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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
15:20 - 15:40 Andreas Markwitz, GNS  
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Chair: Chris Ryan  

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

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

10:10 - 10:30 Andrew Baloglow, University of Wollongong  
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10:30 - 10:50 Perry Davy, GNS  
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Ion-beam sputtered germanium thin films – self-assembly of surface nanostructure using post growth annealing

Damian Carder¹, Andreas Markwitz¹,² and H. Baumann¹

¹ National Isotope Centre, GNS Science, Lower Hutt, New Zealand
² The MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand

d.carder@gns.cri.nz

Presented here is a study into the self-assembly of Ge nanostructures using ion-beam sputtering followed by a rapid and uncomplicated post-growth annealing method. The aim of the work is to produce controlled and predictable assembly of the surface features, central to the development of any application.

Our group has recently demonstrated the nanostructuring of untreated Si substrates using an electron beam annealing (EBA) technique [1], with the so-called nanowhisker surface structure showing immediate promise in field-emission and vacuum electronics applications [2].

Experimental:

Ion-beam sputtered layers of Ge, ~200-400nm thick, were deposited near room temperature on a Si substrate. The ion sputter system was operated at a base pressure of better than 2×10⁻⁷ mbar, with an argon gas ion source operating at 1mA. The Ge films were annealed at temperatures ranging from 400°C up to 700°C using the GNS electron beam annealing (EBA) technique.

Results and Discussion: Atomic force microscopy (AFM) measurements were made using an Easyscan 2 AFM from Nanosurf. Figure 1(a) shows an AFM image of the as-deposited Ge surface. In contrast, figure 1(b) shows the scan of the surface after annealing at 550°C for 15s. It is evident from figure 1 that a dramatic surface roughing on the nanoscale has occurred due to the annealing process. Figure 2 shows the average surface roughness calculated from AFM images of Ge films after annealing for 15s at temperatures from 400°C to 700°C.

Figure 1: Atomic force microscope images of a sputtered Ge film (a) before and (b) after electron beam annealing.
Between 400 and 600°C the roughening is an order of magnitude higher than the as-deposited surface layer but remains relatively constant in this region. Over an interval of 100°C (600 – 700°C) the surface roughening increases again to a value three orders of magnitude greater than the pre-annealed value. Further analysis of the height distributions for the nanostructures reveals a large characteristic difference for samples annealed above and below 600°C. At the lower temperatures the nanostructures are all below 50nm whereas larger nanofeatures form at 700°C, with a distribution of heights centred at 450nm [3].

To further investigate the larger feature size at higher temperatures, we performed Rutherford backscattering spectroscopy (RBS) measurements. The experimental details are as detailed in [4], where simulation of the RBS data was performed using the RUMP software program [5].

Figure 3 shows the RBS spectra of four annealed Ge films. The position of the Ge surface, Ge/Si interface and Si substrate are indicated. Notably, the regions of the Ge/Si interface (1.3 - 1.6MeV) and Si substrate (~1.1MeV) show distinct changes as the annealing temperature is increased. At the lower temperatures (450 and 600°C) the Ge/Si interface is abrupt (at 1.6MeV), in contrast to the higher temperatures (650 and 700°C) where the data shows a pronounced gradient across energies of 1.3 to 1.6MeV. Similarly, the gradient is more abrupt for the lower temperatures at the Si substrate. Both these observations show significant intermixing of Ge and Si across the film/substrate interface. It is noted that the film thickness varies between samples. However this does not account for the simulated differences in the following analysis.

The general features of the film annealed at 450°C are shown in detail in figure 4, assessed from a simulation of the measured spectra.
A surface layer of Ge$_{0.9}$O$_{0.1}$ is observed for all samples. The 450°C sample had a film thickness of 230 ± 5nm. Similar analysis for the sample annealed at 500°C resulted in a film thickness of 260 ± 5nm. It is notable that even at 450°C a 2 at. % diffusion of Ge, extending 180 ± 5nm, into the Si substrate is observed. This diffusion becomes more pronounced at the higher temperatures, where a comparison between the 500°C and 700°C sample is shown in figure 5. For the sample annealed at 700°C there is significant diffusion and intermixing of the Ge into the Si substrate, which is illustrated further in figure 6. It is notable that some Si (5%) has diffused through to the uppermost layer. The Ge content reduces from 95% to 4% across a thickness of around 650 ± 5nm. The significant intermixing alters the strain distribution between the film and the substrate which leads to the formation of larger surface features. A similar shift in size distribution has been observed by Jin et al [6] during MBE growth of Ge on a heated Si substrate above a temperature of 600°C.

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References


Interface trap density reduction in thin silicon oxides using ion implantation

Michael Dunn 1, Dr. Jeff McCallum 1, Eric Gauja 2

1Centre for Quantum Computer Technology, University of Melbourne, Australia
2Centre for Quantum Computer Technology, University of New South Wales, Australia

The reduction of interface charge trap density is important in the manufacture of semiconductor devices such as MOSFETS, and for the successful construction of a silicon based quantum computer using single ion implantation. These devices require very thin oxides (<10nm) in order to obtain high readout sensitivity. However, thinner oxides are also sensitive to oxide integrity so techniques such as rapid thermal annealing (RTA) are used to improve the electrical characteristics. The density of charge traps at the interface between the oxide and semiconductor (Fig 1) is a key measure of oxide integrity. A relatively low density is desired as this generally improves device characteristics.

Interface traps arise due to inherent structural defects, or by radiation processes which cause bond-breaking. In a silicon-oxide interface these defects correspond to trivalent silicon bonds, or “Pb centres” that arise as bonds transfer from the bonding configuration in the crystalline Si to that of the amorphous silicon dioxide. For longer growth times (creating thicker oxides) the interface trap density is reduced as the traps are concentrated only at the interface. These traps are physically localized, but have a continuous spectrum of energy levels and are therefore different to traps found within bulk silicon which have distinct energy levels, at a range of locations in the band gap [1].

Growth of silicon oxide nearly always includes a thermal annealing step which reduces the interface trap density by up to two orders of magnitude depending on anneal settings and the specific sample [2]. Further reduction may be obtained if ions are implanted into the sample as noted by Afanas’ev for F ions implanted to stop in the oxide [3]. Peterstrom observed an increase in interface trap density for B and P implants into Si through SiO2 [4].

In contrast to the Peterstrom study, this paper presents results that indicate ion implantation through the oxide can significantly reduce interface trap density, and finds neither significant ion species nor fluence dependency on the level of reduction.

Figure 1. MOS device structure
Experimental Procedure

Si oxide layers were thermally grown in a triple wall oxidation furnace to thicknesses of 5nm and 7nm. Samples were passivated in forming gas for 15 min at 400 °C. P, Si and SiN ions were each implanted through the oxide at respective energies of 15keV, 15keV and 20keV, for a range of fluences between $10^9$ ions/cm² and $10^{12}$ ions/cm². 15keV P was used due to its importance in the silicon quantum computer development; Si to compare if the observed effect was ion species dependent or damage related; and SiN as a third species with the N component being of interest. 20keV ensured that the N atoms had a similar stopping range to the other two implant species. SRIM (Stopping Range of Ions in Matter) data (Fig 2) show that P atoms come to rest at an average depth of ~240Å below the surface of the oxide. The other species show a similar predicted range. Following implantation, samples underwent a 5 s RTA at 1000°C, followed by a H-passivation anneal at 400°C, 15 min in N₂ (95%)/H₂ (5%) and then 110µm diameter Al contacts were deposited.

Electrical analysis was carried out using Deep Level Transient Spectroscopy (DLTS). Spectra are obtained by taking the sample into depletion with a 2.0V bias, then applying 4.0V, 40ms pulses at 1000ms intervals and measuring the transient behaviour as charges are emitted from the electrical traps. Capacitance-Voltage and Capacitance-Temperature scans are also performed which together with DLTS spectra allow interface trap density to be obtained.
Results

Results for the three ion species at a fluence of 10^9 ions/cm^2 are shown in Fig 3, with interface trap density (Dit) presented as a function of energy. The “RTA” sample underwent all of the same processing steps, including RTA, but was not ion implanted. After implantation there is a significant reduction in interface trap density for all three ion species. Furthermore, this reduction does not seem to be dependent on the type of ion implanted.

Comparison of samples with different implanted fluences is shown in Fig 4. No significant fluence dependency is observed indicating that if a threshold fluence exists it is less than 10^9 ions/cm^2. A similar lack of fluence dependency has also been observed in Si and SiN.

CV curves of the non-implanted samples feature an unusual capacitance ‘hump’ as the sample is biased into depletion (Fig 5). After implantation the hump is no longer present indicating that the mechanism causing the capacitance hump could be linked to the reduction in interface traps.

Figure 4. Interface trap density of MOS device after 14keV P ion implantation at various fluences

Figure 5. Capacitance-Voltage curves for 7nm silicon MOS device before and after implantation of 15keV P ions
The lack of ion species dependency suggests that the damage caused by implantation is responsible for the reduction in density. It is thought that the incident ions trigger a reorganization of the bonds at the interface such that a more energetically favourable structure is obtained with fewer charge traps. Further work will include a study of ion energy dependence and whether the associated stopping range has an effect on the reduction of interface traps. In addition to the ion implantation techniques studied here, MOS devices will also be exposed to electron beam and UV radiation to compare the effects on interface density.

Acknowledgements

Ion implantation performed on the Low Energy Implanter at Australian National University, Canberra.

References


Surface fraction statistics of gold nanoclusters of dissimilar sizes
determined by RBS

Dinesh Kumar Venkatachalam¹, Dinesh Kumar Sood¹, Robert G Elliman² and
Suresh Kumar Bhargava¹

¹ School of Applied Sciences, RMIT University, Melbourne 3001, Australia
² Electronic Materials Engineering Department, Research School of Physical Sciences and
Engineering, Australian National University, Canberra, ACT 0200, Australia

Abstract

Recently we reported [1] ordered spiral patterns of gold nanoclusters in silicon (100)
substrates by Au ion implantation followed by thermal (furnace) annealing. This
unique phenomenon was observed only above a critical threshold implantation dose
and annealing temperature. High resolution SEM & TEM analysis showed two
generations of Au nanoclusters of different size distributions. In this work, we have
used Rutherford backscattering spectrometry (RBS) to study the surface fractional
distribution of the Au nanoclusters of dissimilar sizes. Room temperature
implantations of 10keV Au²⁺ ions were performed into Si (100) single crystal
substrates to a dose of 4.5x10¹⁶ Au/cm² followed by thermal (furnace) annealing at
600°C for 60 min. The quantitative information about the lateral non-uniformity of the
sample surface is estimated by analysing the shape of the RBS spectra. The values
determined by RBS are in good agreement with electron microscopy results. This
study shows the capability of RBS in obtaining quantitative information on size
distribution of nanoclusters of heavy elements embedded in light substrates.

Introduction

Surface embedded metallic nanoparticles are of interest as templates for nanowire
growth and as primary components for future nanoscale devices. Self-assembled
nanoparticles, in particular, can facilitate selective bottom-up growth of patterned
one-dimensional nanostructures. While major progress has been made in fabricating
nanoparticles through various top-down approaches, a general direct bottom-up self-
assembly method is still not available. In this context, ion implantation has emerged
as a promising technique due to its ability to produce embedded nanoclusters [1-3].
Recently we reported the direct (maskless) formation of self-assembled spiral patterns
of gold nanoclusters on Si by Au ion implantation and subsequent annealing [1]. A
systematic study (SEM, AFM, XRD, and TEM) was conducted to determine the
formation mechanism underpinning these patterns. High resolution electron
micrographs showed the growth of Au nanoclusters of two different size distributions
after annealing at temperature above the a-Si/Au eutectic melting point. In this work,
we report the use of Rutherford backscattering spectrometry (RBS) to extract
quantitative information about the size distribution of Au nanoclusters by analysing
the shape of the backscattering spectrum as complement to the qualitative information
obtained by microscopy.

