with a few nm of a platinum layer. Images with a range of scan sizes from top surfaces (normal incidence) and profiles (40º degree angle) were acquired to observe the pore structure before and after modifications.

Asylum MFP-3D Atomic Force Microscope (Asylum Research, USA) was used for the characterisation of surface topography of the bare PA and modified PA with plasma polymer films. The imaging is performed in contact mode in air, using silicon nitride tips (NT-MDT, Russia) with spring constant of 0.58 - 5.5 N/m (specified by the manufacturer).
The XPS analysis of plasma modified samples were recorded using a Kratos AXIS Ultra DLD spectrometer with a monochromated Al Kα radiation source (hv = 1486.7eV) operating at 15 kV and 10 mA. The elements present in the sample surface were identified from a survey spectrum recorded over the energy range 0-1100eV at a pass energy of 160eV and a resolution of 1.0eV. High-resolution spectra (0.1eV) were then recorded for pertinent photoelectron peaks (carbon and nitrogen).

The thickness measurements of deposited films on silicon wafers were used as control samples during polymerization and were performed using Imaging Ellipsometer (Beaglehole Instruments, New Zealand).

**Results and Discussion**

A typical FESEM images of the commercial PA membranes (20nm pore size) is shown in Figure 2 (a-c). These images confirm that structure of PA membranes is asymmetric with a bulk pore structure comprised of straight channels with pore sizes from 100-200nm and a thin layer (cca 1 µm) on the top with specified pore size (20nm, 100nm and 200nm). However their pore shape is rather irregular and not circular and pore sizes are often bigger than specified values. The n-heptylamine plasma polymer film was deposited on the top of these PA membranes using the different deposition times (20 s, 50 s, 100s, 150 s and 200 s). The deposition rate was determined by ellipsometry using control samples (silicon wafers) which confirm an average rate of about 1nm/s. To prove the reduction of pore size as a result of polymer deposition, FSEM and AFM images were taken from the top surface. Typical images of modified PA membranes (20nm pore size) are shown in Figure 2 and 3. It is evident that the decreasing of the size of pore was achieved by increasing the deposition time from 20 s to 100 s (Fig. 2 d-f). When deposition times of 20 s and 50 s were used, the size of pores is reduced and pores are still open. The significant reduction of pore size is observed with deposition time of 100 s which makes most of
the pores partially closed (Fig. 2 f). AFM imaging is performed to confirm the morphology of these pores and images show significant decreasing of surface roughness after polymer deposition (Fig. 3 b). The depressions originating from the pores are seen on AFM images. However their height is considerably smaller in comparison with the height of pores on bare PA membranes (Fig. 3 a), which could direct the conclusion that a thin polymer layer is formed over the pores. When a longer deposition rate of 200 s is performed (data not shown) these depressions disappear which confirms the complete covering of pores.

A similar effect on decreasing the pore size was observed using PA with pores of 100nm and 200nm. Regarding to the larger size of their pores, significant decreasing in pore size was observed by using higher deposition times (100s, 150 s and 200 s). These results show that plasma polymerization can be successfully used for pore modifications of PA membranes with controlled reduction of their size. Further experiments will be carried out to explore the filtration properties of these plasma modified membranes in relation to small organic molecules and proteins.

XPS analysis was conducted to investigate the surface elemental and surface chemical composition of deposited polymer on PA. The survey spectrum (Figure 4, left) reveals the presence of three elements, carbon, nitrogen and oxygen which shows approximately 85 % carbon and 11 % nitrogen from the plasma polymer along with small amounts of oxygen arising from film oxidation. Observed chemical composition of the deposited polymer films on PA was in reasonable agreement with expected theoretical values based on the chemical structure of n-heptylamine (C 85 %, N 10%). The lack of elements attributed to the underlying substrate material indicates that the coating is thicker than the XPS sample depth of approximately 10nm for polymer samples. Curve fitting of high resolution N1s and C1s spectra was used to investigate different nitrogen and carbon functional species present at the surface. Functional species were assigned to curve components based on known primary binding energy shifts. High resolution C1s spectra (data not presented) show three curve components fitted to the spectra which comprised of

![Figure 4. XPS of PA membrane (pore size 20nm) modified with n-heptylamine plasma polymer. Survey spectrum is on the left and N1s high resolution spectrum is on the right.](image-url)
aliphatic hydrocarbon at 285.0eV, amine and ether at 286.4eV and carbonyl functional groups at 287.7eV. Figure 4 (right) shows the position of the nitrogen peak to be approximately 299.3eV which is indicative of amine (possibly some imine) functionality. The lack of amide functionality, which is often observed at higher binding energies in plasma polymer coatings of other nitrogen containing monomers indicates that oxidation has not impeded the surface reactivity. These results confirm that PA membrane surface is covered with polymer film with high density of free amino groups that can be used for covalent attachment of specific molecules with functions that are important for building new separation properties of PA membranes for targeting molecules or ions.

Conclusions

The plasma polymerisation process has been successfully implemented in order to deposit n-heptylamine polymer films on commercially available, inexpensive and high-flux anodic alumina nanoporous membranes. A simple approach is demonstrated to modify the structural and chemical properties of PA membranes with the ability to reduce their pore size in a controlled way and introduce new surface chemistry rich with amino groups. Improved sieving properties of plasma modified PA membranes are anticipated with the ability to develop novel functional membranes for separation of targeted molecules or applied for other applications such as drug delivery. The proposed processing scheme can also be extended for development of other types of inorganic membranes.

Acknowledgment:
The authors thank the Australian Research Council (ARC) and the University of South Australia for financial support.

References

Nanostructures are increasingly being employed for opto-electronic applications because of their unique flexibility in choice of properties.

However characterisation of structures with such small components is very challenging. Often very high (nm) spatial resolution and high sensitivity (ppm) are required. No technique can deliver both. Hence a combination of techniques is required with complementary information summing to give an overall quantitative analysis.

This complementary approach applied to the physical, optical and electrical characterisation of silicon based nanostructures for photovoltaic applications, will be discussed.
The refractive index of ion implanted diamond

M. A. Draganski a*, P. Olivero b, J. Jasieniak c, S. Orbons b, E. Finkman d, P. N. Johnston a, D. N. Jamieson b,e and S. Prawer b,e

a Applied Physics, School of Applied Sciences RMIT University, GPO Box 2476V, Melbourne, Victoria 3001, Australia
b Microanalytical Research Centre, School of Physics University of Melbourne, Victoria 3010, Australia
c School of Chemistry, University of Melbourne, Victoria 3010, Australia
d Department of Electrical Engineering and Microelectronics Research Center, Technion-Israel Institute of Technology, Israel
e Centre for Quantum Computer Technology

* Corresponding author. Tel.: +613 9925 9991; fax: +613 9925 5290; e-mail: martin.draganski@rmit.edu.au

Abstract—Diamond undergoes a pronounced physical transformation when subjected to the bombardment of high energy ions. Above sufficient fluence there is visible darkening of the crystal suggesting significant changes to the refractive index. This suggests diamond-based photonic devices could be fabricated by ion beam lithography. We investigate the refractive index of diamond subject to ion implantation with a focused ion beam. We have measured the refractive index for varying ions fluences over many orders of magnitude for gallium and carbon ion irradiation. Measurements are performed using ellipsometry over a wide spectral range; from UV to near IR. Knowledge of the refractive index as a function of the number of lattice defects and the ionisation induced by the ions is required to evaluate the potential of ion beam lithography for realisation of a photonic crystal. We are investigating the possibility of fabricating a device with a photonic band gap based on the difference in optical properties of pristine and irradiated diamond with the required spatial variations provided by a scanned microbeam.

Keywords: Diamond, Refractive Index, Ion Implantation, Photonic Crystals.
Hierarchically porous inorganic structures have been synthesised and applied for the sequestration of the vanadyl oxo anion and cations. In the first instance these were used as surrogates for uranium species with the advantage that the coordination environment of the vanadium oxo ions could be interrogated in a straightforward manner relative to uranium. Studies of uranium adsorption will be conducted in the future.

Sol-gel chemistry and organic templating techniques were used to prepare mixed titanium and zirconium oxides with trimodal pore size distributions. These materials were characterised with gas sorption, SEM, TEM, TGA and XRD.

Figure 1 shows the gas adsorption-desorption isotherm and BJH pore size distribution of a 85:15 TiO$_2$:ZrO$_2$ mixed metal oxide. These plots show that there are three distinct pore sizes: micropores which are less than 2nm in diameter; mesopores between 4-6nm; and macropores greater than 50nm. Nitrogen porosimetry is the most appropriate method for the detection of mesoporosity, while other techniques, such as TEM and SEM are needed to study the micro and macroporous architecture.

Figure 1. N2 sorption isotherm of 85:15 TiO2:ZrO2 materials templated from agarose gel. Inset: BJH pore size distribution.

Metal oxides produced from sol-gel templating of agarose gel applied
to vanadium adsorption
Glenna L. Drisko $^{1}$, Vittorio O. Luca $^{2}$, Rachel A. Caruso $^{1}$

$^{1}$ PFPC, The School of Chemistry, The University of Melbourne, Melbourne Vic 3010,
$^{2}$ Institute of Materials Engineering, ANSTO, Menai NSW 2234

gleanna@pgrad.unimelb.edu.au
SEM images (Figure 2.a) clearly show the open macroporous framework. This morphology is produced from coating the structure of the agarose gel template [1]. The size of the macropores is therefore determined by the original gel. Explicitly, gels of higher wt% organic matter produce denser structures with higher surface areas and smaller macropores.

