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Ion beam excited optical spectroscopy of inorganic compounds

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Abstract:
"Focussed Ion Beam Optical Spectroscopy" (FIBOS) has been used to identify elements at surfaces of inorganic materials. In general characteristic atomic emission lines were observed but measurements on diamond, thorium halides and thorium oxide also showed a broad band in the blue region between 300 and 500nm with maxima at 450, 450, 425 and 360nm for ThO_2, ThF_4, ß-$ThBr_4$ and ß-$ThCl_4$ respectively. These curves corresponded closely with those observed in luminescence spectra observed using optical methods and were found to broaden progressively during exposure to the ion beam. Remarkably strong signals were recorded from europium doped thorium oxide. Additional applications involve the study of inclusions in minerals and the analysis of electronic materials.

Introduction

Recently we have been investigating a new technique for materials analysis involving atomic emission of light produced when a finely focussed ion beam strikes a sample. The use of this phenomenon in end point detection using unfocussed inert gas beams was first described by White and his co-workers almost twenty years ago (1) and more recently investigations using focussed ion beams have been reported (2). These have been used in our laboratory for secondary ion spectroscopy (SIMS) for a decade and our first ion microscope was constructed in 1986 (3). Here we report results from a number of investigations using instruments constructed or modified for Focussed Ion Beam Optical Spectroscopy (FIBOS).

Experimental

Two UHV systems have been used in the FIBOS experiment. The first was a specially constructed system incorporating a Fisons Instruments duoplasmatron source and an Oxford Instruments monoCL system incorporating a 1200 line/mm grating with an operating slit width of 0.8mm giving a full-width half-maximum resolution of 2.5nm approximately. The optical detector was a Hamamatsu R942-02 photomultiplier in a Peltier cooled housing, with single photon counting electronics giving a background count rate of a few photons per second. The second system was a Fisons Time-of-Flight SIMS instrument incorporating a liquid metal gallium ion gun. A 20keV, 1nA Ga^+ ion beam rastered over a 400μm square was used to bombard the target at 30° incident angle. An optical collection system incorporating a 45° mirror and a reflecting objective lens was used to transfer the light into the same 0.5m monochromator and detector as used in the duoplasmatron system above. The generalised experimental configuration is given in Fig. 1. Metallic or crystalline samples were mounted on 1cm diameter aluminium stubs and inserted into the chamber at working pressure of ~10^{-9}mbar at room temperature before being positioned to give the strongest total photon signal before each spectrum was acquired. Powdered samples were prepared by pressing into pellets using a 10T force over a 13mm diameter pellet. These were then attached to sample stubs using spring-loaded grids.

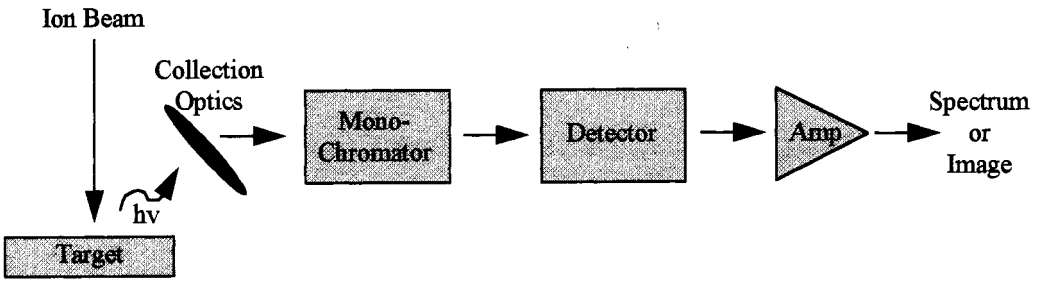

Fig 1. General experimental arrangement for Focussed Ion Beam Optical Spectroscopy (FIBOS)

Applications of FIBOS

A wide range of target materials have been investigated including metals, inorganic compounds and minerals. The optical emission observed from these materials during ion bombardment is attributed to radiation from excited states. For metals, the photon spectrum is composed of sharp emission lines from sputtered particles above the target surface. A typical spectrum from iron is shown in the magnetite spectrum in Fig. 4. The intensity of these spectral lines