RBS has emerged as a powerful analytical tool to investigate the distribution of heavy
elements in light substrates. It has been applied to investigate the kinetics of phase
formation, amorphous re-crystallization and for depth profiling of laterally uniform
targets. Rough targets, on the other hand, are often considered as unsuitable for such
analysis. Thirty years ago, Campisano et al. [4] drew the attention of scientific
community to solve the ambiguity in RBS spectrum interpretation of laterally non-
uniform targets. Following his work, in mid 90s, Marin et al. [5] developed an
algorithm to extract lateral non-uniformity statistics by analysing the shape of RBS spectra. In this report we present statistical information of surface fraction of different populations of Au nanoclusters segregated to substrate surface from a shallow near-surface a-Si/Au alloy produced by ion implantation and thermal annealing. The quantitative information obtained from RBS is confirmed by several low magnification scanning electron micrographs.

**Experimental**

Prime grade single crystal p-type (100) oriented, Czochralski silicon substrates were implanted at room temperature with Au$^{2+}$ ions to an ion fluence of 4.5x10$^{16}$ cm$^{-2}$ using a MEVVA (metal vapour vacuum arc ion source). The lowest possible extraction voltage of 10keV to produce a stable ion beam (with average energy of 20keV) was chosen to ensure maximum surface concentration of implanted Au. A metal (Al) mask with 16 equi-spaced circular holes of 4mm diameter was used in contact with the 2” diam substrate held at room temperature to produce identical and well separated zones of gold ion implanted regions. Later, these implanted regions were cleaved into samples for post-implantation treatments. The depth of the resulting amorphous layer was estimated using SRIM. After implantation, the samples were annealed in an open alumina tube (4” diam) furnace at 600 $^\circ$C (temperature accuracy $\pm$1%) for 60 min. High purity argon (Ar) gas was used as a carrier gas and the flow rate was maintained at 100cm$^3$/min throughout the course of heating/cooling. Before annealing, the furnace was ramped to the desired temperature in the presence of Ar ambient. The sample was then introduced and heated for the required time. In all the cases the sample was cooled rapidly by moving it to the cold end of the furnace tube after the anneal.

Rutherford backscattering with 2MeV $^4$He$^+$ ions was used to evaluate the surface fractional distributions of Au nanoclusters of different populations. The detector was positioned at a scattering angle of 110$^\circ$ (glancing angle to the sample surface) to obtain better depth resolution from the shallow amorphous region. The beam size was maintained large enough (1mm$^2$) to contain a statistically representative sampling of the target to ensure a single spectrum is representative of the sample. The surface morphology and the size distribution of the nanoclusters were analysed using field emission scanning electron microscopy (FEI Qanta 200).

**Results and discussion**

Figure 1 shows the principle observation of our work, namely the formation of a bimodal distribution of Au nanocluster from a molten amorphous-silicon / gold (a-Si/Au) alloy layer after heating 4.5x10$^{16}$ Au/cm$^2$ at 600$^\circ$C for 60 minutes. The as-implanted substrate shows a smooth topology (see inset in figure 1a) with a spatially random distribution of Au droplets in the size range 0.5 - 10µm deposited during MEVVA implantation. These solid Au droplets (labelled by an arrow in the inset) are called “macroparticles” to emphasize their size compared to Au nanoclusters generated during the crystallization of a-Si/Au alloy layer during annealing. These “macroparticles” are generated at the vacuum arc cathode, travel along with the plasma and deposit on the target surface during MEVVA implantation [6].

Figure 1a shows the lateral non-uniformity of the sample surface caused by clustering of zone-refined Au on Si after heating at 600$^\circ$C for 60 min. It also shows that variations of the structure and composition are not so microscopic that no difference with the approximation of a homogeneous medium can be detected. The presence of
two generations of Au nanoclusters of different sizes is shown in figure 1b. The bigger clusters are of the size range 400-500nm whereas the second generation clusters range between 50-75nm. The size of the Au nanoclusters has been determined from several low magnification scanning electron micrographs. The increase in width of the size distribution is similar to ‘Ostwald ripening’ process where the bigger clusters grow at the expense of smaller ones at higher annealing temperatures.

Figure 1: SEM micrographs showing surface morphology of 4.5x10^{16} Au/cm² implanted into Si (100) and annealed at 600°C for 60 min a) low magnification image showing de-wetting of Au on Si (Inset showing as-implanted substrate); and b) high magnification image showing bimodal distribution of Au nanoclusters.

Figure 2 shows the corresponding backscattering spectra obtained with 2MeV He⁺ ions. The spectrum obtained from the as-implanted (un-annealed) sample shows a well defined Gaussian distribution of a 30nm near-surface a-Si/Au alloy layer. The small tail of Au profile in the as-implanted sample is due to the random size and spatial distribution of the Au “macroparticles”. After annealing at 600°C for 60 min the implanted Au condensed into Au islands, leaving free a large portion of underlying silicon substrate. This is evidenced by a strong decrease in the Au yield and a gradual decrease in the intensity towards lower energies.

The Au profile after annealing at 600°C in figure 2 confirms the presence of two generation of Au nanoclusters of different size distributions. The long Au tail is due to the lateral non-uniformity of the substrate surface and the size distribution of the larger Au nanoclusters. (Similar effects were observed by Campisano et al. [4] in a laterally non-uniform lead (Pb) thin film on Si.) In contrast, the smaller clusters lead to resolution limited surface peak [7].

By analysing the shape of the Au profile before and after annealing, it is estimated that after heating at 600°C, Au nanoclusters of the size range 400-500nm account for 70% of the Au coverage, whilst the smaller nanoclusters account for the remainder. To strengthen this estimation, the samples were annealed at temperatures above and below 600°C for very short annealing cycles (5-30s) to study the early stages of Au nanocluster formation. The early stages of Au de-wetting and Au nanocluster formation is estimated by comparing the RBS spectra recorded after different annealing conditions (results will be reported elsewhere).
Conclusions

By analysing the shape of RBS spectra of Au implanted Si before and after annealing, the surface fraction of two different generations of Au nanoclusters is obtained. Good agreement with SEM measurements confirms the accuracy of this method. The above results show that RBS can provide quantitative information about laterally non-uniform samples with more descriptive information provided by SEM. It is sometimes possible to conclude the presence of lateral non-uniformity by comparing several RBS spectra.

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References

Photonic nanostructures and their influence on Er luminescence

Electronic Materials Engineering Department, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia.

Abstract

The properties of Er-doped silica wires are investigated and shown to exhibit properties characteristic of the material nanostructure. Specifically, the 1.5µm emission from Er³⁺ is shown to exhibit a longer luminescence lifetime and enhanced thermal quenching in comparison to similarly doped bulk silica samples. The former is attributed to a reduction in the optical density of states of the nanowire samples and the latter to their large surface-to-volume fraction.

Introduction

Whilst there has been intense interest in the synthesis, structure and properties of silica nanowires [1-5], little work has been performed on optical doping and functionalisation of such materials. Several studies have noted the strong intrinsic luminescence from as-grown nanowires and a recent study by Zhang et al. [5] reported results for Er implanted nanofibre bundles. However, this latter study only examined samples implanted to very high fluences where strong concentration quenching effects are expected. In the present study, we report new results for Er-doped silica nanowires, including the impact of the nanowire structure on the Er luminescence and a novel ion-implantation technique that enables simultaneous nanowire growth and doping.

Experimental

Silicon wafers of (100) orientation were coated with a 20nm thick Pd layer by sputter deposition. Portions of the wafer were subsequently annealed at 1100°C for 4 hours in an Ar ambient to produce a dense, randomly-oriented array of silica nanowires on the sample surface. Doping of the nanowires was achieved by ion-implantation with 110keV ErO⁻. Samples were implanted to fluences in the range from 5×10¹⁴ to 1×10¹⁶ Er/cm² together with fused silica samples for comparison. The implanted Er has a mean-projected range in SiO₂ of 45nm and its peak concentration ranges from 0.3 at. % to 5 at. %. All samples were then annealed at 900°C for 1 hour in either N₂ or O₂ to optically activate the erbium. These experimental procedures are summarized in Fig. 1.

![Fig. 1: Schematic of experimental procedures employed in this study.](image-url)
Physical characterisation of nanowires was undertaken by scanning electron microscopy using a Hitachi field-emission scanning electron microscope (FE-SEM) equipped with energy-dispersive x-ray (EDX) analysis. Photoluminescence (PL) measurements of the Er emission were performed at room temperature using the 488nm line of an argon ion laser as the excitation source. The luminescence emission was analysed with a Triax 320 spectrometer equipped with a high-sensitivity liquid-nitrogen cooled germanium detector. The excitation laser was mechanically chopped at 15Hz and standard lock-in techniques employed to collect the spectra. For time-resolved PL measurements, the output of the detector was connected directly to a digital storage oscilloscope and the response averaged over 128 cycles. The time response of the system is estimated to be less than 0.5ms.

**Results and Discussion**

Fig. 2 shows SEM images of silica nanowires produced by the metal-induced growth process described above. The nanowires have an average diameter of around 150nm and lengths exceeding 100 µm. The nanowire growth mechanism has been investigated and found to depend on the formation of volatile Sao via a reaction between trace oxygen in the annealing ambient (present at the ppm level) and the silicon wafer.

Fig. 3 shows an RBS spectrum of the nanowire sample after implantation with ErO' to a fluence of 5x10^{14}cm^{-2}. The spectrum shows that Pd is distributed throughout the nanowire layer, consistent with its role as a growth catalyst. The implanted Er is located in the near-surface region of the nanowires, as expected from the fact that the projected range, (∼45nm), is less than the average nanowire diameter (∼150nm). Analysis also suggests that the nanowires consist of silicon-rich-oxide rather than stoichiometric SiO_2.
Fig. 4 shows a typical PL spectrum from the Er implanted nanowires together with a schematic of the optical transitions involved. The 1.5μm emission corresponds to the \(^{4}I_{13/2} \rightarrow ^{4}I_{15/2}\) transition of the Er\(^{3+}\) ion.

![Fig. 4: Room temperature PL spectrum from a nanowire sample implanted with ErO\(^{-}\) to a fluence of 6x10\(^{14}\)cm\(^{-2}\).]

Fig. 5 shows measured PL decay curves for nanowire samples implanted to a fluence of 6x10\(^{14}\)cm\(^{-2}\) after annealing in N\(_2\) and O\(_2\), together with a similarly implanted bulk silica sample annealed in N\(_2\). The luminescence lifetime of Er in the nanowire sample is longer than that of the bulk sample. Analysis suggests that this is a direct result of a reduced optical density of states in the nanowire samples.

![Fig. 5: PL decay curves for nanowire samples implanted with ErO\(^{-}\) to a fluence of 6x10\(^{14}\)cm\(^{-2}\) and annealed in N\(_2\) and O\(_2\). Results for a similarly implanted bulk silica samples are included for reference.]

Fig. 6: Integrated PL intensity as a function of temperature for nanowire and bulk silica samples implanted with ErO\(^{-}\) to a fluence of 1x10\(^{15}\)cm\(^{-2}\) and annealed in N\(_2\).
Fig. 6 shows the temperature dependence of the PL intensity for nanowire and bulk-silica samples. This shows enhanced thermal quenching of the luminescence in nanowire samples compared to bulk silica samples. This effect is attributed to interaction between the excited state of Er and surface defects, with the effect enhance in nanowires due to their high surface-to-volume fraction.

**Summary and Conclusions**

The properties of Er-doped silica wires have been examined and shown to exhibit properties characteristic of the material nanostructure. Specifically, the 1.5 µm emission from Er\(^{3+}\) was shown to exhibit a longer luminescence lifetime and enhanced thermal quenching in comparison to similarly doped bulk silica samples. The former is attributed to a reduction in the optical density of states of the nanowire samples and the latter to their large surface-to-volume fraction.