TEM images (Figure 2.b) show the interparticle spaces between clusters of metal oxides. During synthesis, the solution formed nanoparticles through hydrolysis and condensation reactions. These nanoparticles aggregated, resulting in the formation of a gel network around the fibres of the template. Because these particles were roughly spherical, they could not perfectly pack together, which produced cavities between the particles. The micropores are believed to be formed from the metal oxide coating the individual fibres of the agarose gel. When the template was removed through calcination, a void was produced where the fibres used to exist. These spaces are unfortunately difficult to see in the TEM image.

The vanadium adsorption properties were studied as a function of the surface area using ICP analysis. The kinetics and capacity were investigated by monitoring adsorption as a function of time over a period of two days. It was found that vanadate adsorption was very fast. For a 10 ppm solution, maximum adsorption occurred within 5 minutes. The vanadyl adsorption was much slower, most likely due to positive charge repulsions between the surface of the material and the metal cations. Future studies will address measurement of surface charge using zeta potential to investigate the relationship between metal oxide composition and the isoelectric point. Also, uranium adsorption properties will be measured.

Acknowledgements

This research was supported by an AINSE Award (AINGRA07025) and funding from The University of Melbourne/ANSTO Collaborative Research Support Scheme

Reference:
Optimisation of Density Functional Theory (DFT) parameters for calculating the electronic and optical properties of diamond.

Daniel W. Drumm, Faruque M. Hossain, Steven Prawer, Lloyd C. L. Hollenberg
Quantum Communications Victoria University of Melbourne, Parkville 3010, Australia

Colour centres in diamond are of considerable interest to the growing quantum information processing industry. Diamond offers an alternative bulk material to silicon, with attractive mechanical, optical and quantum properties [1]. Understanding the physics of defects and their interaction with the bulk is only possible through modelling. The current study is part of a larger body of work endeavouring to model potential dopant properties accurately and easily.

Operational Density Functional Theory (DFT) [2,3] parameters for Cambridge Serial Total Energy Package (CASTEP) [4] were explored to identify an optimal set for calculating electronic and optical properties of bulk diamond. The effects of supercell size and choice of exchange-correlation energy functional on band structure and density of k-point mesh on the optical properties were investigated to refine modelling (prior to incorporating defects).

CASTEP is a standard industry ab initio simulation package using a plane-wave pseudopotential (PWP) total energy method based on DFT. The program minimises the total energy of a structure (at zero temperature) by modifying nuclei position, and is able to calculate bandstructures, dielectric functions and density of states of crystalline solids. The computations were undertaken on either a Dell Optiplex desktop (2 × 2.40GHz Intel® Core™2 Duo processors, 2GB of RAM) or a Silicon Graphics Altix 3700 supercomputer (32 × 1.5GHz Intel® Itanium® 2 processors, 64GB of RAM).

Within CASTEP, models with supercells incorporating 1, 2, 4, 8 (2×2×2), 3, 9 and 27 (3×3×3) face-centred cubic unit cells (each containing 8 carbon atoms) were constructed and optimised using the Perdew-Burke-Ernzerhof (PBE) functionals in the Generalised Gradient Approximation (GGA) [5], and an ultrasoft pseudopotential with plane-wave basis set cutoff energy of 280.0eV. The valence atom configuration for carbon was 2s22p2. The k-point mesh applied was a Monkhorst-Pack (n×n×n) grid with n ∈ {8,4,2} for corresponding dimension length ∈ {1,2,3}. Points situated within the first Brillouin zone were evaluated. The band structure and optical properties for each model were calculated using the same functional, cutoff and k-point mesh.

The effect of exchange-correlation functional on band structures was studied by taking optimised structures from the first trial (1 unit cell and 8 unit cells) and calculating the band structures using either a norm-conserving pseudopotential with energy cutoffs of 280.0 and 600.0eV, or an ultrasoft pseudopotential with cutoff 280.0eV. The larger cutoff energy provides a more accurate self-consistent charge density and more variational freedom when searching for wavefunctions of unoccupied (excited) states; ultrasoft pseudopotentials are designed to be more robust with lower cutoff energies. The functionals used were the CA-PZ functional developed by Perdew and Zunger [6] with data from Ceperley and Alder [7] in the Local Density Approximation (LDA), the PBE functional in the GGA, the Hartree-Fock (HF) scheme, the CA-PZ functional in the HF-LDA hybrid system, the Screened Exchange (sX) scheme, and the CA-PZ functional in the sX-LDA hybrid method. The natural symmetry of the diamond lattice was exploited to simplify computation and only 20 k-points within the first Brillouin zone were required.
A further study was conducted on an 8-unit cell supercell (taken from above; optimised using 32 k-points) of bulk diamond to observe convergence of the imaginary part of the dielectric function. The optical properties were calculated using a norm-conserving pseudopotential with cutoff energy 600.0eV, the PBE functional in the GGA, and k-point meshes of 1, 4, 14, 32, 63, 108, 172 and 256 k-points. Gaussian smearing of 0.5eV was applied to the calculated spectrum.

Preliminary results for the supercell analysis can be seen in Fig. 1, and may be compared to values of: 7.4eV (direct band gap), 5.6eV (indirect band gap), and ~5.5eV (fundamental absorption edge; not well-studied) [8]. Supercell size appears to have no significant effect on the calculated indirect band gap, although the other data appear to vary considerably, as discussed below.

The calculated values for the direct band gap appear to depend upon the longest dimension of the supercell, and are further from the experimental value with larger supercell side length. The fundamental absorption edge is indicative of direct transitions only, but not necessarily originating at the Γ point. Calculated values appear to diverge with increasing supercell size. One complicating factor in the study is the density of the k-point mesh; computation time is non-linear in response to an increase in the density. The larger supercells in this initial section (e.g. 27 unit cells) used a 2×2×2 mesh, of which 4 k-points were within the first Brillouin zone. The unit cell “supercell” used an 8×8×8 grid, with 256 points evaluated. At this point, it is unclear whether the changing mesh density has confounded the supercell work, hence the later work focusing on the effects of different k-point meshes.

Initial results for calculation dependence on choice of functional can be seen in Table 1. The first trial was calculating the diamond bandstructure using each of the six functionals on a basic unit cell. A norm-conserving pseudopotential with cutoff energy 280.0eV was selected. As can be seen, all but the HF-LDA model converged (within 100 iterations); the sX-LDA values were closest to experiment, but took 4 orders of magnitude longer to compute than the LDA and GGA calculations. The sX and HF models were similarly lengthy but less accurate than the sX-LDA. The LDA, GGA, sX and sX-LDA models gave better results for the indirect gap than for the direct gap; the HF model showed converse behaviour.

The choice of pseudopotential was another possible factor, and ultrasoft pseudopotentials (cutoff 280.0eV) were used to produce alternative LDA and GGA models. (CASTEP does not support the use of ultrasoft pseudopotentials for the other schemes.) Whilst changing the pseudopotential significantly improved the LDA and GGA values, they were not as accurate as the sX-LDA.

The cutoff energy for the pseudopotential was another possible factor leading to error; CASTEP suggests a higher cutoff energy e.g. 600eV for any calculation using norm-conserving pseudopotentials. The study was repeated over the six functionals using a norm-conserving pseudopotential with cutoff 600.0eV. Only the LDA and GGA models converged, showing an improvement slightly less than that of using an ultrasoft PWP. Using a cutoff of 600.0eV for the ultrasoft PWP in the LDA led to a slight improvement of ~0.07eV; the GGA value was poorer.
Repeats of the parameters with an 8-cell supercell were attempted for (norm-conserving) LDA, GGA, sX-LDA and (ultrasoft) LDA and GGA with cutoff 280.0eV, and for (norm-conserving) LDA and GGA with cutoff 600.0eV. A very small improvement (~0.03eV) was seen in all cases except sX-LDA which failed to converge. The best results were seen for the unit cell sX-LDA case (direct 5.64eV, indirect 5.20eV), followed by the 8-cell (ultrasoft) GGA. The running time difference was still 3 orders of magnitude, even with the increase to an 8-cell supercell.

The convergence of calculated optical properties with respect to density of k-point mesh can be seen in Fig. 2. It is evident that, up to density $4\times4\times4$ (thick lines), significant changes to the calculated spectrum are observed. Further increases in density do not have a great effect upon the general shape; this may be due to the large smearing width, or that the prior geometry optimisation was conducted using a $4\times4\times4$ k-point mesh also.

In conclusion, supercell size may affect optical properties and the direct band gap, though the observed differences may also arise from differing k-point mesh densities. The sX-LDA functional appears to be the most accurate, but takes orders of magnitude longer to calculate than using the LDA or GGA. The next best parameters considered are to construct an 8-cell supercell using an ultrasoft pseudopotential with cutoff energy 280.0eV and 20 k-points within the Brillouin zone (for a tetrahedrally symmetrised lattice). Finally, optical properties of an 8-cell model (optimised as above with 32 k-points) appear to converge for k-point meshes incorporating at least 32 k-points.

