DOI: 10.1017/S1431927603445479

Microsc Microanal 9(Suppl 2), 2003
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New Methods in Raman Spectroscopy – Combining Other Microscopes

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Introduction

The advantages of using an optical microscope coupled to a Raman spectrometer have been well documented over the last three decades. The advent of notch filter technology made it possible to develop the "bench top" Raman microscope systems that have dominated the market place for the last ten years. The ease of use which has accompanied these advances in instrumentation has led to a rapid expansion in the use of the Raman technology over many diverse fields, such as materials research, chemical catalysis, biochemical and biomedical, through to art restoration and gemmology. Given the level of interest and the diversity of applications, new demands are now being made by researchers to move away from using traditional optical microscopy to visualise their samples. The purpose of this presentation is to detail the very recent advances that have been made in combining a variety of alternative microscopes to identify the sample area of interest on which a Raman analysis can be performed. We have been working with Nanonics Imaging Ltd (Israel) to combine the Renishaw Raman microscope with their atomic force and near field scanning microscope, to produce a combined Raman/NSOM/AFM system. In addition we have worked with a selection of scanning electron microscope manufacturers to provide Raman analysis from materials inside the SEM.

Results and Discussions

The benefit of combining the worlds of AFM and Raman spectroscopy is illustrated in Figures 1 and 2. A 14 µm x 14 µm AFM image of a nanoindentation in silicon is shown in Figure 1, along with a cross section through the indentation. The lettered points on the AFM cross section represent the points at which Raman spectra were collected. The AFM image shows that the indentation has caused plastic deformation of the silicon, but does not give any indication whether the deformed regions have undergone any phase changes. However, the Raman spectra (Fig 2) clearly show the presence of different phases of silicon, along with shifting and broadening of the main silicon(I) 520 cm^{-1} Raman band caused by residual stresses. Other applications in the fields of polymer science for both AFM and NSOM will be given. In addition the ability to use surface enhanced NSOM Raman will also be discussed.

The SEM structural and chemical analyser (SEM-SCA) combines both SEM and Raman techniques into one system, so that users can take full advantage of the high spatial resolution afforded by the SEM, and the chemical information revealed by Raman. This unique combination enables SEM manufacturers to supply a SEM-Raman system that enables the spectrometer to "see" the same area as the SEM - a micrometer-scale laser spot is projected onto the surface of a sample visible in the SEM image. The SEM-SCA hardware can be fitted to most SEMs without compromising the SEM performance in any way. The nature of Raman spectroscopy means that its performance is unaffected

https://doi.org/10.1017/S1431927603445479 Published online by Cambridge University Press

by the SEM environment - high vacuum (HV), low vacuum (LV), environmental (ESEM), and high or low (cryogenic) temperatures. The advantages of this method are from the SEM view that SEM overcomes the limitations of optical microscopy with respect to: (a) depth of field - the SEM retains good depth of field even at high magnifications. (b) contrast - SEM contrast mechanisms can easily distinguish optically identical or similar materials. (c) spatial resolution - SEM spatial resolution is typically 3-4 orders of magnitude better than optical microscopy.

Raman spectroscopy meets unfulfilled SEM/EDS analytical requirements: (a) EDS yields elemental information only whilst Raman provides structural, chemical, and physical information. (b) EDS is poor for analysing light elements whilst Raman is sensitive to light element chemistry.

The instrument can also perform photoluminescence (PL) and cathodoluminescence (CL) studies as the SEM-SCA collection optics are fully compatible with both PL and CL spectroscopies. The former uses a laser as the excitation source, the latter the electron beam. Each technique can reveal both electronic and physical information about the sample, with CL being sensitive to very subtle changes in composition and residual strain.

Examples will be presented from various application areas using materials science, semiconductors, pharmaceuticals, and forensic science.

FIGURE 1. AFM height map (a) and cross section (b) across a nanoindentation in silicon.

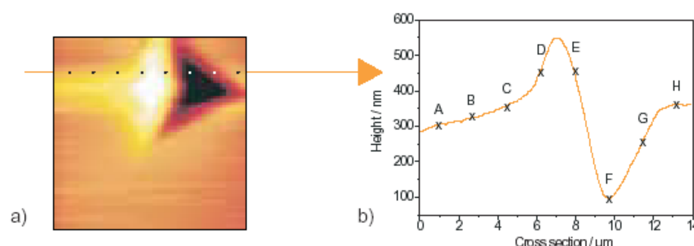
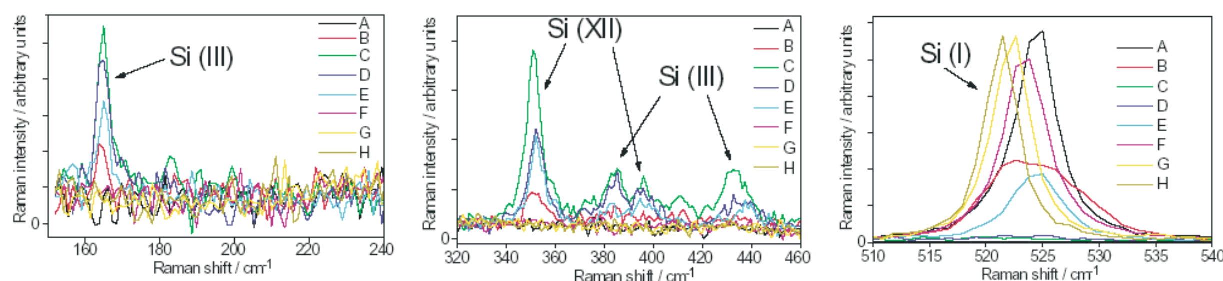


FIGURE 2. Far field Raman spectra taken from the 8 positions indicated in Figure 1.



Acknowledgements

The experiments on the nanoindentation of silicon were performed in collaboration with Professor Y Gogotsi (Department of Materials Engineering, Drexel University), G Cox (Renishaw Inc), and R Noons, R Forrest, S Ward, and Dr R Devonshire (Department of Chemistry, University of Sheffield). The Nanonics/Renishaw system uses additional software from Cavendish Instruments plc that is integrated with Renishaw's WiRE control software.

https://doi.org/10.1017/S1431927603445479 Published online by Cambridge University Press