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**References**

Zinc oxide (ZnO) is a low-priced, powdery white substance that is harmless to humans. It has found use in a wide range of medical and cosmetic applications. The ability to absorb ultraviolet light makes zinc oxide an active ingredient of choice in suntan lotions. ZnO is also incorporated in dietary supplements and vitamin tablets as source of the essential micro-nutrient zinc for the human body. It is widely used in paint pigments, paper coatings, UV-absorbing pigments, voltage spike suppressing varistors, touch-screen transparent conductive films, gas sensors and filler for rubber goods, etc. Although ZnO is used in commonplace, it also possesses semiconductor-like properties. It has a direct band gap of 3.36eV at room temperature and a higher excitation binding energy (50meV) which assures more efficient emission at higher temperatures, compared with other wide band gap materials such as GaN (28meV). Owing to these properties, ZnO has been identified by researchers in world wide as a next generation material that has the potential to create more efficient optoelectronic devices such as LED’s, Lasers, CDs and high definition DVD players [1-2].

ZnO is a natural n-type semiconductor, because of the presence of intrinsic defects such as Zn interstitials and O vacancies causing deviation from stoichiometry. Progress in ZnO research for optoelectronic applications remains limited due to constraints encountered in producing p-type materials in either thin films or bulk crystals. The growth of n-type material has proven to be relatively simple, as shallow donor impurities (Al, Ga and In) are readily incorporated into the ZnO lattice [1,3]. The fundamental difficulty in p-type doping of ZnO arises from a number of reasons. For example, the donor level may be especially deep so that thermal excitation into the valence band is low. Other reasons could be a low solubility of the dopant or induced self compensating processes [4]. Recent theoretical studies have suggested that zinc vacancies in the ZnO matrix act as possible deep acceptors. However, nitrogen (among group V elements of P, As, N) atoms substituting for oxygen in the ZnO film have shown to be the most promising shallow acceptor in ZnO [4]. The aim of this investigation is to establish the doping protocol for nitrogen ion implantation into ZnO thin films using the GNS low energy ion implantation facility and ion beam analysis techniques.

**Experimental procedure and results**

We have deposited a range of ZnO thin films on silicon (100), quartz, glass and glassy carbon substrates using radio frequency (RF) magnetron sputtering under the optimised deposition parameters described in ref.3. The ion beam analysis techniques of RBS, Elastic Recoil Detection Analysis (ERDA) and Nuclear Reaction Analysis (NRA) [5,6] were used to measure the stoichiometry of the films and impurities such as hydrogen concentrations. Large variations in film thickness and composition were found in most of the as deposited films. It was also found that less than 1-2% hydrogen was present on the films deposited on Si. XRD analysis revealed that a strong (002) preferential orientation in the ZnO films deposited Si irrespective of thickness, indicating a polycrystalline hexagonal structure characteristic of ZnO, and preferential orientation along c-axis. It is due to the lowest surface free energy of (002) plane in ZnO.
Ion implantation for doping semiconductor materials (i.e. introducing dopants into the semiconductor) is a well established technique for the fabrication of electronic and optoelectronic devices. We have implanted 23keV nitrogen ions at under normal incidence with fluences ranging from $1 \times 10^{15}$ to $1 \times 10^{17}$ ions cm$^{-2}$ into ZnO films deposited on Si. The ion beam was raster scanned over the surface to produce a laterally homogeneous implantation into the films. DYNAMIC-TRIM [7] calculations have been performed to determine theoretical implanted ion profiles for the various fluences. The calculations predict a mean projected range of 45nm coupled with a maximum implantation depth of around 80nm. For these fluences, the N peak concentration varies between 0.05 and 18 at.%. At fluences larger than $1 \times 10^{16}$N cm$^{-2}$, the N profile intersects with the surface. Annealing was performed using an electron beam annealing system [8] at sample temperatures of 700°C for 10min. This system operates with an electron energy of 20keV and current up to 2mA. The annealing chamber is evacuated with a turbomolecular pump to a base pressure better than $1 \times 10^{-7}$mbar.

NRA measurements were carried out to determine the nitrogen concentration in the implanted samples. Nuclear reactions induced by bombardment with energetic protons, deuterons or alpha particles cause the emission of other energetic particles that can be used for elemental analysis. The sensitivity of the technique is very high for light elements[6].

Deuteron beams of an energy of 920keV (ion current = 20nA, ion beam diameter = 1mm) were used. The emitted particles were detected with a surface barrier detector (active area of 300mm$^2$, Mylar absorber thickness 10.6μm) mounted at 150° to the beam. Standard materials of anodically oxidised Ta$_2$O$_5$ and TiN were used for calibration purposes.

Fig. 2 shows independent nuclear reaction peaks for the implanted ion N along with the O from the film and Si from the substrates. Carbon impurities can also be seen. The peak width corresponds to the thickness of the film. The peak height can be converted into concentration by taking into account the values of cross sections and stopping power. In the present study the nuclear reactions $^{14}$N(d,$\alpha$)C (dσ/dΩ =
0.07mb sr⁻¹) and \(^{14}\text{N}(d,p)^{15}\text{N} (\text{dσ/dΩ} = 0.56\text{mb sr}^{-1}) \) were used to determine the N ion concentration in the implanted films. These reactions were chosen because their peaks do not interfere with peaks from the film and substrate material. It was found that the measured N concentrations at a fluence of \(2 \times 10^{16} \text{ ions cm}^{-2}\) are around 4.1 at.\% which is close to the DYNAMIC-TRIM calculated values as shown in Fig. 1. Nitrogen concentration can be measured at fluences above \(5 \pm 1 \times 10^{15} \text{ ions cm}^{-2}\), which convincingly proves that NRA is suitable for detecting low levels of nitrogen in implanted semiconducting materials.

### Electrical and optical measurements

The resistivity, carrier concentration and carrier mobility of the deposited and nitrogen implanted ZnO films on silicon were measured using an Ecopia HMS-3000 Hall Effect measurement system [9]. A high purity Ti coating was used for ohmic contact to all the films. Table 1 summarises the electrical characteristics obtained from the implanted and annealed films.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Film thickness (nm)</th>
<th>Sample treatment</th>
<th>Carrier Concentration (cm(^{-3}))</th>
<th>Mobility (cm(^2).V(^{-1}).s(^{-1}))</th>
<th>Resistivity (Ω cm)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>302</td>
<td>as-deposited</td>
<td>-4E19</td>
<td>4</td>
<td>0.04</td>
<td>n</td>
</tr>
<tr>
<td>51</td>
<td>170</td>
<td>Implanted (F=1x10(^{15}) cm(^{-2})) &amp; annealed</td>
<td>-4.9E18</td>
<td>1.5</td>
<td>0.04</td>
<td>n</td>
</tr>
<tr>
<td>52</td>
<td>200</td>
<td>Implanted (F=2x10(^{15}) cm(^{-2})) &amp; annealed</td>
<td>-2.2E19</td>
<td>9</td>
<td>0.032</td>
<td>n</td>
</tr>
<tr>
<td>53</td>
<td>314</td>
<td>Implanted (F=2x10(^{15}) cm(^{-2})) &amp; annealed</td>
<td>3.39E18</td>
<td>305</td>
<td>0.0047</td>
<td>p</td>
</tr>
<tr>
<td>54</td>
<td>302</td>
<td>Implanted (F=2.5x10(^{16}) cm(^{-2})) &amp; annealed</td>
<td>-2.1E19</td>
<td>3</td>
<td>0.01</td>
<td>n</td>
</tr>
<tr>
<td>55</td>
<td>338</td>
<td>(F=2.5x10(^{16}) cm(^{-2})) &amp; annealed</td>
<td>3.4E18</td>
<td>278</td>
<td>0.006</td>
<td>p</td>
</tr>
<tr>
<td>56</td>
<td>302</td>
<td>Implanted (F=5x10(^{16}) cm(^{-2})) &amp; annealed</td>
<td>-1.9E19</td>
<td>3</td>
<td>0.12</td>
<td>n</td>
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<tr>
<td>57</td>
<td>326</td>
<td>(F=5x10(^{16}) cm(^{-2})) &amp; annealed</td>
<td>2.34E18</td>
<td>40</td>
<td>0.06</td>
<td>p</td>
</tr>
</tbody>
</table>

It is found that the N implanted and annealed targets showed p –type carrier concentration values from \(-1.0 \times 10^{13} \text{ to } -5.0 \times 10^{19} \text{ cm}^{-3}\), hole mobility from \(1 \text{ to } 500 \text{ cm}^{2}.\text{vs}^{-1}\) and resistivity of \(0.0001 \text{ to } 5 \text{ ohm.cm}\) [10]. All the implanted samples show n-type conductivity. After annealing, the films were showing p-type behaviour. The carrier concentration decreases after implantation since the implanted region becomes amorphous. However, the carrier mobility does not change. Once the implanted films are annealed, the carrier mobility has increased two orders of magnitude and the carrier concentration value remain in the same order of magnitude value.

The optical properties have been investigated by photoluminescence (PL) [10]. PL measurements are performed at 77K. The results are shown in Figure 3. A strong donor bound exciton peak near 374nm (~3.32eV), which is typical for n doped ZnO, is observed in addition to the broad peak in the visible region near 600nm. The exciton peaks correspond to p-type ZnO formed as a result of the acceptor doping process of low-energy acceptor ion implantation and EB annealing are observed between 360 – 450nm. The most prominent line at 3.31eV is observed in our p-type ZnO samples. In addition to that few other acceptor bound exciton peaks at 3.31 and 3.35eV are also observed.
Summary

We have successfully developed a protocol to produce a p-type ZnO via low energy ion implantation and electron beam annealing. We have implanted low energy nitrogen ions into thin films deposited on Si (100). The implantation depth was calculated to be 50nm using Dynamic-TRIM. The implanted N was measured quantitatively using nuclear reaction analysis. The structural, electrical and optical properties were determined by XRD, Hall effect and PL. It is found that the N implanted and annealed targets show p-type carrier concentration. PL revealed exciton peaks in the region between 300-450nm. These exciton peaks correspond to p-type ZnO formed as a result of the acceptor doping process of low-energy acceptor ion implantation and EB annealing.

Acknowledgments

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Reference

Towards a formula for optimized production of single NV centres in diamond by ion implantation

J.O. Orwa¹, A. Cimmino¹, B. Gibson², D. Simpson² and S. Prawer¹,²,³
¹ Microanalytical Research Centre, School of Physics, University of Melbourne, Victoria 3010, Australia
² Quantum Communications Victoria (QCV), University of Melbourne, Victoria 3010, Australia
³ Centre for Quantum Computer Technology, Melbourne node, Australia

Corresponding author. Tel.: +613 8344 7651; fax: +613 9347 4783; e-mail: jorwa@physics.unimelb.edu.au

Abstract

Single NV centres in diamond have been the subject of many studies in recent years due to their potential applications in quantum information processing. Compared to other single photon sources such as attenuated lasers, single atoms, molecules and semiconductor quantum dots, the NV diamond colour centre has the advantage of simplicity, photo-stability and room temperature operation. Despite these excellent properties, a recipe for maximizing the efficiency of NV production is yet to be optimized. This study is a step towards this optimization and uses photoluminescence and confocal fluorescence spectroscopy to investigate the NV yield of high purity single crystal type IIa diamond samples implanted with nitrogen followed by thermal annealing. The parameters varied include implanted nitrogen species, implantation energy, temperature, fluence and annealing temperature. Further, the study distinguishes between the yields of NV- and NVo and offers theoretical basis for the observed differences.

Keywords: Diamond, N-V centre, Ion Implantation, Single photon source.

Neutral atom microscopy: a non-destructive, high-resolution surface analysis technique

K. O'Donnell¹, P.C. Dastoor¹, D.J. O'Connor¹, W. Allison²
¹ School of Mathematical and Physical Sciences, University of Newcastle, NSW 230
² Cavendish Laboratory, Cambridge University

In recent years there has been much interest in neutral atom microscopy for surface studies. A neutral helium beam with an energy of 30-110 meV has a sub-angstrom de Broglie wavelength, making it an extremely sensitive surface probe. In addition, the energy range allows for simultaneous thermal and chemical contrast.