Further investigation of these effects is necessary; attempts will be made to re-run the unconverged calculations, the k-point convergence will be investigated with less smearing, both over the current data and for an 8-cell model optimised using a different k-point mesh (e.g. $5\times5\times5$). Analysis of the convergence of bandstructure will
also be conducted. Repeats of the study should be done for systems involving defects to check the consistency of any conclusions drawn from this work.

Table 1: Effect of exchange-correlation (approximation scheme) functional, pseudopotential and size of supercell on band gap (converged results only)

<table>
<thead>
<tr>
<th>Pseudopotential Approximation Scheme</th>
<th>Energy Cutoff (eV)</th>
<th>Supercell (unit cells)</th>
<th>Direct Band Gap (eV)</th>
<th>Indirect Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norm-conserving LDA</td>
<td>280.0</td>
<td>1</td>
<td>4.27</td>
<td>3.70</td>
</tr>
<tr>
<td>Norm-conserving GGA</td>
<td>280.0</td>
<td>1</td>
<td>4.66</td>
<td>4.00</td>
</tr>
<tr>
<td>Norm-conserving HF</td>
<td>280.0</td>
<td>1</td>
<td>11.50</td>
<td>10.5</td>
</tr>
<tr>
<td>Norm-conserving sX</td>
<td>280.0</td>
<td>1</td>
<td>4.85</td>
<td>4.4</td>
</tr>
<tr>
<td>Norm-conserving sX-LDA</td>
<td>280.0</td>
<td>1</td>
<td>5.64</td>
<td>5.20</td>
</tr>
<tr>
<td>Ultrasoft LDA</td>
<td>280.0</td>
<td>1</td>
<td>4.69</td>
<td>4.09</td>
</tr>
<tr>
<td>Ultrasoft GGA</td>
<td>280.0</td>
<td>1</td>
<td>5.03</td>
<td>4.36</td>
</tr>
<tr>
<td>Norm-conserving LDA</td>
<td>600.0</td>
<td>1</td>
<td>4.60</td>
<td>4.00</td>
</tr>
<tr>
<td>Norm-conserving GGA</td>
<td>600.0</td>
<td>1</td>
<td>4.97</td>
<td>4.31</td>
</tr>
<tr>
<td>Ultrasoft LDA</td>
<td>600.0</td>
<td>1</td>
<td>4.76</td>
<td>4.15</td>
</tr>
<tr>
<td>Ultrasoft GGA</td>
<td>600.0</td>
<td>1</td>
<td>4.76</td>
<td>4.15</td>
</tr>
<tr>
<td>Norm-conserving LDA</td>
<td>280.0</td>
<td>2</td>
<td>4.30</td>
<td>3.85</td>
</tr>
<tr>
<td>Norm-conserving GGA</td>
<td>280.0</td>
<td>2</td>
<td>4.70</td>
<td>4.20</td>
</tr>
<tr>
<td>Norm-conserving LDA</td>
<td>600.0</td>
<td>2</td>
<td>4.62</td>
<td>4.03</td>
</tr>
<tr>
<td>Norm-conserving GGA</td>
<td>600.0</td>
<td>2</td>
<td>5.00</td>
<td>4.33</td>
</tr>
<tr>
<td>Ultrasoft LDA</td>
<td>280.0</td>
<td>2</td>
<td>4.71</td>
<td>4.12</td>
</tr>
<tr>
<td>Ultrasoft GGA</td>
<td>280.0</td>
<td>2</td>
<td>5.05</td>
<td>4.39</td>
</tr>
</tbody>
</table>
Figure 2: Imaginary part of dielectric function of 8-unit cell diamond; varied k-point mesh density (Optimised using 4x4x4 mesh, smearing width 0.5eV)

Acknowledgements
D. W. Drumm gratefully thanks A. D. Greentree and J. H. Cole for several fruitful discussions. This work was supported by Quantum Communications Victoria (QCV), which is funded by the Victorian Government’s Science, Technology and Innovation (STI) initiative.

References
XANES from ROI vs. DA deconvolution of full spectral SXRF data
Barbara Etschmann abc, Chris Ryan ac, Joël Brugger de, Mark Pownceby f,
Weihua Liua e, Pascal Grundler d and Dale Brewe g
a CSIRO Exploration & Mining Australia
b CODES Centre of Excellence, University of Tasmania, Australia,
c School of Physics, University of Melbourne, d The University of Adelaide, Australia, e South Australian Museum, Australia
f CSIRO Minerals, Australia and g The Advanced Photon Source, USA

Abstract

XANES spectra obtained using a Region-Of-Interest (ROI) centered on a major X-ray line of a trace element in a complex matrix may be dominated by significant interferences from other elements. To combat this, full fluorescence spectra were collected at each energy point in a XANES scan. These fluorescence spectra are deconvoluted using Dynamic Analysis (Ryan, 2000), subtracting off interfering signals to extract pure elemental XANES spectra. Applied to the measurement of the oxidation state of Eu (100-300 ppm) in natural Scheelite, this method provides better quality XANES data, as evidenced by improved statistics and flatter pre- and post-edge regions.

Introduction

X-ray fluorescence microprobes can achieve high spatial resolution (beams of micron to sub-micron sizes), high sensitivity (detect elements in the 10-100s ppm) and provide information regarding chemical speciation using X-ray Absorption Near Edge Structure (XANES).

XANES spectra are traditionally measured by collecting all counts within a defined energy window centred on a prominent X-ray peak. This works well for simple systems where there are no elemental interferences. In more complex systems, interfering fluorescence peaks may be eliminated with the use of a Wavelength Dispersive Spectrometer (WDS), however this usually implies that the element of interest exists in large enough concentrations to obtain a statistically reasonable number of fluorescence counts in the narrow acceptance of the WDS. For example, using a WDS, Rakovan et al. (2001) were able to discriminate between Eu Lα1 (5849.5eV) and Mn Kα (Kα1 = 5900.3, Kα2 = 5889.1eV).

For XANES analyses of trace elements in complex natural samples using a WDS is not a feasible option. Low concentrations of the trace elements (10-100s ppm) require the use of the lower resolution Energy Dispersive Spectrometer (EDS), where the signals from the trace elements may be dominated by significant interferences from other elements.

Similar problems of extracting information from trace elements are also encountered when fluorescence mapping with EDS detectors (e.g. SXRF, PIXE) and is a well established problem in the microprobe community. One way of combating this has been to implement a spectral decomposition transformation called the Dynamic Analysis (DA) method that enables the projection of accurate elemental images (Ryan, 2000). The aim of this paper is to demonstrate how this concept can be extended to XANES analysis of trace elements.
**Test sample – background**

Scheelite (CaWO₄) samples containing ~100-300 ppm Eu and a number of other rare earth elements with interfering fluorescence peaks were used in this experiment. Scheelite is of geological interest as it is a minor phase controlling REE geochemistry in many gold ore deposits. Under the conditions of formation of these deposits (i.e., T 250-350 °C; near neutral pH; redox condition next to CO₂(g)/CH₄(g)), the speciation of Eu is expected to be sensitive to the chemistry of the ore forming fluid, in particular the pH, redox state, and salinity (Brugger et al., 2007). Hence, the measurement of the oxidation state of Eu in minerals such as Scheelite can shed light on the physico-chemical conditions leading to Au precipitation.

**Experimental**

Eu L₃ XANES spectra and SXRF maps were collected at beamline 20-ID-B at the Advanced Photon Source (APS) at Argonne National Laboratory, USA. 20-ID-B has a Si (111) monochromator, resulting in an energy resolution ΔE/E of ~1.4 x 10⁻⁴ at 10keV with a flux of ~10¹¹ photons/s at 9.3keV. KB mirrors were used to focus the beam to 5 x 5µm². A liquid N₂ cooled 7 element Ge fluorescence detector was located at ~90° to minimize detection of the scattered X-ray beam. The monochromator energy was calibrated by using a pellet of Eu₂O₃ + BN as a reference standard. XRF maps were collected at 9.3keV to avoid the W L₃ edge and minimize resonant Raman scattering from W (Brugger et al., 2006); XANES spectra were collected from 6953 to 7003eV with a step size of 0.3eV, 2 s per step. XANES spectra were collected using both a region-of-interest centered on the Eu Lα₁ peak and full fluorescence spectra at each energy point of the XANES scan.

**Method & Results**

GeoPIXE uses the DA method to project quantitative elemental images (Ryan, 2000) from fluorescence spectra (PIXE, SXRF). The DA technique is a matrix transform algorithm that unfolds overlaps and subtracts background, escape peaks and other detector artifacts.

![Figure 1 SXRF spectrum of Scheelite sample DRY3, showing the first and last fluorescence spectra of a XANES scan (E = 6953eV and E = 7003eV).](image)
Pure elemental XANES spectra can be extracted by deconvoluting the SXRF spectral data using the DA method. While this is costly in terms of the time taken to record the full SXRF spectra, it reaps the benefit that interferences are removed; as opposed to ROI, where all counts in a particular energy window are recorded. This option has now been implemented in GeoPIXE (Ryan, xxxx).