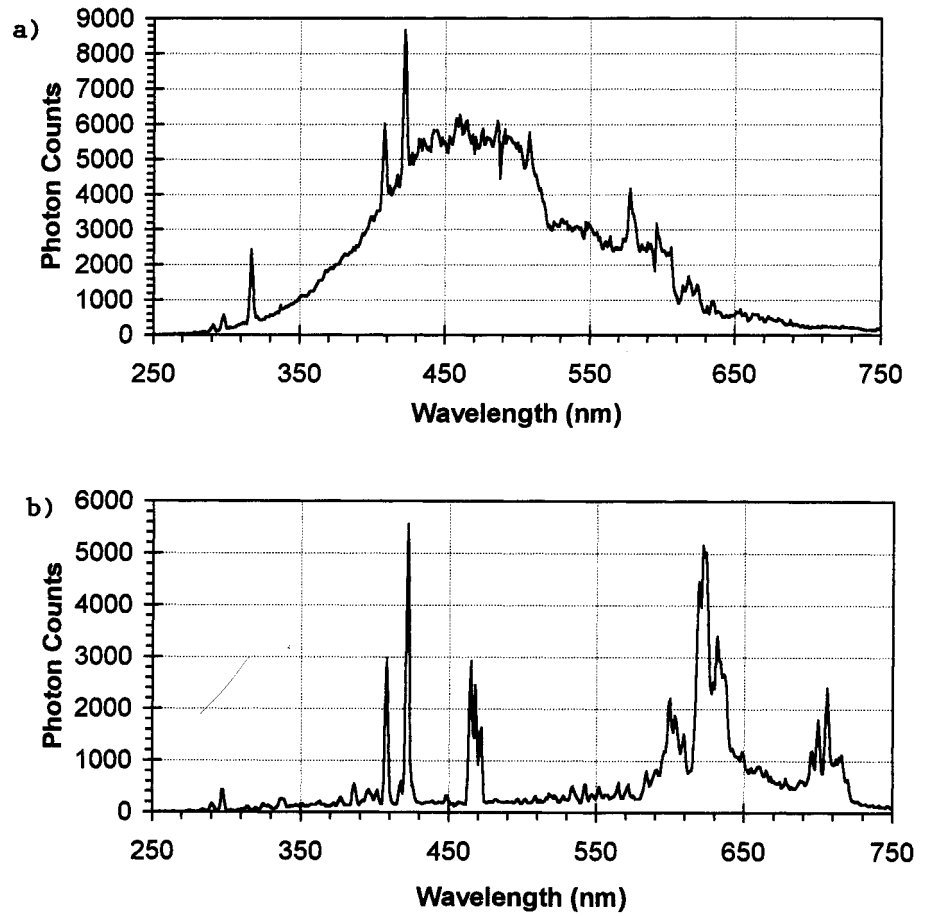

Fig. 2 FIBOS spectrum of a) thorium oxide and b) europium oxide.

from Ni/Fe alloys under argon ion bombardment has been fitted to a Boltzmann distribution to investigate the possibility of a thermodynamic equilibrium state for quantitative analysis (1). In an analysis of a similar series of Fe/Cr alloys, Martin and MacDonald noted the dependence of the intensities of the Fe and Cr emission also under bombardment on the oxygen background pressure (4). Similar studies in our laboratory indicated a variation in the photon intensity/concentration relationship for different spectral lines (5).

Optical emission has also been observed from compounds of lanthanide and actinide elements. Pressed powder samples of ThF_4, $ThCl_4$ and $ThBr_4$ and ThO_2 irradiated with a focussed gallium ion beam showed broad-band luminescence emission superimposed upon atomic emission lines from gallium and thorium atoms and the appropriate ligand (6). The intensity of the luminescence was very dependent on beam damage and the rapidity with which the spectrum was recorded. The intensity diminished with duration of exposure to the ion beam. Nevertheless the relative intensity from the series of compounds studied followed the nephelauxetic series of ligands,

$$ThCl_4 > ThBr_4 > ThO_2 > ThF_4$$

derived from the ligand polarisability. A similar order was observed in the satellite-to-main peak separation in X-ray photoelectron spectra from a similar series of uranium compounds (7,8). Figure 2 shows the spectra recorded from ThO_2 together with that from Eu_2O_3. In the latter luminescence was not observed.

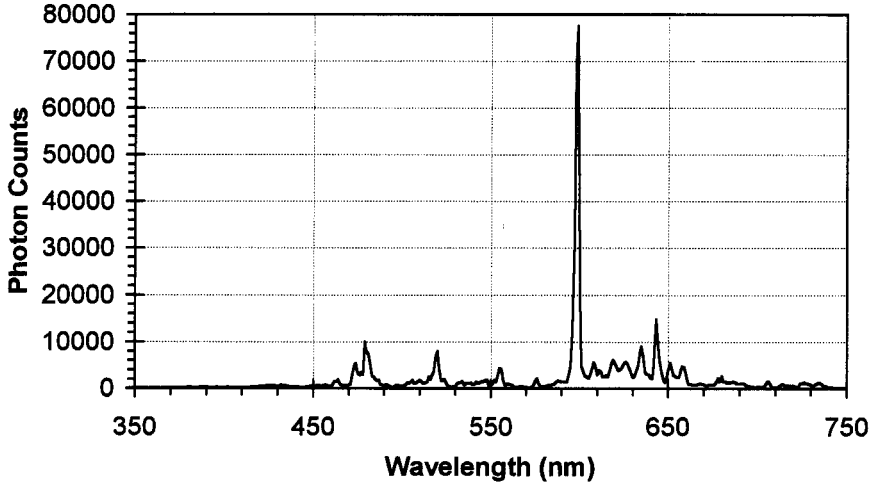

Fig. 3. FIBOS sample of ThO_2 doped with 0.02% Eu^{3+}.