Development of a microscope based on neutral helium atom beams has previously been held back by the lack of sufficiently advanced optical elements for focusing and detection, however it is believed that there are now viable approaches to both problems. Ultra-thin single-crystal, hydrogen-passivated Si(111) surfaces have been created at the Cavendish Laboratory, which when electrostatically bent can be used to focus a helium beam for microscopy.

For an imaging microscope configuration, the University of Newcastle is developing a spatially-resolved field ionization detector allowing for the first time true imaging with a neutral atom beam source. In this talk the author will describe the concepts and technology behind both the Cavendish Laboratory's Scanning Helium Microscope (SHeM) and the University of Newcastle's spatially resolved helium field ionization detector.
Characterization of silicon detectors utilized in an on-line dosimetry system for microbeam radiation therapy
A.M. Baloglow 1, M.L.F. Lerch 1, M. Reinhard 2, R. Siegele 2, E. Brauer-Krisch 3, E. Siegbahn 3, V. Perevertailo 4, A. Bravin 3, A.B. Rosenfeld 1
1Centre for Medical Radiation Physics (CMRP), University of Wollongong, NSW, Australia
2Australian Nuclear Science and Technology Organization (ANSTO), Lucas Heights, NSW, Australia
3European Synchrotron Radiation Facility (ESRF), Grenoble, France
4SPO-BIT, Ukraine

Microbeam radiation therapy (MRT) is a new form of radiation treatment being developed for children with inoperable and otherwise untreatable brain tumours. A new on-line dosimetry system is currently under development at the Centre for Medical Radiation Physics, University of Wollongong, Australia [1], which will be used to measure peak dose for each microbeam and the instantaneous MRT peak-to-valley dose ratio (PVDR). The peak dose and PVDR is an important physical parameter in MRT that indicates the quality of the MRT beam and must be measured with an accuracy of better than 5%.

The detector will also be used to act as a fast beam-stop trigger to avoid an undesirable dose being delivered to the patient undergoing MRT treatment within milliseconds time treatment delivery. Therefore the radiation damage induced in these detectors is important for understanding the reliability of the deduced dose using these detectors and will determine the useable lifetime of the detectors. The work outlined in this article discusses radiation damage studies induced in the bulk silicon strip detector utilized in the dosimetry system. Such radiation damage studies have not been widely studied under the very intense pulsed, low energy (average energy 100keV) synchrotron x-ray photons.

Materials and methods

The strip detector was fabricated by ‘SPO-BIT’ Ltd., Ukraine, according to the CMRP design. The detector is made up of 128 p+n junction strips each with a width of 10 microns, length of 500 microns and with a strip-pitch of 200 microns produced on a 375 micron n-silicon substrate of resistivity of 5 kOhm cm. Current-voltage I-V measurements were taken of individual strips of the detector using a Keithley237 current source device. A BOONTON7200 capacitance bridge was used to measure the capacitance-voltage, C-V, characteristics of the silicon strip detector as above. The device was placed under evacuated conditions and measured at room temperature.

The Ion Beam Charge Collection (IBIC) study was performed on the ANTARES tandem accelerator at the Australian Nuclear Science and Technology Organization (ANSTO), using a 5.5MeV alpha particle beam with a diameter of 2 microns under reverse and zero bias. All three of the above mentioned techniques were performed before and after the irradiation of the detector with 60kGy from biomedical beamline (ID17) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The detector was irradiated under standard MRT beam conditions [2].
Results and Discussion

Fig. 1 displays the I(V^{1/2}) characteristics of some of the strips that make up the silicon strip detector, after MRT synchrotron beam irradiation. The neighbouring strips were suspended. Due to the penumbra of the 1mm microbeam the strips in the centre of the beam received higher radiation dose. One can clearly identify the heavily irradiated strips compared to the lightly/unirradiated strips. The non-irradiated and lightly irradiated p+ strips have demonstrated a typical linear relationship I vs V^{1/2} in a wide range of the reverse bias. However, the relation no longer exists for heavily irradiated strips for bias above 20V.

![Figure 1. Current-voltage characteristics of the post-irradiated Silicon Strip Detector.](image1)

Fig. 2. shows a distinct difference in the CV curve between the heavily irradiated strips to the lightly irradiated or unirradiated strips. One important notable feature is the change occurring to the kink within the C-V curve within (1-15)V.

![Figure 2. Capacitance-voltage characteristics of the post-irradiated Silicon Strip Detector.](image2)

Both of the effects mentioned above can be explained by build up positive charge in the field oxide by synchrotron ionizing radiation. The mechanism of increasing current is related to the creation of a MOS structure by the Al contact above the field oxide outside of the p-n junction area of the p+ strip. The build up of positive charge within this field oxide layer results in an electron enhancement channel at the silicon surface, leading to lateral shrinkage of the depletion layer at the p+ strip/n layer. An increase of the negative bias above the critical voltage (~20V) will overcome this induced electron channel and result in abrupt lateral depletion. Increasing of the depleted volume of the p-n junction increases the reverse current proportionally.
A similar explanation can be related to the kink present within the C-V characteristics of irradiated p+ strips. The MOS capacitance, produced by the Al contact above the field oxide and outside of the p-n junction, is connected in parallel to the capacitance of the reverse biased p-n junction. The effect of this MOS capacitance on the total capacitance can be seen on Fig.2. With the positive charge accumulated in the field oxide layer, this MOS component requires a greater reverse bias to reduce the term and for the capacitance exhibited by the depleted p-n junction to dominate. This can be seen in the C-V curve for the heavily irradiated strips. A more detailed explanation with theoretical modelling of this structure will be presented in the full paper.

![Image of the collected charge on IBIC experiment.](image)

For verification of the nature of the radiation damage within the strip detector under the synchrotron radiation and the explanation of the behaviours of I-V and C-V characteristics presented above, an Ion Beam Charge Collection (IBIC) study has been carried out on the device. IBIC was performed on the ANTARES tandem accelerator at the Australian Nuclear Science and Technology Organization (ANSTO), using a 5.5MeV alpha particle beam with a diameter of 2 microns under zero and reverse bias. Fig.3 shows a colour coded representation of the collected charge on 7 consecutive p+ strips irradiated with the 1mm synchrotron beam under various reverse bias conditions (0, 5, 10, 20, 30, 50V). The Al connection pads containing the wire bonding to the detector board can be clearly seen at the bottom of each strip.

It is clear that for bias 0 and 5 V full charge collection was observed in a central part of the 10 µm strip and no charge collection was observed under Al pads due to build up charge in the field oxide as discussed above. With increasing bias up to 10V (upper right image) improvement of the charge collection has been observed for the three far right strips which have received less dose due to beam penumbra and therefore less build up charge in the field oxide. The next image (lower row, left image) a bias of 20V demonstrates the effect of the accumulated positive charge within the field oxide layer, due to the irradiation of intense x-rays, on the charge collection efficiency of the device. A further increase in bias leads to full
charge collection under the Al pads of the strips on the left hand side and laterally to P+ strips due to spreading of the depletion region.

**Conclusion.**

The proposed model of radiation damage of the n-Si strip detector for MRT dosimetry on ESRF synchrotron beam based on build up charge in a field oxide only has been proved. This model was successfully applied for explanation of peculiarities of I-V and C-V characteristics changes. No bulk defect due to the irradiation of intense x-rays was observed in this application. Build up charge effect can be avoided by overbias of the strips or by regular annealing under 150°C if detector is to be used in a passive mode [3].

**References**


Low-energy ion implantation of Group IV elements into wafer silicon has been used to investigate the fabrication of novel nanomaterials. For example 7keV Pb\textsuperscript{+} atoms have been implanted into p-type Si wafer material at room temperature with the ion fluence of 4 \times 10^{15} \text{ at cm}^{-2} [1]. The analysis of the physical properties of implanted materials includes determination of the elemental depth distribution by RBS, elemental loss under high vacuum conditions after computer controlled electron beam annealing at 200 to 1000\degree C; and the determination of surface topography by AFM [2]. The results of the experimentally determined elemental loss and structural properties need to be compared to theoretical calculations in order to understand and explain the physical structure of implanted substrates. This paper presents theoretical calculations for the rate of Pb and Sn loss from Si implanted substrates under vacuum during electron beam annealing over a range of temperature regimes.

Electron beam annealing of Si wafer material itself can produce nanostructures called nanowhiskers with potential applications as field emission devices [3]. The process of implanting ions into Si substrates results in amorphisation of the Si crystal lattice at the implanted area. Electron beam annealing of the implanted area recrystallises the Si or co-recrystallises Si with the implanted atoms to produce materials with novel and interesting nanostructures [4-5].

An important part of the process is determining the atomic concentration and depth profile of the implanted material. The annealing of substrates can result in diffusion of implanted atoms into, and out of, the bulk material. Theoretical calculations of the rate of loss of implanted atoms can be compared to experimentally determined values.

In the absence of any other interaction with the substrate, kinetic theory can be used to determine the rate of atomic loss from a substrate surface. The rate of migration of a property (mass, energy) is measured by its flux \textit{J} and for mass this is expressed in kg m\textsuperscript{-2} s\textsuperscript{-1}. The general form of the equation known as Fick’s First law of diffusion is given as [6]:

\[
J = -D\left(\frac{dN}{dz}\right)
\]

(1.1)

where:

- \textit{D} = the diffusion coefficient
- \textit{N} = the number of particles per unit volume (atoms cm\textsuperscript{-3})
- \textit{z} = some axis

With respect to the case of atoms leaving a solid surface under high vacuum conditions we assume that the flux is mono-directional and equation 1.1 can be used to derive the flux of atoms from the surface such that:

\[
J = \frac{1}{4}\pi \sigma^2
\]

(1.2)

\(\sigma\) = mean speed = \(\frac{8kT}{\pi m}\)\textsuperscript{0.5} = \(\frac{8RT}{\pi M_{\text{mol}}}\)\textsuperscript{0.5} from the Maxwell distribution.

Since we are interested in the change of state from solid to gas we can incorporate the vapour pressure and atomic mass and rearrange equation 1.2 to give:

\[
J_m = 4.38 \times 10^{-4} \times p \times (M_{\text{mol}}/T)^{0.5}
\]

(1.3)

where:
$J_m =$ mass flux (g cm$^{-2}$ s$^{-1}$)  
$p =$ vapour pressure (Pa)  
$T =$ temperature in Kelvin  
$M_{mol} =$ molar mass (g)

Figure 1 Calculated remaining dose of Pb in Si after annealing at $T_{\text{max}}$ for different times, the dashed vertical line is the melting point of Pb

We can use equation (1.3) to calculate the loss of Pb and Sn from Si at different temperatures using the vapour pressure at that temperature (from [7]). For comparison with electron beam annealing the calculation can be modified to also account for atomic loss during ramping up and down and the time that the material is held at target temperature.

Figure 2 Calculated remaining dose of Sn in Si after annealing at $T_{\text{max}}$ for different times, the dashed vertical line is the melting point of Sn
Starting from an initial dose of $4 \times 10^{15}$ atoms cm$^{-2}$, Figure 1 presents the calculated remaining dose (atoms cm$^{-2}$) for Pb in Si after annealing over a range temperature regimes using a temperature ramp of 5°C s$^{-1}$ and holding at the target temperature ($T_{\text{max}}$) for 10s, 30s, and 80s respectively.

In the case of annealing Si implanted with Sn at an initial dose of $4 \times 10^{15}$ atoms cm$^{-2}$, Figure 2 presents the calculated remaining dose (atoms cm$^{-2}$) for Sn in Si after annealing over a range temperature regimes using a temperature ramp of 5°C s$^{-1}$ and holding at the target temperature ($T_{\text{max}}$) for 10s, 30s, and 80s respectively.

The difference between Sn and Pb loss rates are immediately evident. Even though the melting point of Sn (211.97°C) is significantly lower than that of Pb (327.5°C), the determining factor is the vapour pressure. At room temperature, the vapour pressure of Sn is $10^{20}$ less than that of Pb.