Depending on compositional variation in this natural mineral, the ROI and DA Eu XANES vary between similar (Fig. 2 a and b) and showing significant differences (Fig. 2 c and d; the DA Eu XANES have much cleaner pre and post regions), which is probably related to the subtraction of interfering fluorescence peaks.

Clearly, for major elements, and for systems with little to no interferences using a ROI works well. However, for trace element XANES, and for samples that have substantial interferences this new technique of collecting full fluorescence spectra has significant advantages.

a. DA deconvoluted Eu XANES spectrum at point 1
b. ROI Eu XANES spectrum at point 1

c. DA deconvoluted Eu XANES spectrum at point 2
d. ROI Eu XANES spectrum at point 2

Figure 2 XANES scans from DA deconvoluted SXRF spectra and ROI window for different spots on the Scheelite sample DRY3.

Acknowledgements

This work was supported by the Australian Synchrotron Research Program, which is funded by the Commonwealth of Australia under the Major National Research Facilities Program. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Contract No.W-31-109-Eng-38. JB acknowledges Australian Research Council QEII fellowship (DP0208323).
References


Fabrication of periodic $\text{Al}_2\text{O}_3$ nanomasks

Jing-Hua Fang, Paul G. Spizzirri, Alberto Cimmino and Steven Prawer.
School of Physics, Microanalytical Research Centre,
University of Melbourne, Parkville, Australia 3010.

Introduction

Periodic $\text{Al}_2\text{O}_3$ nano-masks are made of nano-porous alumina, which are formed by the anodization of aluminium metal. Historically, these anodized layers were developed to help protect aluminium (metal) from erosion. However it was soon realised that these layers could not fulfill this role as the metal continued to wear. At the same time it was noted that the anodized layer comprised regular nano-pore arrays which extended almost completely through the oxide, leaving just a thin barrier layer between the electrolyte and the aluminum metal. These features, coupled with the convenience and low cost of fabrication, have made these nano-pore arrays very attractive as a nano-membranes or templates.

Nano-scale periodic arrays have since found a variety of applications including: nano-filtration, nanotube / nanowire / nanodot fabrication and as substrates for micro-reactors [1-3]. Active areas for application also now include the development of photonic crystals and quantum dots where they may play a significant role in quantum computing architectures [4]. Methods for fabricating these periodic arrays include ion implantation and single crystal growth through nano-apertures onto controlled substrates.

In this work, we describe a method for fabricating nano-porous membranes (i.e. nano-templates) which have a high aspect ratio and would be applicable to the applications described. Termed an anodically etched, aluminium oxide template (AAO), periodically ordered $\text{Al}_2\text{O}_3$ nano-pores with diameters of 50nm and an interpore spacing of about 100nm can be realized using an electrolytic cell. Details of the template synthesis will be presented and their application to the preparation of quantum dots using ion implantation and crystal growth techniques will be discussed.

Experimental

Nano-porous AAO templates were prepared using a two-step oxidation process [5]. Clean, high purity aluminium foil (99.999%) with a thickness of 250µm was electropolished in a mixture of HClO$_4$ and C$_2$H$_5$OH (1:9 v/v) for 2 to 5 minutes. Next, the foil was anodized in an electrolytic cell where the aluminium is configured as the anode and metallic lead (high purity) as the cathode. The cell is operated with a potential of 40V - 60V DC using oxalic acid (0.3 mol dm$^{-3}$) as the electrolyte at 10°C for 30 to 60 minutes. The anodized alumina was subsequently dissolved in an etchant solution comprising phosphoric acid (6 % by weight) and chromic acid (1.8 % by weight).

A second oxidation step was then performed under the same anodization conditions for another 1 to 3 hours. In order to separate the AAO template from the aluminium foil, the voltage reduction sequential method (VRS) was adopted which resulted in the membrane “peeling” away from the foil [6]. Finally, the pore channels were cleared by dipping the membrane in 1% to 5% phosphoric acid at 20°C for various times. The resulting structure and morphology of the templates were then characterized using scanning electron microscopy (SEM).
Results and Discussion

Figure 1(a) shows a typical SEM image of the top (i.e., electrode solution interface) of an Al₂O₃ nano-mask which was fabricated and then etched in a 5% phosphoric acid solution for 1 hour. It is evident in this image that the pores are semi-periodic and have an average diameter of about 50nm. From the cross-sectional SEM image of Figure 1(b), the high-aspect-ratio of the AAO templates can also be seen. The depth of the channels depicted is ~10µm following the second 2 hour anodization step. However, as shown in Figure 2, the top and bottom openings of the channels have some residual disordered structure which is related to the remaining barrier layer. This residual structure, which results in occluded channels, will adversely impact on the application of these AAO templates in their use as nano-masks, especially for ion implantation purposes.

In order to understand the underlying processes that result in the occluded pores and in an attempt to try and make them more applicable for nano-fabrication, a more detailed analysis of the etching and peel off process was performed. Normally when the template is peeled off from the aluminum, the bottom of the channels (i.e. in contact with the metal) remains blocked. It is believed that a barrier layer forms between the aluminum and the template during the anodization process. Different acids with different concentrations and exposure times were studied and we observed...
that by using 5% (by weight) phosphoric acid, successful etching of this barrier layer
resulted in clear channels. Figure 3 shows the influence of different etching times on
the template using phosphoric acid after it has been removed from the aluminium.
From the data in Figure 3, we can see that a 2 hour etching time results in the
complete removal of the barrier layer. Furthermore, continued etching for times >2
hours (data not shown) results in the destruction of the top of the template with a
subsequent loss in its pore like structure and ultimately, that of the channels.

![Figure 3. The influence of etching time on the formation of the AAO template depicting (a) 1 hour, (b) 1.5 hour and (c) 2 hour etching. “Open pores” are clearly observed after 2 hours of etching.](image)

**Conclusion**

Semi-periodic Al$_2$O$_3$ nano-masks were successfully synthesized using a two-step
anodization process in an electrolytic cell. The diameter of the resulting nano-pores is
\( \sim 50\text{nm} \) and the thickness of nano-masks was found to be dependent upon the duration
of the second anodization step. We have observed channel formation rates of \( \sim 5\mu\text{m} \)
per hour. With straight channels of high aspect ratio and clear pores, these Al$_2$O$_3$
 nano-templates are suitable for preparing quantum dots using ion implantation or
nano-crystal growth techniques.

**References**


High temperature electronic properties of field-effect transistor based on SiC nanowires
Fang Fang 1,2
1 GNS Science, National Isotope Centre, 30 Gracefield Road, Lower Hutt, New Zealand
2 Institute of Micro/Nano Science & Technology, Shanghai Jiaotong University, Shanghai, 200030, P.R.China

Abstract
SiC is a potential material for a large bandgap semiconductor (Eg = 2.4 V) with its superior electronic, physical, and chemical properties, making it an excellent candidate for high-temperature nanoelectronic devices. SiC nanowires were synthesized on activated carbon fiber in large quantity by the way of high-frequency induction without metal catalyst. The morphologies of those nanowires were studied by XRD and SEM. Field-effect transistor (FET) was fabricated by deposition of Au-electrode pairs on the surface of SiO2 film, with SiC nanowires placed between two Au electrodes with the help of microfabrication techniques. Semiconductor analysis equipment as Agilent 4156C was used to test the electronic properties of those FETs. The I-V curves for samples at different high temperatures (473K, 673K and 773K) in an ambient atmosphere were tested. It was found that the higher the temperature, the more increase of the drain current. The carrier mobility versus 1000/T agreed well with the Arrhenius function. It is recommended that the SiCFETs in this work would be used as electrical devices operated in high temperatures because of their superior properties.

Key words: SiC nanowires; field-effect transistor (FET); high temperature

1. Introduction
In recent years, nanoscale one-dimensional materials, particularly carbon nanotube and SiC nanowire, etc, have attracted much attention due to their remarkable physics properties and their great potential applications in nanoscale electronics and optoelectronics [1]. The semiconductor nanowire field-effect transistors (FETs) is one of the promising devices which is considered to be building blocks for the application in the next generation of nanodevices. SiC is a potential material for a large bandgap semiconductor (Eg = 2.4 V) with its superior electronic, physical, and chemical properties [2]–[4], making it an excellent candidate for high-temperature nanoelectronic devices. However, little work has been done to record the high-temperature electronic property of SiC-nanowire FET. In this paper, we report the electronic property of such SiC-nanowire FET device at different temperature based on our previous work [5]. The SiCFETs were fabricated and tested at different high temperatures (200 °C, 400 °C and 500°C) in an ambient atmosphere. The carrier mobility corresponding to SiC-nanowire FET devices work at different temperature was calculated. It was found that the carrier mobility versus 1000/T agreed well with the Arrhenius function.

2. Experiment
The SiC nanowires were synthesized on activated carbon fiber in large quantity without a metal catalyst in a vertical high-frequency induction furnace. By heating SiO, the formed SiO gas was carried to an activated carbon fiber surfaces (lower temperature, ~ 1450 °C) by Ar, and then their reactions led to the formation of a large amount of β-SiC nanowires. Devices were fabricated by some microfabrication techniques. Figure 1 shows the configuration of the field-effect-transistor. SiC
nanowires were placed between two Au electrodes. In order to get good connection between metal and the SiC nanowires, chemical treatments must be applied on the obtained SiC nanowires. The electronic measurements were performed using an Agilent 4156 C semiconductor characterization system under an ambient condition at room temperature and different high temperatures (200 °C, 400 °C and 500°C).