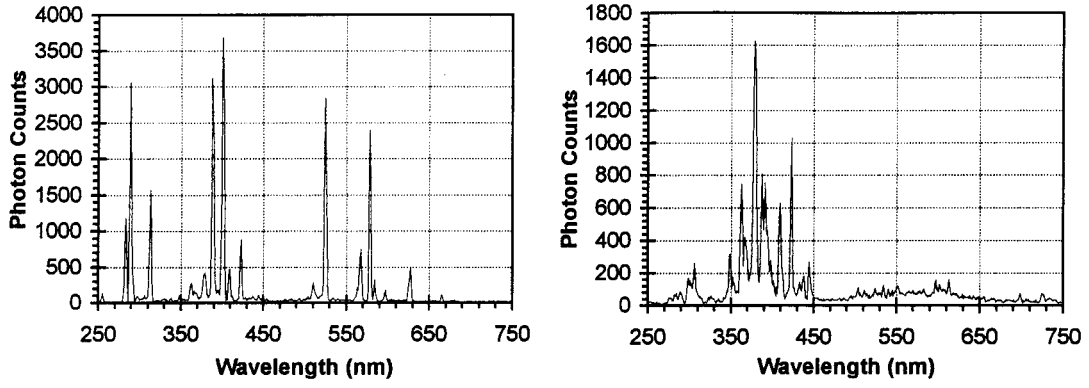

Fig. 4. Left: FIBOS spectrum of Schist deposit from Anglesey, North Wales, UK.
Right: FIBOS spectrum of an area of magnetite in the same sample.

We have also examined the effect of dopants in ThO_2 with spectacular results. A crystalline sample of ThO_2 doped with 0.02% Eu^{3+} gave the emission spectrum shown in Fig. 3. It is dominated by the single strong line at ~590nm due to the magnetic dipole transition $5D_0 \rightarrow {}^7F_1$ (8). The intensity of this line is staggeringly high even with the beam current of 1nA A signal of 80,000 counts was obtained indicating a detection limit of Eu^{3+} below the part-per-million level in such materials.

The analysis of inclusions in metals and minerals requires direct solid sampling of the material without elaborate sample preparation. FIBOS meets this requirement. We have examined crystallite inclusions of magnetite in schist deposits from Anglesey in North Wales, UK. The results are shown in Fig. 4. By selecting the strongest line in the iron spectrum it is possible to obtain a map of the distribution of magnetite in this mineral.

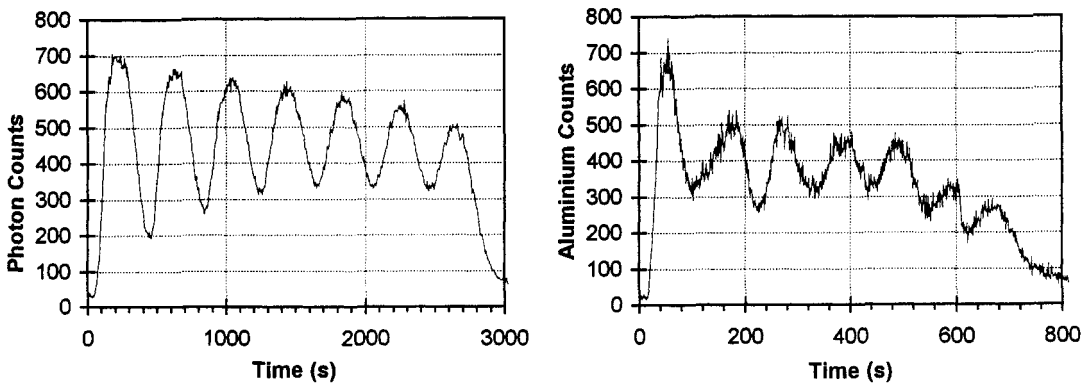

Fig. 5. Depth profiles of a seven layer 500A GaAs/AlAs superlattice
Left: 395nm (Al) FIBOS profile; Right: Mass 27 (Al) SIMS profils (Sample courtesy of D. Westwood, University of Cardiff).

Finally the application of the FIBOS technique to reveal buried interfaces, end-point detection is demonstrated for a seven layer 500A GaAs/AlAs superlattice. Fixing on the 395nm line from Al and monitoring its change in intensity as the focussed ion beam sputtered through the GaAs and AlAs layers gave the profile shown in Fig. 5. For comparison the corresponding secondary ion profile for the Al^+ species at 27 amu is shown. Here the secondary ion mass spectrum (SIMS) was obtained using the same focussed ion beam. The profile is less well-resolved and tails to a greater extent as the depth of the profile increases.

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