Kinetic theory calculations provide a useful way of comparing expected behaviour of Si implanted substrates during the annealing process with experimentally derived results. Deviations from calculated results are likely to be explained by physical changes in the Si substrate material either by Si surface recrystallisation of the amorphous implanted area providing a barrier to diffusion of implanted atoms out of the bulk material or by inclusion of implanted atoms into the crystal lattice itself thereby forming novel nanostructured materials.

**References**


Porous titanium dioxide materials fabricated by using templating techniques

Rachel A. Caruso
PFPC, School of Chemistry, The University of Melbourne, Melbourne, Vic. 3010, Australia
rcaruso@unimelb.edu.au Phone: +61 3 8344 7146 Fax: +61 3 9347 5180

Abstract

The ability to control the morphology of materials is highly desirable as structure plays an important role in the final properties of the material. This can lead to enhancement of the performance of materials in applications due to changes in characteristics such as the accessible surface area and porosity. A study of the synthesis of titanium dioxide structures with controlled morphology will be presented. The tailoring of both outer morphology and inner porosity will be demonstrated by the use of templating techniques. Characterisation allowed the determination of bulk and intricate structural details, the crystallinity of the particles, the surface area and pore sizes of the structures and the temperatures at which crystal phase changes occurred.

Porous titanium dioxide structures have been produced using a variety of organic templates. The titania precursor, titanium isopropoxide, initially fills the pores of the template. When the infiltrated template is introduced to water hydrolysis and condensation reactions occur, resulting in an amorphous titania coating of the organic structure. The samples are dried and then calcined to achieve the highly porous titanium dioxide structures. The outer morphology is dependent on the form of the template,1 producing for example, films, spheres or tubes (Figure 1).

![Figure 1. Titanium dioxide porous structures produced using a filtration membrane, chromatography beads or polymer fibres as templates.](image)

The inner porosity of the titania structures is achieved by the coating of the original template with the inorganic. During the sol-gel process the amorphous titania forms at the surface of the template, leaving the open porosity of the template in the final titania structure. For example, although shrinkage occurs during the sol-gel process, the porous structure from a 2 wt % agarose gel can still be observed in the final TiO₂ material fabricated in the presence of the agarose gel template.2 A smaller pore is also observed when the sample has been calcined to induce crystallisation of the titania. This small pore results from interparticle crevices, and is in the mesopore range when anatase nanocrystals are produced.
Figure 2. SEM images of the 2 wt % agarose gel and the titania structure fabricated using this agarose gel as a template.

The surface area of the porous titania structure can vary from 30 m²g⁻¹ to over 100 m²g⁻¹ depending on the crystal size of the titania and the overall porosity of the materials produced. By introducing small quantities of a second metal oxide to the titania synthesis, leading to metal doping of the titania, the crystal phase behaviour of the material can be altered: This influences the final crystal size and therefore the surface area. For example, doping 4 wt % Al into the TiO₂ structure resulted in a decrease in crystal diameter from 30 to 20 nm, and an increase in surface area from 48 to 98 m²g⁻¹.³

Titanium dioxide has a wide range of applications, including as photocatalysts and electrodes in photovoltaic cells. As many of these applications require chemical reactions or physical interactions at the surface of the titanium dioxide, an increase in accessible titanium dioxide surface area would be expected to enhance the efficiency of the materials. We are currently studying how the controlled morphology, porosity and increased surface area influence the performance of the titania materials in the photodegradation of organic pollutants in aqueous solutions, and in photovoltaic devices.

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References
Helium ion microscope – high resolution, high contrast microscopy for nanotechnology

D. J. O’Connor
School of Mathematical and Physical Sciences, University of Newcastle, NSW 2308

The Helium Ion Microscope is the marriage of a crystal tip field ionisation source and an electron microscope column to attain high resolution images of surface and interfaces. The high brightness and small spatial distribution of the field ionisation source is used to create a 20keV He ion beam which is refocused onto surfaces. The higher mass of the projectile and the nature of secondary electron emission for energetic ions leads to a potential lateral resolution of 0.25nm though so far the best obtained is 0.8nm.

The different electron emission resulting from ions compared to electrons leads to greater contrast in secondary electron mode and it is possible to image both surface and subsurface simultaneously. In lithography applications, the incorporation of He into a surface has no chemical impact to the subsurface region compared to other ion beam etching processes.

This instrument is still under development by Carl Zeiss SMT, Inc and new features incorporating chemical identification via elastic particle scattering are expected to be part of future options.
Next generation x-ray microspectroscopy: towards full-spectral XANES and high-throughput fluorescence imaging using massively parallel detector arrays and real-time spectral deconvolution


1 CSIRO, Exploration and Mining, Geoscience, Monash University, Clayton VIC, Australia
2 National Synchrotron Light Source, Brookhaven National Laboratory, NY, USA
3 CSIRO Materials Science and Engineering, Clayton VIC, Australia
4 Instrumentation Division, Brookhaven National Laboratory, Brookhaven NY, USA.
5 Australian Synchrotron, Clayton VIC, Australia
6 School of Physics, University of Melbourne, Parkville VIC, Australia
7 CODES Centre of Excellence, University of Tasmania, Hobart TAS, Australia
8 South Australian Museum, North Terrace, Adelaide SA, Australia

Introduction

Present limits placed on synchrotron x-ray microprobe fluorescence imaging by detectors and data acquisition approaches result in poor image definition, defined as the number of pixels. The approach taken here aims to set the pixel count to suit the needs of the sample (between ~0.2-4 mega-pixels) and use a fast multi-parameter data acquisition approach, with each x-ray event tagged by X,Y position and detector number, and tight coupling with direct stage control, to accumulate full-spectral data for all pixels without imposing dwell time constraints per pixel.

The attraction of energy-dispersive detectors for imaging and trace analysis, which stems from high data-rates and full-spectral data collection, is tempered by the need to unravel the complex overlaps between interfering elemental signatures and detector artefacts, background and scattered beam. A method, called Dynamic Analysis (DA), has been developed [1] to deconvolute these overlapping signatures, which enables the elemental images to be projected successfully, even for trace elements and rare mineral phases. Moreover, the method lends itself to real-time imaging as the underlying matrix transforms can be executed on each x-ray event as it arrives.

The large dynamic range of imaging applications between major elements and trace elements at ppm levels leads to poor statistics for trace element images when a small number of detector elements are used due to the major elements setting the count rate limits in each detector. However, to improve trace element image quality means increasing the collection solid-angle of the detector system which increases overall count rates. This demands a large number of detector elements (hundreds) to maintain a manageable count rate in each detector channel and a data acquisition approach that can handle many millions of events per second.

Demands on fast scanning and high throughput data acquisition is further tested if 3D applications are to be tackled. These include x-ray absorption edge spectroscopy techniques, such as XANES imaging, and 3D fluorescence tomography. In these cases, we need to collect multiple full-spectral image frames, one for each step in $E_{\text{photon}}$ (for XANES) or $\theta$ (for tomography).

New Detector Concept

A new spectroscopy detector system is under development by BNL and CSIRO that combines a large planar Si detector array, custom pulse-processing ASICs, and a
pipelined, parallel processor with embedded DA image projection, which aims at large solid-angle, close coupling to stage control and count-rates approaching \(10^8\) events/second, with full real-time processing and deconvoluted image projection [2,3]. The final concept aims for a 384 element detector array. This work reports on a series of tests using 32 and 96 element detector system prototypes.

The detector comprises low-leakage Si pad arrays under development at BNL [2], and CMOS application specific integrated circuits (ASICs) providing a 32 channel integrated low-noise preamplifier plus high order shaper with baseline stabilizer (HERMES [4]), and a 32 channel peak-detecting derandomizer and multiplexer (SCEPTER [5]) to enable time-over-threshold determination for pile-up detection and rejection. The detector pad array is wire-bonded to one or more 32 channel HERMES ASICs. The detector array (water cooled with additional Peltier cooling of the detector array to -35°C) has demonstrated an energy resolution of 184eV (Mn K\(_\alpha\)).

Pulses from the SCEPTER ASICs representing both energy (E) and time-over-threshold (T) are digitized by dual 14-bit fast synchronous ADCs interfaced to the parallel processing engine HYMOD, developed at CSIRO for high speed instrumentation applications. HYMOD consists of a wide input data interface (128 bit), 166 MHz field programmable gate-array (FPGA) connected to 6 large static RAMs, a 166 MHz Motorola PowerPC co-processor, and ample fast serial (12 x 3.125 Gb/s) and Ethernet ports (2 x 1Gb/s). Code for the FPGA is developed using an in-house pipelined, parallel processing compiler called 3PL, and will handle pile-up rejection, energy calibration mapping, DA projection and directly drive the sample stage. The PowerPC handles image accumulation and display and in the final version will handle external control requests as an EPICS node. Tests of the HYMOD implementation of the DA algorithm, using a second HYMOD to simulate a detector data-source, have demonstrated event processing and real-time DA image projection at \(10^8\) events per second.

The DA method builds a matrix transform to perform the task of spectral deconvolution of overlapping element spectra and detector artefacts [1]. The method was developed at CSIRO to project quantitative elemental images derived from proton induced x-ray emission (PIXE) data and has been extended to handle Synchrotron x-ray Fluorescence (SXRF) data [6]. The DA approach lends itself to real-time processing of detected x-ray counts on an event-by-event basis. Each event is tagged by detector number and current XY position of the sample stage for imaging (and potentially E\(_{\text{photon}}\) for XANES and \(\theta\) for fluorescence tomography). The detector number is used to select energy calibration tables appropriate for the detector to map channel number onto DA matrix column. This column provides the image increments for each elemental image at the current XY position. This close coupling of scan coordinates with data acquisition removes the common constraint of ~second dwell time per pixel, enabling high definition images to be collected with dwells of ~1ms.

**Prototype Tests**

Prototype tests in late 2006 at the NSLS, beam-line X27A [8] demonstrated the concept using a 32 element prototype (called Maia-32) with the array wire-bonded to a single HERMES-SCEPTER pair. This experiment provided some illustrative examples, which featured short dwell per pixel (6ms), mega-pixel images (up to 2000 x 2000 pixels) and real-time deconvolution into separated elemental images [7].
Recent tests in 2007 at X27A used a 96 element prototype (called Maia-96) with the array bonded to 3 HERMES-SCEPTER pairs and a faster stage. The geometry of this prototype test is shown in Fig. 3. These tests demonstrated (i) count rates up to 6 Mcps, (ii) dwell times as short as 0.8ms (7.5µm pixels), (iii) further mega-pixel images of geological and biological samples, which show extraordinary detail in major and trace elements (Figs. 1,2), and (iv) schemes designed to compress or filter the raw data-flow in anticipation of even higher rates with larger arrays.

Conclusions

Plans for a 384 detector system, integrating full-spectral data collection with high speed stage control and real-time data processing and image display are on track with successful tests of 32 and 96-channel prototypes at the NSLS, which featured mega-pixel imaging at dwell times as short as 0.8ms and count rates up to 6 Mcps. Given the capabilities of the new system, the choice of pixel number and dwell time are now dictated by the needs of the applications and adequate counting statistics and not by data acquisition limitations.

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References

Fig. 1  Fe (left), Y (above) in iron-oxide nodules, Rose Dam, WA, imaged using the Maia-96 prototype detector array, NSLS beam-line X27A [8], 17.2 keV photons, 13 x 21 mm$^2$, 1625 x 2625 pixels at 5 ms/pixel.

Fig. 2 (right)  Ca in stems of Acacia Aneura from Western Australia, imaged using the Maia-96 prototype detector array, beam-line X27A, 17.2 keV photons (9 x 17 mm$^2$, 1200 x 2267 pixels at 7.5 ms/pixel)

Fig. 3 (below) Layout of the 96 element detector (detector at 90° to the beam, target rotated -45°), showing its solid-angle at 20 mm from target. The final 384-element detector array will have 6-7 times larger effective solid-angle.
Extended interface analysis using high energy electron scattering
M R Went and M Vos
Atomic and molecular physics laboratories, RSPhysSE, ANU, Canberra 0200.