3. Results and discussion

Fig. 2. (a) The synthesized fluffy-like SiC nanowires. (b) XRD pattern of SiC nanowire samples. (c) and (d) are SEM images of large quantities of randomly oriented nanowires.

Fig. 2 (a) shows the real blue fluffy-like SiC nanowire samples we obtained in hand. The X-ray diffraction (XRD) pattern of as-prepared samples is shown in Fig. 2(b). All the peaks were indexed as $\beta$-SiC. Fig2(c) and (d) show the SEM images of those nanowire samples. It’s a large amount of straight, curved, randomly oriented and free- standing nanowires before chemical treatments.

Fig. 3 shows the temperature dependence of the drain current of the n-type SiC-nanowire FET at $V_g = 5V$. It can be seen that the drain current increased with the
increase of temperature at the same drain-source voltage. It is commonly believed that
the role of the $V_{g}$ is to change the value of $R_{SiC}$ through Fermi level (EF) modulation,
thus changing the slope. The carrier mobility was calculated thereafter and according
to our previous calculation, it is found that the carrier mobility versus 1000/T agreed
well with the Arrhenius function [5].

![Graph showing $I_{ds}$ vs $V_{ds}$ curves at different temperatures](image)

**4. Summary**

The limitation temperature
for electronic device based on Si is about 350°C while the electronic device based on
SiC can work at around 600°C without cooling system. So there is a great potential for
SiC electronic devices to work in many fields like aviation system for military use.

To sum up, an efficient route has been developed to synthesize large quantity of SiC
nanowires. Field-effect transistor (FET) was successfully fabricated by
microfabrication techniques. I-V curves of SiCFET were tested at different high
temperature in order to study the high temperature property for such device. It is
found that the drain current increased with the increase of the working temperature at
the same drain-source voltage. Thereafter the carrier mobility was calculated and it is
found that the carrier mobility versus 1000/T agreed well with the Arrhenius function.
The SiCFETs in this letter would be used as electrical devices operated in high
temperatures because of their superior properties. Therefore, the synthesized novel
SiC nanowires are expected to have potential application in electronic devices
working at high temperature.

**References**

Age mapping of radioisotopes by daughter trace element analysis

V.S. Gill 1, D.X. Belton 2,1, D.N. Jamieson 1, C.G. Ryan 2,1
1School of Physics, University of Melbourne, Victoria, Australia
2CSIRO Exploration and Mining, Clayton, Victoria, Australia

Introduction

Chemical dating is a technique that uses elemental concentrations within microscopic zircon crystals which can be effectively used to determine the age of associated minerals and has been in use for a number of years (see for example [1,2]). The half-lives of the steps in the radioactive decay chain of U and Th to Pb can be used to determine the age of a zircon crystal. Zircons (composition ZrSiO₄) have played an important role in the dating of sediments associated with the Cretaceous/Tertiary (K/T) extinction event from 65.5 million years ago [3]. At the other end of the timescale, zircons have been used to date the oldest rocks on the planet with an age of over 4.2Ga [4]. A decay system with a long half-life is therefore required. We are developing a new method for dating zircons by measuring trace elements using Proton Induced X-ray Emission (PIXE). By performing the analysis with a focused ion beam in a nuclear microprobe system, the compositional zoning of the zircons can be measured. This method therefore has the potential to map the age of the zones in the zircons that can provide new insights into the episodic growth of zircons in response to magmatic and metamorphic events.

![Zircon crystals mounted in epoxy.](image)

Zircons are uniquely suitable for the recovery of their age from the elemental composition because of a very useful chemical attribute. This is that the chemical processes that produce the zircon crystals from the original melt also purge lead from the growing crystal (common lead). Successful dating of zircons from the elemental composition requires that there is only a minimal level of common lead and that the system is closed to U, Th and Pb after crystallisation. These characteristics are widely accepted to generally apply in zircon, once the mineral has cooled to below the closure temperature [5] and assuming it has not suffered radiation damage (metamictisation). Therefore the age of a zircon crystal can be determined by measurement of the elemental concentrations of parent radioactive elements and their associated daughter elements.

Both U and Th radioactive decay chains terminate with stable Pb isotopes. By using the standard relations between the concentration of a radioactive parent element to the...
daughters and taking into consideration that the PIXE technique is not sensitive to the isotope, the age of a zircon, $\tau$, can be calculated by the following equation [6]:

$$
\begin{align*}
  Pb &= Th \frac{208}{232} \left[ \exp(\lambda_{232} \tau) - 1 \right] \\
       &\quad + U \frac{206}{238,04} 0.9928 \left[ \exp(\lambda_{238} \tau) - 1 \right] \\
       &\quad + U \frac{207}{238,04} 0.0072 \left[ \exp(\lambda_{235} \tau) - 1 \right]
\end{align*}
$$

where $Pb$, $Th$ and $U$ are the concentrations in ppm (measured by PIXE in our case) and $\lambda_{232}$, $\lambda_{238}$ and $\lambda_{235}$ are the radioactive decay constants of $^{232}$Th, $^{235}$U and $^{238}$U respectively. This equation is transcendental and therefore must be solved iteratively.

Figure 2: PIXE spectrum from a zircon crystal induced by 3MeV H$^+$ irradiation.

**Considerations for analysing Zircon**

When analysing zircons, there is a particular limitation that must be addressed. As can be seen in Figure 2, the spectrum is dominated by the Zr K-shell peaks at 15.8 and 17.7keV. The U, Th Lα and Pb Lβ peaks (at 13.6, 13.0 and 12.6keV respectively) are dwarfed by the large Zr peaks, thus reducing sensitivity to the elements of interest due to low energy tails reducing the signal to noise ratio of Th, U and Pb.

For the analysis method achieve optimum sensitivity, the H$^+$ ion beam energy provided by the nuclear microprobe should be optimised to minimise the Zr signal compared to the signal from the U, Th and Pb signals. It is traditional to perform PIXE with a H$^+$ energy of 3MeV. This energy is chosen to maximise the characteristic x-ray yields across a useful range of elements from Al ($Z=13$) to U ($Z=92$). Also, the x-ray production cross section is a function of incident beam energy and differs with element ($Z$) and shell (K, L or M) of excitation. In this work we investigated the optimum beam energy required to maximise x-ray yield of U, Th and Pb in preference to Zr.
**Method of determining optimal incident beam energy**

The error that is most important to minimise is that for the age. By performing a standard error treatment on the age equation (for example see reference [7]), it can be seen that reducing the error for concentrations of U, Th and Pb will also reduce the uncertainty in age as expected.

Although it is possible in principle to determine the optimum beam energy from theory, uncertainties associated with beam energy loss and x-ray attenuation in the zircon crystals made it preferable to perform an empirical measurement. There we performed a series of zircon analyses over a range of beam energies from 1.2 to 3.5MeV, in 0.1MeV steps, in an attempt to optimise operating conditions. We collected x-ray spectra using the CSIRO nuclear microprobe over a range of beam energies and determined the uncertainty (or experimental error) in the U, Th and Pb signals. The error associated with a measured elemental concentration is related to the FWHM of the peak corresponding to the element of interest in the x-ray spectrum. One aspect of minimising uncertainty in age is helped by maximising the proportions of the concentrations of Th:Zr and U:Zr, but there are other factors that also must be taken into consideration.

There are other experimental parameters that also need to be taken into account when optimising the beam energy. At high energies (above 3.5MeV), there is a possibility of producing neutrons due to interactions of the beam with oxygen and carbon in the sample, thus operator safety becomes an issue. Also at higher energies, the constraints of the equipment, such as bending magnets, become important so we also propose to limit the beam energy to that achievable with small ion beam accelerator/nuclear microprobe systems which typically operate with beams below 3.5MeV.

![Figure 3: Relative yield of Th (L ) and U (L ) to the Zr (K ) matrix signal as a function of the H + beam energy.](image)

When running the proton beam at lower energies (around 1.5MeV) there are other considerations that must be addressed. When taking data in this range, more counts must be taken to obtain good counting statistics, as the x-ray yield drops with beam
energy [8], so analysis times become prolonged. The current the beam is operated at is used to keep the count rate constant but there is a limit to how far it can be increased. Variations in beam rigidity mean that stability, electrostatic scanning and focus must also considered in the optimisation process.

Conclusions

Preliminary results from initial experiments are shown in Figure 3. Although further analysis is necessary, this appears to suggest that an energy of around 2MeV would be optimal for running the microprobe when analysing zircon.

This optimal energy has implications for the chemical dating of monazites and the mineral apatite, which have similar properties of closed systems with a dominant element masking the U, Th and Pb of interest. These accessory phases, along with zircon, are important to geological research and mineral exploration.

References

Enantioselectivity of chiral molecules on chiral copper surfaces
M. J. Gladys 1,3, A. Stevens1, N. Scott1, G. Jones4, D. Batchelor2 and G. Held1.
1 Department of Chemistry, University of Cambridge, Lensfield Rd, Cambridge, CB21EW.
2 Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany.
3 School of Mathematical and Physical Sciences, University of Newcastle, Callaghan 2308, NSW Australia.