Abstract
We demonstrate that high-energy, high-resolution reflection electron energy loss spectroscopy (REELS) can provide unique insights into interface formation, especially for the case where an extended interface is formed. By changing the geometry and/or electron energy the electronic structure is probed over a range of thicknesses. Simultaneously the elastically scattered electrons are resolved into different components, corresponding to scattering of atoms with different mass. Thus these high-energy REELS/elastic scattering experiments obtain information on both atomic composition and the electronic structure of the overlayer formed.

Introduction
Reflection energy loss spectroscopy (REELS) has long been used to study the interaction of electrons with a surface, and is an important tool to help understand photoemission, as the latter necessarily involves the transmission of electrons from the material under investigation into the vacuum. In this paper we present REELS spectra taken at energies up to 40keV. As the mean free path of electrons increases with energy this allows us to probe rather thick layers. Here we want to demonstrate that high-energy REELS can be used as an in-house technique to study the electronic structure of thick layers. It is in this sense an alternative to high-energy photoemission, and is a method that could quite easily be adapted to even higher energies.

Interest in investigating the possibilities of these high-energy REELS measurement was triggered in part by the realization that the elastic peak splits up at high energies in different components, corresponding to electrons scattering of atoms of different mass [1]. This is because if an electron is scattered over a large angle, it transfers a significant amount of momentum to the scattering atom. If the momentum transferred to the atom is $\mathbf{q}$, then the corresponding (mean) recoil energy $E_r$, transferred from the electron to the atom is given by $E_r=\frac{q^2}{2M}$, with $M$ the mass of the atom. Thus, in favourable cases, the elastic peak splits up into different components, due to scatterers with different mass $M$ and the measured structure can be used to determine the surface composition. This technique is then often referred to as ‘electron Rutherford backscattering’ (ERBS) (see e.g. [2]), as it resembles (ion) Rutherford backscattering in many ways. REELS at high energies provides complimentary information to ERBS, mainly on the electronic structure, that is obtained simultaneously with ERBS data.

Experimental details
The main spectrometer is shown in Fig. 1. The spectrometer is equipped with two electron guns. Each gun emits electrons with 500eV energy. The sample is surrounded by a high voltage sphere kept between 4.5keV and 39.5keV. Thus electrons with energies between 5keV and 40keV are scattered from the sample. After being decelerated and focused by a slit lens stack, the electrons enter a hemispherical analyser. At the exit of the analyser a two-dimensional detector was used allowing electrons in an energy window of $\approx30eV$ to be detected simultaneously. For more details about the apparatus design see Refs. [3] and [4]. Data were taken with current
less than 1 nA. Typically a spectrum was obtained over a 2-hr period. Samples were prepared in a separate UHV chamber by sputtering using Xe⁺ ions. Auger spectra taken after cleaning revealed no C or O at the surface. The sample was then transferred under UHV to the main spectrometer for the high-energy REELS measurements. Later aluminium was deposited onto the cleaned (Mo and Pt) surface by thermal evaporation from a boron carbon nitride composite crucible. This was performed in a dedicated evaporation chamber.

**Results and Conclusion**

We want to investigate if we can use REELS for overlayer–substrate systems. In REELS one measures the energy distribution of the electronic excitations for an electron backscattered from a material. This distribution is a signature of the electronic structure. In a substrate–overlayer system one can identify two or more phases (overlayer, substrate and possibly one or more phases formed at the interface), each with its own electronic structure and hence loss function. By monitoring the structures of the loss function as a function of overlayer thickness we can probe which phases are present in the sample.

**Fig. 1.** An overview of the experimental configuration. If gun A is used the sample is positioned as shown and the scattering angle is 120°. Angle between the sample surface normal and incoming and outgoing trajectories is then 45° (but surface normal, incoming and outgoing trajectories are not in the same plane). If gun B is used (scattering angle 45°) the sample is rotated over angle $\alpha$ by 112.5°. The incoming and outgoing trajectories are now more glancing (both 67.5° with the surface normal).

**Fig. 2.** A comparison of the raw (40keV) REELS data obtained for Al deposition on Mo and Pt. For the Mo case the Al plasmon is clearly visible at the lowest coverage. However for Pt this is not the case. The difference between the high-energy spectra before and after deposition (lower panels) resembles the Al loss function in the case of deposition on Mo, but is completely different for deposition on a Pt sample. The structure appearing after evaporation near 2eV energy loss is the Al elastic peak.

The simplest overlayer-substrate system is one where no reaction occurs, and the evaporated layer grows in a layer-by-layer mode. From the work of Kolaczkiewicz et al. it is known that Al grows (at low coverages) on Mo in a layer-by-layer mode [5].
We show spectra of Mo covered with thick (by electron spectroscopy standards) Al layers (40Å and 80Å) (Fig. 2). The spectra were, for convenience, normalized in such a way that they largely overlap for large energy loss values. For the Mo substrate the main effect of Al deposition is a sharp peak at 15.2eV energy loss relative to the Mo elastic peak. 15.2eV corresponds to the Al plasmon energy and this feature is thus attributed to electrons scattering from Mo for which either the incoming or outgoing electron excited an Al plasmon. The main features of the Mo energy loss spectra are still discernable. Thus the measured energy loss spectra for the Al/Mo system can be described, at least in first-approximation, as the sum of a Mo REELS spectrum and an Al REELS spectrum. Taking the difference of the spectra before and after Al deposition we see that the excess intensity corresponds to the energies of the Al bulk and surface plasmon.

The behaviour of Al deposition on Pt contrasts strongly with that seen for Al deposition on Mo. The Al-Pt system is known to form a surface alloy for thin layers at room temperature [6]. Our Pt results are shown in the right panels of Fig. 2. Now no sign of the Al plasmon is found. Above 30eV energy loss and below 10eV energy loss the features of the Pt loss function still stand out. From the difference spectrum it is clear that the excess intensity is centred around 20eV energy loss in a much broader peak (in comparison to the Al plasmon width). Increasing the coverage increases the difference before and after deposition, but the position and width of the peak in the difference spectrum does not change dramatically. We take the difference to be the rough shape of the loss function of an interface compound that is formed.

At very small energy loss (≈2eV) an additional peak appears after Al deposition in the 40keV REELS spectra. It is due to electrons scattering elastically from Al, rather than Pt or Mo. This additional peak appears at the recoil energy \(E_r\) predicted for Al. Thus it is attributed to a feature of the ERBS spectrum, not an additional inelastic energy loss feature. This Al peak appears, for identical coverage, more intense for evaporation on Mo, compared to that on Pt. This is not surprising as the Pt elastic cross section is much larger than the Mo elastic cross section, and the ERBS signal strength is, at least in first order, proportional to the elastic cross section (as all detected electrons have been scattered elastically). Hence the relative strength of the Al peak after 40Å and 80Å deposition is larger for the Mo substrate compared to the Pt substrate.

![Fig. 3](image_url). Elastic region of the spectra taken at 150Å and 600Å Al coverage taken with gun A using a 20keV (left panels) and a 40keV (right panels) electron beam. The full line is a fit using two Gaussian peaks and a Shirley background. The main peak was aligned with the calculated recoil energy of Pt under these conditions.
To now investigate the ERBS signal we examine the region near the elastic peak in Fig. 3 we show the 150Å and 600Å cases as an example. At 150Å coverage it is possible to get a good fit using two Gaussians separated by the calculated difference in recoil energy. However the area obtained from these fits depends very much on the background choice (we used a Shirley background for these fits). The situation has changed at 600Å. Not only has the Al signal strength increased, but the Pt signal has become weaker due to attenuation in the Al layer (the latter is evident from the decrease of the total count rate in the elastic peak area for a given beam current). Now the peak separation can be left free in the fit, and indeed values very close to those calculated for the recoil energies are obtained, further confirming our interpretation of this feature at low energy losses. This also suggests that the single-scattering approximation is valid, i.e. the electrons are deflected over a large angle by one collision only. The relative intensity of the Al peak in the 20keV measurement is stronger than in the 40keV case, as at lower energy attenuation in the Al layer is stronger, and the thickness of the Pt layer that contributes effectively to the elastic peak is less.

We have described high-energy reflection electron energy loss experiments and confirm that these experiments are bulk-sensitive. Interfaces formed by evaporation of Al on the substrates were monitored by REELS over a large range of overlayer thicknesses using a range of energies. In this way one can vary the depth probed, and the picture obtained in this way gives clear insights in extended interface formation. Besides the dramatic changes in the REELS spectra it was found that deposition of Al on high Z substrates results in a splitting of the elastic peak, due to recoil effects. In general, the spectra are all very dependent on the electron energy, but, at least qualitatively, the spectra can be interpreted as the sum of the bulk loss functions of the materials that contribute (overlayer, substrate and reacted layer). Changes due to energy variations are then a simple consequence of a variation in probing depth. Hence it is clear that REELS at high energies is often a very convenient way of probing surface elemental composition as well as the electronic structure up to considerable depth (=1000Å in favourable cases). A prerequisite for this method is that the energy loss spectra of the overlayer and substrate have well-resolved distinguishing features.

Avalanche detector technology for keV single ion detection and implantation for quantum bits construction

C. Yang 1, D.N. Jamieson 1, T Hopf 1, E. Gauja 2, A.S. Dzurak 2 and R.G. Clark 2

1ARC Centre of Excellence for Quantum Computer Technology, School of Physics, University of Melbourne, Victoria 3010, Australia
2ARC Centre of Excellence for Quantum Computer Technology, University of New South Wales, Sydney 2052, Australia

Abstract
Avalanche photodiode (APD) technology offers high sensitivity in the detection of visible light and x-rays based on the high internal charge gains. It is ideal for the measurement of ionization energies with very high sensitivity. It can potentially be used for the detection of single low-energy-heavy ion particles at keV energy range, especially for the detecting and controlling of 5-10keV P⁺ single ion implantation events for the construction of Si:P based quantum bits. We used the method of ion-beam-induced-charge (IBIC) to investigate the internal charge gain and charge collection efficiency (CCE). We achieved a charge gain larger than 300 in commercial APDs through the IBIC measurement using MeV He⁺ ions. A special detector structure is outlined for counting keV single ion implantation events aiming for the construction of Si:P based quantum bits (qubits) and single-donor nano-devices.

Keywords: Avalanche photodiodes (APD), ion-beam-induced-charge (IBIC), charge collection efficiency (CCE), internal charge gain, ionization energy, keV single ion implantation, qubits, nano-devices

Introduction
We have established a single-ion-implantation method for the qubits construction based on the ionization energy measurement of single ion induced charge in silicon through using PIN detector structure [1-4]. The on-going project is aiming for the improvement of the detection limit of the ionization energy measurement by adapting the APD detector technology for the keV single ion detection.

APDs are conventionally configured to work in non-linear Geiger mode in most optical applications. The Geiger mode is for an operation with a maximum gain; the drawback is impossible to tell and reject pile-up events. The work presented here we successfully operated APD detectors in a linear mode with an output of signal pulse height linearly proportional to the ionization energy of the incident particles; this gave us an advantage of being able to distinguish single ion events from two or multiple ions pile-up events. We used the method of ion-beam-induced-charge (IBIC) to measure the internal charge gain and charge collection efficiency (CCE). We observed a strong correlation of internal charge gain with the ions implantation depth in avalanche detectors with a charge gain larger than 300 in commercially available APDs. An avalanche-PIN design structure is outlined for counting keV single ion events aiming for the construction of Si:P based qubits and single-donor nano-devices.

IBIC characterization of single ion detectors
IBIC imaging method in a nuclear Microprobe was applied in the characterization of the detectors. This IBIC method was previously used for a prototype of PIN detector’s optimization aiming for keV single ion detection [5]. The PIN detector structure and
its typical IBIC map revealing the charge collection efficiency is displayed in the Figure 1. The PIN detector has constant charge collection efficiency 100% at the device’s centre area with a wide range of bias voltages. The IBIC analysis was also applied to a selected commercial APD detector with increased bias voltages up to 160 V. Figure 2 displays a uniform CCE map indicating a charge gain of 2.0 with a bias voltage of 95 V. A structural defect was also evident in the CCE map. A further effort will be focused on modifying an existing PIN device by introducing an avalanche zone into the detector design for achieving a large internal charge gain (>1). IBIC analysis on the new devices will provide key information on the internal charge gain of the future avalanche-PIN (APIN) devices.