Abstract
Chiral (Enantiomeric) molecules often exhibit drastically different reactivity in living matter. Our current work focuses on generating chiral surfaces that exhibit selectivity for single enantiomers for chiral molecule synthesis and molecular sensors. Using a variety of techniques we have studied the adsorption of S and R-Alanine enantiomers on Cu(531) and found for the first time, a self assembled chiral overlayer on a chiral substrate. HR-XPS was used to retrieve information about the chemical states and adsorption sites and show the molecule is bound to the surface with a triangular footprint. Carbon K-edge NEXAFS using linear and circularly polarized synchrotron radiation shows the variation of the carboxylic acid (O-C-O) π* resonance and therefore the molecular orientations on the surface. Large differences are observed between the adsorption geometry of the two Alanine enantiomers.

Introduction
To generate enantiospecific reactions, animals have developed a complex system of lock and key mechanisms. This design utilises the 3D shape of enzyme molecules to match specific chemicals which form countless biological functions. Thus enzymes act as chiral catalysts, and include what is known as “active sites” which stereo-direct the reactions. Stereoselective catalysis is rapidly becoming a crucial phenomenon in the pharmaceutical industry where new chiral drugs are synthesized. Single enantiomer drugs are more active, require lower doses and exhibit fewer side effects than racemic (50:50 mixture of enantiomers) drugs [1] The ‘wrong’ enantiomer of a chiral pair may have such damaging side effects, that far outweighs the benefits of the correct enantiomer. [2] This means that of these many available drugs, one form is good, while the other is ineffective or even dangerous. As a consequence, there is a current and pressing demand to either select or create only one of the enantiomers in drug manufacturing. [3,4] Current methods to produce a single enantiomer rely on homogenous catalysis which has the inherent problem of removing the catalyst molecule from the product solution without destroying the target drug. As an alternative, the use of a heterogeneous catalyst would circumvent the majority of separation problems that exist. Analogous to 3D enzymes, chiral surfaces contain an inherent 2D chiral interface that provide a ‘lock’ so that only one of the enantiomers, the ‘key’ will fit, i.e. the surface will recognise the chirality of the molecule.

Significant success with regards to the enantioselective hydrogenation of α and β-ketoesters has been achieved by modifying achiral Pt or Ni catalyst surfaces with chiral molecules such as cinchonidine/cinchonine and tartaric acid, respectively, (see [5-8] and references therein). In order to identify the underlying reaction pathways it is crucial to know the adsorption geometries of the relevant reactants and modifiers as well as their adsorption energies. Two different generic microscopic mechanisms have been discussed in the recent literature, which both would lead to stereoselectivity of chirally modified metal catalysts [8]: the template model states that the modifiers template the metal surface in such a way that it provides a chiral reaction environment
for the reactant molecule; in the active chiral site model the metal substrate essentially provides a platform for the modifier molecules to adsorb; the stereochemical effect is predominantly due to the geometry of the chiral modifiers.

Metal single crystals on the other hand are inherently non-chiral in nature and generally do not possess enantioselectivity. Nevertheless, it was established that certain single crystal fcc surfaces with high Miller indices contain step-kinks, that is, two steps constituting a kink site that are inequivalent [9] and therefore chiral. To classify the enantiomers of these surfaces, the kink site (A in Fig.1) is defined as the junction of the following faces {111}, {110} and {100}. In terms of atomic surface density, a hierarchy exists such that \{111\} > \{100\} > \{110\}. The D (right-handed)-kink contains the sequence \{111\} → \{110\} → \{100\} which runs clockwise as viewed from the vacuum while for the L(left-handed)-kink, the sequence is anticlockwise. The (531)R and (531)S surfaces are shown in Figure 1, and illustrate the chiral differences inherent in these surfaces. On a cut crystal, the right-handed surface will appear on the ‘front’ side, while the left-handed surface is present on the reverse. The idea behind intrinsically chiral surfaces is that only one enantiomer will fit to the kink sites (“active sites” analogous to enzymes) on the surface, while the other does not.

The earliest reports of enantioselective reactions on chiral single crystal surfaces came from a series of electrochemical studies by Attard et al. [9-10] showing clear differences in the cyclo{voltammograms for electro-oxidation of (L)- and (D)-glucose on Pt electrodes terminated by chiral \{643\}, \{431\}, \{531\} or \{321\} surfaces. Changing the enantiomer of the reactant molecule from (L) to (D) in these experiments had the same effect as changing the chirality of the electrode surface.

In this paper we describe the adsorption of Alanine on Cu\{531\}R produces an ordered p(1x4) chiral overlayer. This is the first ordered self assembled layer on a chiral surface to be observed. Furthermore, NEXAFS data show differences in adsorption geometry are observed between Alanine enantiomers on this surface. Finally Density Functional Theory calculations were used to model stable structures of Alanine on Cu\{531\} to compare to experimental work to illustrate the magnitude of the interface and intermolecular bonding forces at work to produce these effects.

![Figure 1: The two enantiomer surfaces of the fcc(531) step-kinked surface. This surface has the smallest unit cell of all fcc chiral surfaces, which makes it an ideal model surface for investigating chiral systems. On this surface the step-kinks are made up of alternating [311] and [100] steps as illustrated.](image)
Experimental

The Cu single crystal used in the synchrotron experiments was terminated by a (531) surface (equivalent to \{531\}R \[4\] or \{531\}D \[20\] shown in figure 1. The crystals were cleaned by repeated cycles of sputtering at room temperature and annealed in vacuum to at least 1000K. In all experiments the crystal was mounted with the [-112] crystallographic directions at horizontal (in the plane of the storage ring for the synchrotron experiments). The synchrotron experiments were performed at beamline UE52 PGM of BESSY II in Berlin (Germany). XP spectra in the C 1s, N 1s, and O 1s regions were recorded using a Scienta 200mm electron energy analyser with a pass energy of 40eV and linearly polarised synchrotron radiation with a photon energy of 630eV. The angle of incidence was close to the surface normal and the emission angle around 60° away from the surface normal. Enantiopure R or S-Alanine (99 % from Aldrich) crystalline powder was adsorbed by evaporation from a glass crucible heated to the desired temperature. Saturation coverage was achieved via background dosing in excess of the amount actually needed was deposited at room temperature followed by annealed to the desired temperature. Submonolayer coverages were generated through incremental dosing at the same dosing conditions.

In addition to the previously described experiments, the adsorption of alanine on the Cu\{531\} surface was studied by means of density functional theory (DFT) calculations using the CASTEP computer code. The generalised gradient approximation as proposed by Perdew et al. \[11\] was applied (henceforth referred to as GGA-PW91) for electron-ion interactions, combined with Vanderbilt ultrasoft pseudopotentials \[12\] for exchange and correlation. For the clean Cu\{531\} surface, the plane wave basis set was truncated at a kinetic energy of 340eV to describe the electronic wavefunctions. The bulk lattice constant (a = 3.606Å) for use of the Cu surface calculations was determined by the Brillouin zones sampled with a 8,8,1 Monkhorst Pack Mesh. Calculations of Alanine on Cu\{531\} were carried out on [1 1, 2 -2] unit cells to correspond to the ordered overlayer observed in LEED. The slab contained 20 layers of Cu\{531\} and a vacuum depth equivalent to 15 atomic layers was placed between the periodically repeated slabs to ensure that the adsorbate and the subsequent slab do not interact. A Monkhorst Pack Mesh of 5x1x1 was used to sample the Brillouin zone

Results and Discussion

The adsorption geometry of alanine on Cu\{531\} was characterised using LEED, NEXAFS and XPS A p(1x4) alanine structure was observed with LEED and is the only intrinsically chiral surface for which an ordered molecular superstructure has been observed so far. The chemical shifts of the C 1s, N 1s and O 1s core level signal in XPS are essentially the same as for alanine on Cu\{110\} at low coverage, which indicates that the molecules assume the same 3 alaninate adsorption complex as shown in Figure 2. There are two adsorption sites on the \{531\} surface that can match the triangular footprint, namely \{110\} and a \{311\} facets. The azimuthal orientation and, hence, the adsorption site can be determined through the angular dependence of the carbon K-edge NEXAFS spectra. According to the dipole selection rule, the intensity of the $\pi^*$ resonance at 288eV (cf Fig. 2(a)) which is localised at the carboxylate group (O-C-O) is at a maximum when the polarisation vector, $\sim E$, of the exciting synchrotron radiation is perpendicular to the O-C-O triangle and goes to zero when $\sim E$ lies in the plane of the triangle, irrespective of how the molecule is adsorbed. The intensity of the $\pi^*$ resonance for a single molecule is proportional to $\cos^2\gamma^\circ$, where $\gamma^\circ$ is the angle between $\sim E$ and the surface normal of the O-C-O plane \[13\].
The angular dependence for a saturated layer of alaninate on Cu\{531\}R shows very shallow intensity variations with minima well above the zero level, as seen in Figure 2(b). This indicates that the signal arises from molecules with two different azimuthal orientations (additional information comes from the fact that the adsorbate layer forms a p(1x4) superstructure which can only accommodate two molecules per unit cell). There is also a distinct difference in the angular intensity variations between the (R) and the (S) enantiomers of alaninate, which indicates significant enantiospecific differences in the local adsorption geometries of the two enantiomers.

These results imply that both enantiomers occupy both triangular adsorption sites on the \{311\} and \{110\} microfacets of the Cu\{531\} surface. DFT model calculations for glycinate (NH2\{CH2\}COO) do not indicate a particular preference for one of the two adsorption sites but strongly favour an adsorption complex with two first layer (kink) Cu atoms and one second layer atom involved [14], which is the geometry depicted schematically in Figure 2d. This adsorption geometry allows all kink atoms to participate in the adsorbate bond. It also allows the molecules on \{110\} microfacets to form strong hydrogen bonds between their amine groups and the oxygen atoms of neighbouring molecules (hydrogen atoms are not shown) with O-H distances close to the ideal value of 1.5Å. The resulting distortion of the molecule causes the methyl group, which is on the 'downhill side' of the \{110\} facet for the (S)-enantiomer, to move further away from the surface plane, minimising the interaction with the metal atoms.

Figure 2: (a) Carbon K-edge NEXAFS spectra of (R)-alaninate on Cu\{531\}R for two different angles of the polarisation vector; (b) angular dependence of the \(\pi^*\) resonance at 288eV for saturation coverage of alaninate (p(1 x 4) overlayer, from [17]); (c) for 55% saturation coverage; (d) Geometry model for the p(1x4) overlayer of alaninate on Cu/531g at saturation coverage [17].
From a steri point of view this model appears most plausible since the methyl group of the (R)-enantiomer is on the 'uphill side' of the \{110\} microfacet and requires less molecular distortion in order to reduce the interaction with the surface atoms. The associated angle \(\alpha_{110}\) should therefore change, whereas for the more symmetric adsorption site on the \{311\} facet the interaction of the methyl group with the surrounding Cu atoms is weak with both enantiomers and should not induce molecular distortions that would change \(\alpha_{311}\) significantly. The fit results for this model also imply that there are about twice as many molecules adsorbed on \{110\} than on \{311\} adsorption sites. This may explain the significantly lower degree of ordering that is observed for this enantiomer.

The angular dependence of the \(\pi^*\) resonance is very different for a dilute alaninate layer around half the saturation coverage, as shown in Figure 2(c). Both enantiomers now show the same angular dependence. The fit to the data shown in Figure 2(c) shows a 4 : 1 preference for the adsorption sites on the \{311\} facets with the molecules rotated by about 20° with respect to the adsorption geometry at saturation coverage [15]. This is the result of missing inter-molecular interactions. Table 1 lists these different alanine overlayers with their respective adsorption energies, \(\Delta H_{\text{ads}}\). Of primary interest here are the \(\Delta H_{\text{ads}}\), and what can be seen is that for (R) alaninate there is a preference for the (311R/311R) structure; this can be compared to the S-alaninate which is also found to favour the (311S/311S) structure. What we actually see in the adsorption energy trends is a similar tale to that observed for the Cu\{110\} surface where the most stable structures all lie within a small range on the boundaries of DFT reliability. Furthermore, this suggests that we are unlikely to observe any enantioselectivity in experiments such as temperature programmed desorption (TPD) or in the LEED patterns, and is indeed found to be the case for the TPD. In fact, examining the \(\Delta H_{\text{ads}}\) shows that the R-alaninate has a preference for (311/311) and (110/110) occupation whilst the S-alaninate shows a preference for (311/311) and (110/311) occupation. Moreover, the difference in \(\Delta H_{\text{ads}}\) from the least favoured structures are beyond the energy differences observed for conformation changes found from studies on the Cu\{110\}[16] and Cu\{311\}[14] surface.

**Summary**

Our findings allow three important conclusions for the adsorption of alanine on Cu\{531\}: (a) the isolated molecules have higher adsorption energy on the \{311\} facets where alanine can adsorb without major lateral distortions; (b) the adsorption energy difference between \{311\} and \{110\} must be higher than possible energy gains from the formation of hydrogen bonds with molecules on the \{110\} adsorption sites (in essence this leads to a substrate-mediated repulsive interaction); (c) the enantiospecific adsorption behaviour at higher coverage is induced by (repulsive or attractive) inter-molecular interactions between molecules on \{311\} and \{110\} sites or by repulsive molecule-substrate interactions on the \{110\} adsorption sites. The most important type of inter-molecular interaction are hydrogen bonds. Their importance for the arrangement of adsorbed amino acids has been pointed out by

<table>
<thead>
<tr>
<th>System</th>
<th>(\Delta H_{\text{ads}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>½ ML</td>
<td>+1.40</td>
</tr>
<tr>
<td>(110)(^R)</td>
<td>+1.35</td>
</tr>
<tr>
<td>(311)(^R)</td>
<td>+1.39</td>
</tr>
<tr>
<td>(110)(^S)</td>
<td>+1.36</td>
</tr>
<tr>
<td>(311)(^S)</td>
<td>+1.36</td>
</tr>
<tr>
<td>+1/2 ML</td>
<td>+1.36</td>
</tr>
<tr>
<td>(110)(^R)/ (110)(^R)</td>
<td>+1.36</td>
</tr>
<tr>
<td>(311)(^R)/ (311)(^R)</td>
<td>+1.45</td>
</tr>
<tr>
<td>(110)(^S)/ (311)(^R)</td>
<td>+1.24</td>
</tr>
<tr>
<td>(110)(^S)/ (110)(^S)</td>
<td>+1.28</td>
</tr>
<tr>
<td>(311)(^S)/ (311)(^S)</td>
<td>+1.43</td>
</tr>
<tr>
<td>(110)(^S)/ (311)(^S)</td>
<td>+1.38</td>
</tr>
</tbody>
</table>
several authors before [55, 66]. Repulsive interactions for the present case are most likely related to the methyl group.

**References**

Delineating groundwater flowpaths using $^{14}$C dating in the Upper Loddon catchment, central Victoria

Sarah K. Hagerty $^{1}$, John A. Webb $^{1}$, Geraldine E. Jacobsen $^{2}$

$^{1}$Department of Environmental Geoscience, La Trobe University, Bundoora, Victoria, Australia

$^{2}$Institute for Environmental Research, ANSTO, Lucas Heights, NSW, Australia

Radiocarbon dating of groundwater has been used to delineate flowpaths and calculate hydraulic conductivity as part of a detailed hydrogeological/hydrogeochemical study of the Tullaroop catchment in the Upper Loddon, central Victoria. The dating confirms that both the basalt and deep lead aquifers in the study area are recharged through scoria cones at volcanic eruption points. The radiocarbon dating also shows that flow paths in the basalt aquifer are complex since ages do not always increase downflow; any hydraulic conductivity calculations must take this into account. One anomalously old $^{14}$C date supports other hydrogeological evidence that suggests groundwater in the deep lead is trapped upflow of horsts created by ENE Cainozoic faults.
ANSTO heavy ion ToF for analysis of light elements in thin films

M. Ionescu 1, Y. Zhao 2, R. Siegele 1, D. D. Cohen 1, D. Lynch 1, D. Garton 1,
E. Stelcer 1, M. Prior 1

1Australian Nuclear Science and Technology Organization Sydney, Australia
2University of Wollongong, Australia.

Abstract

Thin films have various potential applications in electronic devices, and their performance is intricately linked with the electric and magnetic properties of the film, in which an important role is played by the presence of light elements, in particular Hydrogen, Oxygen and Nitrogen. The source of light elements, the form in which they are incorporated into the thin film, and how this is influencing the MgB2 thin film properties is currently under scrutiny by various research groups. Typically these films are grown on oxide ceramic substrates, such as Al2O3-C and it is possible that the source of Oxygen is the substrate itself or the growth atmosphere. Here we report on a study of light elements in MgB2 thin films grown on various substrates, using heavy ions recoil and a time-of-flight detector. A series of MgB2 thin film samples produced by PLD (pulsed laser deposition) were analyzed, including films produced in-situ on Al2O3-C substrates with an on-axis and off-axis geometry, one film produced in-situ with an off-axis geometry, and one film produced ex-situ, with a bulk-like Tc. We also analyzed one film produced with on-axis geometry under the same conditions on Si (001) substrate. The amount of Oxygen detected by ToF, appears to be correlated with the Tc of the films, the higher the Tc the lower the oxygen content. Also, the superconducting properties of the examined thin films are discussed in the context of the results.