Large charge gain for single ions in APD devices

We used MeV He⁺ ion to measure the charge gain. The charge gain in the commercial APD detector is a strong function of the bias voltage. IBIC analysis using 2.0MeV He⁺ ions was applied to the APD with bias voltages scanned from 10 to 160 V. The result of the charge gain versus bias voltage is displayed in Figure 3. The internal charge multiplication process was evident at a bias voltage above 60 V. The charge gain reaches above 10 at bias voltage of 150 V and larger than 300 at bias voltage above 155 V.
Construction of APIN device for Single ion implantation

It is not feasible to use commercial APDs for the single ion implantation application due to its metal coating and impurity doping at the device’s frontal area. We have developed a prototype of PIN detectors for the keV single ion implantation. It is possible to construct an avalanche zone at the backside of this type of PIN device for achieving a large internal charge gain. Figure 4 displays a layout of a proposed avalanche-PIN structure for the single ion implantation application.

Acknowledgements

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References

Towards a better understanding and prediction of the bremsstrahlung background in PIXE spectra

David D. Cohen, Ed Stelcer, Michael Prior, Rainer Siegele and Mihail Ionescu

ANSTO, PMB1, Menai, NSW, 2234, Australia.

Abstract

Murozono and Ishii et al recently published theoretical QFEB, SEB and AB bremsstrahlung cross sections which, when modified by typical x-ray detection efficiencies, provide excellent predictions of the backgrounds in PIXE spectra for a range of light target matrices.

Introduction

MeV ions impinging on solid targets produce bremsstrahlung radiation. For MeV ions on light to medium atomic numbered targets this radiation has at least three components; quasifree electron (QFEB), secondary electron (SEB) and atomic bremsstrahlung (AB)[1-4]. The QFEB process is represented schematically in Fig. 1. A target electron is scattered by the Coulomb field of the projectile producing bremsstrahlung x-rays. The cross section becomes large when the projectile velocity is much larger than the target electron velocity. The maximum energy transferred to the electron at rest is \[ T_r = \frac{m_e E_p}{M_p} \]. The SEB radiation is produced when the projectile ejects a target electron which is then scattered by the Coulomb field of another target nucleus. This process is shown in Fig. 2.

The maximum energy transferred to the target electron in this SEB process is \[ T_m = 4T_r = \frac{4m_e E_p}{M_p} \]. The final bremsstrahlung process we consider here is AB shown in Fig. 3. This occurs when a bound target electron is excited to the continuum, by the projectile and then returns to its original bound state. This results in a continuous spectrum from a few eV to tens of keV depending on the bound state of the electron. Following Murozono et al [4] we only consider K and L shell bound states here. Typical cross sections for 3MeV protons on carbon for these three mechanisms are shown in Fig. 4. The QFEB process is significant below 2keV, SEB dominates the total bremsstrahlung cross sections from 2-8keV and AB becomes significant above 8keV x-ray energies. For 3MeV protons on carbon \( T_r = 1.6 \text{keV} \) and

Fig. 1. Schematic QFEB

Fig. 2. Schematic SEB.

Fig. 3. Schematic AB.

Fig. 4. Typical cross sections for QFEB, SEB and AB processes for 3MeV protons on carbon after Murozono et al [4].
$T_m=6.5\,\text{keV}$ which is reflected well in the cross section fall off in the QFEB and SEB data of Fig. 4 (see vertical dashed lines). These bremsstrahlung cross sections are monotonic and continuous with x-ray energy and increase significantly with decreasing energies below 10keV.

Particle Induced X-ray Emission (PIXE) experiments [5,6] are generally performed using 3MeV protons on carbon like matrices with silicon based detection systems. Fig. 5 shows the calculated detection efficiency for a typical Si(Li) detector with 25µm beryllium entrance window thickness and two different crystal dead layer thicknesses of 0.1µm and 0.5µm [7]. Discontinuities are produced in the detection efficiency at the Si K edges and the gold contact M edges as shown [8].

The drop in efficiency from 100% above 10keV to less than 1% at 1keV folds the cross section plots of Fig. 4 over below 2keV, producing the classic measured PIXE bremsstrahlung shapes shown in the simulations of Fig. 6 for 3MeV protons on thin carbon. The discontinuities at the Si Kedge and the gold contact layer M edges have been used by Cohen et al [8] to estimate the detector silicon dead layer and the gold contact layer thicknesses.

**Bremsstrahlung Yields**

Scaling the QFEB, SEB and AB cross sections of Murozono et al [4] and convoluting their sum over the 0-15keV x-ray energy region with the detection efficiencies of Cohen [7] we can calculate the total bremsstrahlung yields for different ions on selected targets. Fig. 7.
Fig. 7. Calculated bremsstrahlung yields for 100 μC of 3MeV protons, using a detector with 80 μm Be window and solid angle of 1.3msr. All targets were 1,000μg cm^{-2} thick.

Fig. 8. The variation in bremsstrahlung yields with target self absorption, using 5%, 25%, 50% and 100% of the target thickness for self absorption corrections on a Cu target.

shows such a calculation for 100μC of 3MeV protons on 1,000μg cm^{-2} Be, C, Si, Ca and Cu targets. Note the target thickness is much less than the proton range. These yields have been corrected for detection efficiency and self absorption of 3MeV protons for all targets. As the target atomic number Z increases the x-ray yields increase in the 7-20keV region. The peak in the bremsstrahlung shifting from 2keV for Be to 4keV for Cu targets is produced by self absorption in the target. This is clearly demonstrated by Fig. 8 where yields for 3MeV protons on 1,000 μgcm^{-2} thick Cu are plotted as a function of the percentage depth at which the self absorption was calculated. Self absorption shifts the low energy cut off and the apparent peak in the yield to higher x-ray energies as the size of the correction increases with depth.

We have measured bremsstrahlung yields from a range of pure thin targets including Be and C. Fig. 9 shows such yields for 200μC of 2, 3 and 4MeV protons on 1,767 μgcm^{-2} thick carbon. For proton energies above 2.2MeV on carbon an additional Compton scattered gamma ray background component appears in the spectrum above 10keV. This can be adequately fitted by an exponential function in x-ray energy and subtracted off, leaving the pure bremsstrahlung component, between 0 and 10keV, see Cohen et al [9].

The solid curves of Fig. 9 show the background shapes of these PIXE spectra were well fitted by the bremsstrahlung plus gamma ray backgrounds calculated above. Indeed Figs 10 and 11 show that this technique for bremsstrahlung prediction can be used to fit thin targets for compounds as well as pure elements. Fig 10 is the PIXE spectrum for 2.6MeV protons on thin Teflon. The Teflon was relatively very pure and hence the spectrum well represents bremsstrahlung background. The flat continuous background above 10keV was due to Compton scattered gamma rays from F(p,p'γ) reactions and was well fitted by an exponential function in x-ray
energy all the way down to zero keV. The solid curve under the experiment between 1 and 9keV was the predicted bremsstrahlung background for (CF\textsubscript{2})\textsubscript{Teflon} with only one extra parameter for scaling its peak height to fit the experiment between 2keV and 3keV. Closer inspection shows a good fit to the experimental shape, with significant deviation only above 4keV where the AB component maybe underestimated by theory.

This may be expected since the AB contributions calculated by Murozono et al [4] only included the K and L shell target electrons and only transitions from these levels to the continuum and back to the K or L shell. Whereas one might expect transitions from inner shell target levels to the continuum (Radiative Ionisation, RI) may also contribute in this x-ray energy region [2]. The excess counts in this region may be due to pileup of the bremsstrahlung radiation with itself although experimental count rates were kept low so that dead time corrections were typically well below 5% for most runs.

Fig. 11 is a similar plot to Fig. 10 except for thin Kapton (C\textsubscript{22}H\textsubscript{10}N\textsubscript{2}O\textsubscript{5})\textsubscript{n}, this was plotted on a linear scale so the background fit below the characteristic peaks for P, Cl K and Fe could be better assessed. Again the fit was excellent with the only fitting parameter being a single scaling factor to match theory and experiment in the 3keV region where there were no characteristic x-ray peaks.

**Summary**

Theoretical QFEB, SEB and AB cross sections have been used to estimate the experimental bremsstrahlung backgrounds found in typical thin target PIXE spectra of pure elements for proton energies between 1 and 4MeV. This has been extended, again with good results, to compounds containing lighter elements like carbon, oxygen, nitrogen and fluorine. If the Compton scattered gamma ray background was simulated with an exponential function in x-ray energy, then the total background for most common PIXE spectra were successfully modelled from first principals. These concepts can now be included into standard PIXE analysis codes like PIXAN [10,11], GUPIX [12,13] and GeoPIXE [14].

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References


Fully-automated counting of fission tracks in natural minerals for fission track dating and thermochronology

Andrew J.W. Gleadow 1, Stewart J. Gleadow 1, Barry P. Kohn 1, and Michael S. Krochmal 3

1School of Earth Sciences, University of Melbourne, Melbourne, Victoria 3010, Australia
3Autoscan Systems Pty Ltd, PO Box 112, Ormond, Victoria 3204, Australia

The automated counting and analysis of fission tracks in natural minerals has been one of the most long-sought goals in fission track dating. But despite extensive exploration of possible approaches, and some promising developments [eg 1-3], essentially all attempts up to this time have failed in one or more key aspects. There are specific challenges and difficulties to be overcome in the automated image analysis of spontaneous fission tracks in natural minerals. These include discriminating genuine tracks from non-track defects, resolving multiple track overlaps, and identifying small tracks in a background of similar-sized spurious features, such as surface dust particles and fluid inclusions. The optical variability of individual grains of natural minerals also poses challenges for digital image analysis systems that are inherently poor at pattern-recognition tasks compared to the eye and brain combination of a human operator. Developments in computing have largely solved other problems of image quality, lack of sufficient computing power, and of sufficient image storage.

Rapid advances in optical microscopy, such as confocal laser scanning microscopy, have so far had little impact on the imaging of etched fission tracks in minerals. Notwithstanding claims to the contrary [4], confocal microscopy has little benefit for the imaging of fission tracks because it remains inherently a reflected light technology at the present time. Some individual fission tracks are revealed superbly, but others are made almost invisible by this observation mode. This situation is not likely to change until a truly transmitted light confocal imaging system is developed. However, these developments have led to the emergence of a new generation of microscope control systems that now enable the acquisition of digital microscope images of unprecedented quality using conventional imaging modes in transmitted and reflected light.

Our digital image acquisition system is based on a Zeiss Axiotron microscope with motorized stage and focus mechanism, motorised objective nosepiece and light source shutters. All of the main microscope configuration functions are thus under computer control. To this set-up a Physik Instrumente PIFOC piezoelectric microscope-objective nanofocussing device has been added for the 100x objective. The PIFOC device is capable of positioning the objective lens with sub-nanometer resolution over a total scanned range of 100 µm with near-instantaneous response and no mechanical backlash. The motorised stage and focus motor are used for preliminary positioning of the specimen to previously-labelled points of interest. The PIFOC device is then used for precise control of focussing and highly stable image acquisition using an Olympus ColorView 1 CCD digital microscope camera with 3.3 megapixel resolution. Our procedure captures a surface-focussed reflected light image followed by a precisely spaced Z-stack series of images in transmitted light. This image series is then archived to disk before processing using a custom developed image analysis system based initially on the ImageJ cross-platform image analysis program. All custom software has been written in Java to maximise its cross-platform implementation.
We first concentrated attention on the problem of automating the fission track counting and our initial attempts centred on using the information in a Z-Stack sequence to resolve the problem of multiple track overlaps. Various approaches for projecting and analysing the Z-Stack were tried and, whilst some of these produced potentially useful information on track dimensions, they were processor intensive and most were ineffective at resolving overlaps. Our attention then turned to utilising the information in the reflected light image and from this we have developed a remarkably simple digital image analysis system that solves most of the typical track recognition and discrimination problems encountered in routine fission-track analysis in natural minerals.

We have called the method ‘Coincidence Mapping’ and it involves combining the reflected light image with a single transmitted light image, as shown in Figure 2. The transmitted and reflected light images (Figure 1, (a) and (b) respectively) are segmented by applying a custom developed thresholding routine to give the binary images of features (c) and (d). Inspection of Figure 1 shows that both kinds of binary images include spurious features that are not tracks. However the intersection of these two images obtained using a Boolean AND operation selects for the genuine track features and against spurious objects. The coincidence map, Figure 1(e), shows the selected features and (f) the rejected features from this analysis. The analysis is extremely efficient and takes only a few seconds to complete the analysis of images that may contain hundreds of tracks. Figure 1 illustrates fission tracks etched in a muscovite external detector but experience so far shows that the discrimination obtained with this method is also highly effective for counting spontaneous fission tracks in apatite.

The method is extremely effective at discriminating tracks from surface dirt and dust, polishing scratches, microlites and fluid inclusions. It is also remarkably effective at resolving multiple track overlaps even at track densities well beyond that which a human operator would normally attempt. The system achieves this success in resolving overlaps by capturing the higher spatial resolution of the track entrance pits.
in the reflected light image. At even higher track densities, where the reflected light pits themselves begin to overlap, we have used an analysis of the areas of the individual pit features to resolve the number of tracks represented by larger compound track features. In this way we have successfully been able to count track densities up to \(5 \times 10^7\) cm\(^{-2}\), well beyond the range that is normally countable in transmitted light by a human operator. We see no reason why this method should not work effectively up to track densities as high as 108 tracks cm\(^{-2}\). The error rate in our experimentation so far is about the same or better than that achieved by a human operator counting in transmitted light. At high track densities the error rate is significantly lower.

We are now very confident that coincidence mapping will provide the first successful image analysis system for the fully-automated counting of fission tracks in natural minerals. Automated counting should significantly improve data quality in fission track dating through better counting statistics, measurement of additional track description parameters not currently collected, and increased objectivity in fission track analysis. The technique is extremely fast and promises a much more rapid sample throughput than can be achieved by a human operator. Combined with direct-uranium determination by laser-ablation ICP-MS [5], coincidence mapping will provide a revolutionary new approach to fission track dating. Automated measurement of track lengths is a more challenging problem that is not yet resolved, although several promising leads are being investigated.

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References


PIXE imaging of a developing corrosion front beneath a protective coating on galvanized steel

David X Belton a, David N. Jamieson b, Chris G. Ryan a, Aaron K. Neufeld c

aCSIRO Exploration and Mining, Melbourne, VIC, Australia
bSchool of Physics, MARC, University of Melbourne, VIC, Australia
cBlueScope Steel Limited, Coatings Research, Port Kembla, NSW, Australia

Abstract

Despite their wide application in construction and manufacturing, unprotected metals are largely unsuited to applications where they are exposed to moisture and potentially corrosive agents. This has led to the development of engineering solutions such as pre-painted galvanized steel strip and sheet, which combines chemical and mechanical protection against aggressive environments. However, if the integrity of this barrier is compromised, then the structural element – in this case the steel – may be exposed to progressive and irreversible deterioration leading ultimately to failure of specific performance criteria. In this paper we used the CSIRO-GEMOC nuclear microprobe to investigate in-situ, the nature of chemical reactions at the interface between the outer paint coating and the underlying hot-dipped galvanized layer in a specimen that has been exposed to extreme marine atmospheric conditions. By using 3MeV protons, we were able to penetrate the outer paint coating, the underlying zinc plating, and the steel substrate below. The combination of layers acted to attenuate the x-ray yields from the Fe-rich substrate while permitting abundant counts from Cl-rich corrosion product compounds and dehydrated electrolyte beneath the paint coating to be detected with only a 125µm Be filter. We present a series of elemental images showing spatially, in extraordinary detail the physical degradation of the paint coating and the effects of corrosion processes.

Keywords: x-ray imaging, corrosion, galvanized steel, PIXE, nuclear microprobe

1. Introduction

Zinc coating is an economical means of protecting steel from the ravages of exposure to the elements. Galvanized steel products resist corrosion in two fundamentally different ways [1]. First, the zinc plating provides a mechanical barrier that prevents exposure of the steel substrate to moisture and potentially aggressive environments. Secondly, zinc acts as an active coating that provides sacrificial or galvanic protection. Modern protection of hot-dip zinc galvanized (HDG) steel products includes a paint coating which provides exceptional resistance to corrosion [2]. However, the finished coating may be damaged either during installation, or subsequently when the material is in use. If the integrity of the barrier system is compromised the steel may deteriorate and ultimately fail. HDG steel coated with an inferior paint or with imperfections, is susceptible to blistering when exposed to a corrosive ambient. Blistering is initiated by cathodic processes at the interface between the paint coating and the zinc layer. Chlorides form here through the corrosion of zinc in the area of the delaminated blister, and if the underlying steel is exposed, additional oxidation of zinc is introduced. The crucial property of zinc is that under these circumstances, it protects the steel from oxidation.

The spatial distribution of the elemental products and reactants provides clues to understanding of corrosion initiation [3] and allows us to better define the key characteristics of an effective paint coating. However, obtaining chemical information
about corrosion reactions buried beneath the paint topcoat (typically >25 µm) is a challenge, since removal of the coating without disturbing the elemental composition and distribution within the corrosion zone is rarely successful. [4]

Nuclear microprobe analysis provides a method for capturing high resolution images of spatial variation in composition without the removal of the paint coating. The ion beam can penetrate through the topcoat to allow Proton Induced X-ray Emission (PIXE) from the “buried” steel substrate, the galvanized zinc layer and the corrosion product compounds. The arrangement of the layering in these samples coincidentally ensured that high x-ray yields resulting from both the Fe-rich and Zn-rich layers were sufficiently attenuated by the intervening paint coating. Use of a 125µm Be filter ensured optimum yield of easily attenuated Cl and Si X-rays.

2. Experimental Method

Panels of prepainted HDG steel sheet were exposed to a severe marine environment for 3 years. During this period, physical imperfections in the paint coating and poor wet adhesion between the zinc layer and the paint coating have formed the initiation points for blistering corrosion. For analysis using the CSIRO-GEMOC Nuclear Microprobe, a sample 1 cm in diameter was cut from the panel. Using the optical microscope capabilities of this microprobe, the scan region was readily positioned over a blister which presents as a distinctive feature resulting from corrosion product build-up under the paint coating. The scan region was selected to image both undamaged and blister regions of the sample. X-ray data for the sample was collected with a Canberra UltraGe X-ray detector fitted with a 125 micron Be filter. The ~1.8 micron, 3MeV H⁺ beam at 0.1 nA was rastered in the Y-direction and the sample stage stepped in the X-direction to achieve a total scan of approximately 4mm². Routine procedures are available within the GeoPIXE software package [5] to determine elemental concentrations from the raw spectra in the undamaged zone.

Layered targets require more detailed treatment to allow for the variation in composition with depth. Nevertheless, it is possible to image, in extraordinary detail, the transition from undamaged to the corroded zinc-paint coating interface whilst leaving the entire multilayer sample intact. For this investigation, we were primarily interested in the reduction of the zinc layer and the chloride distribution. However, regions of poorly constrained thickness (eg. the blister) meant that the PIXE spectrum did not provide sufficient information to model a complete analysis of a multi-compositional, layered specimen. To address this, a suite of experiments using progressively milled (removed) paint coating were conducted to characterise the response of both Zn and Fe X-rays to varying thicknesses of overlying material.

3. Results and Discussion

The organic-rich paint coating is characterised by Si, K, Ti and Cr. The x-ray element map for Ti is reproduced in Figure 4. TiO₂ is used to optimise a whole range of paint properties including colour, opacity, dispersion and durability [6]. With the exception of some small artefacts introduced by the combination of irregularities in the sample surface and the detector geometry (the detector is located to the right of the scan area at 135° to the beam), the concentration of Ti (and Si, K, Cr) is essentially unvarying over the entire element image. One can infer that the paint coating has not suffered significant wear nor chemical decomposition and thus does not appear to participate as a reactant in the corrosion process.
Figure 1: Schematic of the corrosion growth process following a breach in the paint topcoat of hot-dip galvanized steel substrate exposed to a corrosive ambient. The 3MeV H\(^+\) ion beam is able to penetrate the ~25 micron topcoat and induced x-rays from the elements of interest (Cl and heavier) emerge through the topcoat to be detected.

In contrast, zinc in the HDG layer represented by the element map (Fig. 4) shows a number of features in both the undamaged and corroded regions, not all of which are related to the corrosion reaction. Cl (Fig. 4) is present under the paint coating in the form of corrosion product compounds and dehydrated electrolyte. A first order comparison of the Cl and Zn element maps highlights the significant lowering of Zn x-ray yield in those regions where Cl is present. With higher energy x-rays such as Zn (K\(\alpha\) - 8.64KeV), this reduced yield cannot be explained by attenuation in a modest thickness of corrosion products between the paint coat and an unaffected zinc layer. Modelling in GeoPIXE indicates that within the region of early de-lamination (Fig 1) characterizing the corrosion front, the loss of Zn yield is consistent with a reduction in thickness of the HDG layer on the order of 1.2\(\mu\)m.

Figure 2: Elemental maps (Ti, Cl, Zn, Fe) of the propagating corrosion front obtained from the characteristic x-ray peaks. Corrosion propagated radially from the approximate centre of the scan region. Note the presence of a sub-vertical fabric in the Zn and Fe images, unrelated to the scan direction (see the single faulty scan line in the Cl image). The lower images are element maps draped over a derivative image generated from the Zn map [7] and highlight some of the element relationships.
Zinc-hydroxychlorides are formed by oxidation of zinc in aggressive marine atmosphere. Thus, a reduced thickness of zinc will generate a marked drop in Zn x-ray yield in the region coincident with the Cl element map. However, estimates of Zn loss using GeoPIXE are hampered by the variable and irregular thickness of the Cl-rich precipitate. Note that Cl appears in the element maps ahead of the external blister margin (Fig. 2) and may indicate that the maximum extent of delamination of the paint coating. Beyond this interface, Cl is absent. There are narrow zones of reduced Zn yield that might suggest the development of cellular features in the Zn. Enhanced Fe yields observed in Figure 4 would support thinning of the Zn in these areas. Since these regions do not generally coincide with the presence of Cl, it may be inferred that they are unrelated to the corrosion process and the cellular structure may be a result of the hot-dip galvanizing process.

Fe x-ray yields (Fig. 2) from within the steel substrate are sensitive to the amount of absorption represented by the overlying HDG zinc and paint layers (and the Cl-rich precipitate where present). Reduction of the zinc layer by the corrosion reaction generates enhanced Fe yields. The increase in Fe x-ray yield is most emphasised in the boundary zone where delamination has occurred but where there is insufficient space to precipitate large quantities of x-ray absorbing corrosion products such as those seen in the centre of the blister. GeoPIXE analysis, and modelling of varying paint coatings in our test samples, suggests that the variation in Fe yields in the boundary zone can be explained by variations in the thickness of the overlying materials (primarily Zn loss) with no loss of the steel substrate itself.

4. Conclusions

Nuclear Microprobe analysis can be used to rapidly investigate the distribution of key elements in the corrosion reactants and products normally obscured beneath a protective paint coating in layered substrates. For pre-painted, hot-dip zinc galvanized sheet, the layered construction permits high precision analysis over the element range Cl to Zn with minimal filtering to avoid detector saturation. The resultant x-ray element maps can be processed using established image analysis techniques which enable us to generate powerful interpretive images and our “layer thickness” experiments will further constrain quantification within the corroded regions. Characterization of the intact corrosion reaction assemblage through the topcoat using the nuclear microprobe provides a superior method for identifying the structure and spatial distribution of the corrosion reaction products. Precise determination of the spatial relationships between reaction components without disturbing the material is crucial for a deeper understanding of the mechanisms behind the corrosion reaction.

References