Keywords—Heavy ions ERDA, MgB2 thin films

Introduction

Thin films characterization by heavy ions time-of-flight ERDA spectrometry is an attractive technique due to its capacity to detect elements over a wide range of Z, and to extract from the recoiled particles both mass and depth information. Over the last 15 years ANSTO has developed and constantly improved such a system [1], used routinely to characterize complex thin film architectures, and optimized for multi-layered, multi-element configurations found in the areas of semiconductor and superconductor device development. One such thin film with device application potential is MgB2, in which Oxygen has been gradually revealed as playing an important role in its electric and magnetic properties. As early as 2001, it was reported that the exposure to low levels oxygen during fabrication of MgB2 thin films could “alloy” the ex situ annealed MgB2 films to form a Mg(B-O)2 alloy, resulting in a much improved critical current Jc but a slightly lower transition temperature Tc of 35 K [2] than the bulk. A study of grain boundaries in Oxygen-alloyed bulk samples by selected area electron diffraction (SAED), suggests that Oxygen was incorporated in the form of MgO phase with a size of about 10nm [3], where periodical Mg-B-O layers were found at the grain boundaries. These studies suggest that oxygen-rich precipitates could provide pinning centers as the precipitates and oxygen-incorporated grain boundaries are of favorable dimensions, between 5-100nm, which is comparable with the coherence length ξ of MgB2 which is around 5nm [4,5]. However, the decrease of the transition temperature with the incorporation of Oxygen observed in bulk and thin films is undesirable, and it is more pronounced in thin films. The cause
appears to be the influence of Oxygen precipitates on the electron-phonon coupling parameters, as suggested by calculation for two possible oxygen-ordered MgB$_2$ compounds of composition Mg$_2$B$_3$O and Mg$_2$B$_3$O$_2$ [6]. The results show that the calculated $T_c$ values of Mg$_2$B$_3$O and Mg$_2$B$_3$O$_2$ are 18.3K and 1.6K, respectively. This result is in accordance with the reported decrease of $T_c$ in some oxygen enriched MgB$_2$ samples, especially in the in situ prepared thin films [7, 8]. There is enough evidence to suggest that in device applications based on MgB$_2$ thin films, the presence of Oxygen and its distribution will strongly influence the device performance, and therefore detailed information of Oxygen form and its distribution in MgB$_2$ films is necessary. In this paper, we report the results of Oxygen distribution measured by heavy ion ERDA in different types of MgB$_2$ films prepared by the pulsed laser deposition (PLD) method.

Experimental details

The ERDA experiment was carried out in a vacuum better than 1x10$^{-6}$Pa, using Iodine ions of 82.5MeV. A schematics of the experimental apparatus used here is shown in Fig.1. The beam was shaped in a rectangular form, 3mm high and 1mm wide, and directed onto the sample at an incident angle of 67.5°, between the beam direction and sample normal. The energy of recoils was measured with a time-of-flight detector placed at an exit angle of 45° relative to the sample normal, resulting in a scattering angle of 45°. The two electrostatic mirrors were placed 0.5m apart, and each contained a 25µg/cm$^2$ C foil to measure the flight time of the recoils. The final rest energy of the recoils was measured with a surface barrier detector, placed at the end of the flight path. The samples are placed on a 2-axis goniometer, and placed in the beam path at the required position. In this experiment, the total charge collected on each sample during the measurement was 12µC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>Deposition geometry</th>
<th>Mg layer</th>
<th>cap layer</th>
<th>Surface etching</th>
<th>$T_c$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Si (001)</td>
<td>On-axis</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>18.7</td>
</tr>
<tr>
<td>2</td>
<td>Al$_2$O$_3$-c</td>
<td>On-axis</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>25.8</td>
</tr>
<tr>
<td>3</td>
<td>Al$_2$O$_3$-c</td>
<td>Off-axis</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>Al$_2$O$_3$-c</td>
<td>Off-axis</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>34</td>
</tr>
<tr>
<td>5</td>
<td>Al$_2$O$_3$-c</td>
<td>Off-axis</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>33</td>
</tr>
<tr>
<td>6</td>
<td>Al$_2$O$_3$-c</td>
<td>Off-axis</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>33</td>
</tr>
<tr>
<td>7</td>
<td>Al$_2$O$_3$-c</td>
<td>Off-axis</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>34</td>
</tr>
<tr>
<td>8</td>
<td>Al$_2$O$_3$-c</td>
<td>Off-axis</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>34.5</td>
</tr>
</tbody>
</table>

Table 1. Summary of sample characteristics used in this study. The $T_c$’s were determined by dc magnetization method

A number of MgB$_2$ films were grown by PLD, as detailed in Table 1, where the $T_c$ of each sample was measured by SQUID magnetometer between 300K and 5K. The details of the PLD apparatus were described previously [8, 9]. Two deposition geometries were applied. For “on-axis” deposition, the substrate normal was perpendicular to the target, and for “off-axis” deposition, the substrate normal was parallel to the target surface. For some films, after the deposition of the MgB$_2$ film, and before the in situ annealing process, pure Mg was deposited by PLD from a
separate Mg target, as the final “cap” layer, in order to compensate for the Mg loss during annealing. The thickness of the Mg cap layer was around 100nm. For some samples, the surface was etched away before the Oxygen and the $T_c$ measurements using the ion beam.

**Results and Discussion**

The raw spectrum of sample 1 is presented in Fig. 2-a, in (Energy-time) space. This data was projected onto the time axis and converted into depth profile (Fig. 2-b) from first principle calculations, using previously published information on the stopping power of ions in matter [10]. The calculations show that at this energy of Iodine, the variation in the stopping power of elements of interest (Oxygen, Boron, Magnesium and Silicon) is only a few percentages between the top and the bottom of MgB$_2$ films. A close inspection of this figure shows a significant presence of Oxygen throughout the entire thickness of MgB$_2$ film, with a slightly higher concentration at the surface. Also, the Oxygen as well as Magnesium appears to have diffused into the Si substrate over a significant depth. As Oxygen was not present in the MgB$_2$ target used to grow the film, the most probable source for it remains the growth atmospheres. This is supported by the fact that, if the base pressure in the deposition chamber prior to the deposition is higher than approximately $1 \times 10^{-5}$Torr, then the resulted film is not superconducting, and presumably all Mg is oxidized before the stable, MgB$_2$ phase is formed.

Fig 3 shows the same result for sample 2, which had the lowest $T_c$ amongst the films grown on Al$_2$O$_3$. The depth profile of elements in the film also shows the presence of Oxygen with a distinct peak at the surface. If we define the film-substrate interface as the depth where Oxygen and Al increase together, we can distinguish the Oxygen present only in the film. In this case, the amount of Oxygen is slightly smaller as compared with the film grown on Si substrate, but there is still a significant diffusion of Mg in the Alumina substrate. Surprisingly, this result also suggests a small diffusion of Boron into the substrate.

The ERDA result for sample 3 is shown in Fig. 4. This sample was also grown on Al$_2$O$_3$ (see Table 1), but with an off-axis deposition geometry, and additionally, an Mg cap layer was used. The depth profile of elements shows that, compared to the sample 2, Oxygen and Magnesium have a similar depth profile, but no diffusion of Boron into the substrate occurs.

The ERDA results for the sample with the highest $T_c$ (sample 8) are presented in Fig. 5-a. In this case the depth profile show a much lower Oxygen content in the film, and also no significant diffusion of Boron into the substrate. However, the same significant diffusion of Mg into the substrate is apparent for this sample.

The amount of Oxygen measured by ERDA in these series of MgB$_2$ thin films was normalized to the thickness of the thickest film (sample 1) and to the maximum value of the Oxygen peak (also found in sample 1), with the result is shown in Fig. 5-b. A clear correlation between the transition temperature $T_c$ and the relative amount of Oxygen is evident. This may explain the cause for some differences in the $T_c$ between films produced under apparently “identical” conditions. This result also shows that Oxygen is higher when the deposition geometry was on-axis as compared to an off-axis deposition.

A surprising result is the presence of a significantly larger amount of Oxygen in the MgB$_2$ film grown on Si as compared to the film grown on Al$_2$O$_3$, but at this stage it is
not clear why this difference exist. The native SiO₂ layer on the Si substrate surface was not removed before deposition, but this is unlikely to be the main cause.

The diffusion of Mg into the substrate appears to be independent of the type of substrate (Si or Al₂O₃) and of the deposition geometry (on- or off-axis). This suggests a barrier against Mg diffusion may have to be created for the growth of these films. On the other hand, the diffusion of Boron appears to take place only when the substrate was Al₂O₃ and the deposition was on-axis.

Fig. 1: Schematics of the ANSTO ERDA-ToF spectrometer: (a) hardware; (b) signal processing

Fig. 2: ERDA results for sample 1: (a) E-time spectra; (b) Depth profile of elements obtained from time-yield projection
The use of a Mg cap layer, a common practice in the PLD fabrication process of MgB$_2$ thin films was investigated (comparison between samples 5 and 6), and a slightly larger amount of Oxygen was detected at the surface of the film 6, for which a Mg cap layer was used. As expected, this small redistribution of Oxygen did not affect the $T_c$ of the film, and is possible that the use of the cap layer may not be as efficient as initially believed to be.

**Conclusion**

Using heavy ion ERDA analysis, we have shown in this work that a considerable amount of oxygen can be incorporated in the in situ PLD MgB$_2$ films. The Oxygen depth profile shows that it is present throughout the whole film, and even it diffuses into the substrate, in films deposited on Si. The results also show Mg is diffusing into both Si and Al$_2$O$_3$ substrates, and its diffusion into Al$_2$O$_3$ takes place for both on- and off-axis deposition geometries. Boron was found to have a limited diffusion into...
Al₂O₃ when the deposition geometry was on-axis, and no diffusion when the film was deposited with off-axis geometry. The use of Mg cap layer appears to have little influence on the Tc, and the results suggest that the small variation of Tc between the films with and without the Mg cap layer may be associated with the small increase of Oxygen at the surface of the films when the cap layer was used.

Acknowledgment

This work was carried out with financial contribution from AINSE and ARC.

References


