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"High-Resolution Heavy-Ion-Induced X-ray Satellite Emission Study of Implanted Sulfur as
a Probe of Co-Implanted Oxygen in an Oxide Substrate"

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HIGH-RESOLUTION HEAVY-ION-INDUCED X-RAY SATELLITE EMISSION STUDY OF IMPLANTED SULFUR AS A PROBE OF CO-IMPLANTED OXYGEN IN AN OXIDE SUBSTRATE

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Using high-resolution measurements, the relative fluorescence yields of the sulfur $K_{\alpha}L^n$ X-ray satellite lines produced by 24 MeV Si^{9+} ion irradiation of a series of quartz glass targets co-implanted to equal doses and depths of sulfur and oxygen have been obtained and compared to the yields from a series of quartz glass targets implanted to the same depth with sulfur only. The data exhibit lower yields in the higher-order KL^n satellite lines for the co-implanted oxygen targets but similar dose dependent curves. These results are consistent with oxygen increasing the valence electron density of the local sulfur environment. It also suggests that, with an appropriate choice of a probe ion, HIXSE may be capable of detecting impurity ions in matrices that normally mask the impurity, e. g., oxygen in oxide substrates.

1. Introduction

One of the most difficult chemical measurement problems is the quantitative characterization of a small change in the concentration profile of a major species in a complex sample. Any analytical technique chosen requires high precision because the problem typically reduces to a comparison of two large numbers. If the small change in concentration is further limited to a narrow spatial band below the surface of the sample, for example, an ion-implanted layer, new or alternative approaches to the question must be developed. One such alternative approach to the problem is to find a chemical difference induced by the localized change in concentration. If a chemical variation can be discerned, the technique must also be able to probe the narrow band without destroying that chemical

information. This latter requirement eliminates techniques which rely on destructive depth profiling to probe the subsurface variations in the analyte profile. Heavy-ion-induced X-ray satellite emission (HIXSE) spectroscopy, because it nondestructively probes the near surface region (5-1000 nm) and yields chemical information, is ideally suited for this task [1]. HIXSE combines the advantages of particle-induced X-ray emission (PIXE), i.e., being able to detect an element in almost any matrix with the chemical information obtainable from electron spectroscopy methods [1-5].

Previous studies have shown that high-resolution HIXSE measurements can be used to yield chemical information about ion-implanted moieties over a range of doses [1,6,7]. Recently, we have extended those results to show that the X-ray satellite spectrum of the implanted ion also yields information about the chemistry of the substrate [8]. In this report, we will show that high-resolution HIXSE measurements of sulfur implanted in quartz glass targets can be used to probe the presence of oxygen co-implanted to equal depths and doses.

2. Experimental methods

A series of quartz glass targets were implanted with 70 keV sulfur and 35 keV oxygen ions at $3 \mu\text{A}/\text{cm}^2$ to equal depths and equal doses ranging from 0.5 to $9 \times 10^{16}/\text{cm}^2$ at the ORNL Surface Modification and Characterization (SMAC) facility. Verification of the sulfur dose, depth (90 nm) and implant uniformity was accomplished at the SMAC facility by analyzing

each sample with 3 MeV He ion scattering. The oxygen dose was analyzed for a select suite of silicon samples which were co-implanted simultaneously with the quartz targets using secondary ion mass spectroscopy (SIMS) (C. A. Evans and Assoc., Redwood, Ca.). A TRIM calculation, using equal doses of 70 keV sulfur and 35 keV oxygen in SiO_2 , demonstrates, as shown in fig. 1, that the profiles overlap spatially. A 24 MeV Si^{q+} ion beam, extracted from the Oak Ridge EN tandem Van de Graaff accelerator, was used to excite the implanted sulfur X-ray spectra. Prior to the excitation with a fast, heavy-ion beam, each target was coated with a 50 nm Al film to minimize charging effects. Typical beam currents ranged from 5-7 particle nA. Total doses range from 10 - 60 μC . The high-resolution S $\text{K}_\alpha\text{L}^\alpha$ X-ray measurements were obtained with the Oak Ridge High-Performance X-ray Spectrometer (HI-PER-X 200). This device, which is described in detail elsewhere [9], employs a 10 cm^2 cylindrically curved quartz ($10\bar{1}1$) crystal with a 2d spacing of 0.6687 nm and a radius of curvature of 25.4 cm to diffract the X-rays. The detector is a sealed position-sensitive proportional counter (Ordela Inc., Oak Ridge, TN) with a 10 cm^2 active area. The energy resolution for these experiments was approximately 2 eV at 2.3 keV. Four sets of targets were prepared, with each set having at least three samples. Each target was analyzed at least twice on separate runs. Spectra were corrected for the detector Be window absorption, summed and normalized to the integrated K_α yield. Corrections for absorption of the sulfur K X-rays by the target were ignored because of the shallow depth of the implanted sulfur. Projectile energy losses were negligible for the same reason.

3. Results and discussion

The high-resolution sulfur K_{α} X-ray spectra produced by the collision of 24 MeV Si^{9+} ions with quartz targets implanted to equal depths and doses of $8 \times 10^{16}/\text{cm}^2$ sulfur and sulfur and oxygen are displayed in fig. 2. Each spectrum is composed of series of intense satellite lines in addition to the normal sulfur K_{α} diagram line. These lines correspond to the K_{α} X-rays emitted from configurations having n L-shell vacancies. A comparison of the spectra in fig. 2 clearly reveals a shift in the relative intensity distribution of the KL^n satellite lines from higher to lower-order lines when oxygen is co-implanted with sulfur. The dashed lines highlight the increase in the intensity of the KL^2 satellite line relative to the KL^4 line when atomic oxygen is co-implanted.

These spectral variations are the consequence of differences in the refilling rates of the L-shell vacancies prior to the emission of the K_{α} X-rays. The refilling of the L-shell probably proceeds through a two-step mechanism of an inter-atomic transfer from the valence-shell of a neighbor to the unoccupied Rydberg levels of the target atom followed by rapid intra-atomic Auger cascading [10]. A change in the chemical environment or, equivalently, the density or distribution of valence electrons available for refilling the L-shell vacancies, will alter the vacancy transfer rates and thus change the observed satellite yield. For example, if the local chemical environment of implanted sulfur changes in such a way as to increase the density of valence electrons available for refilling, the probability of a K X-ray being emitted from a higher-order configuration line, e.g., KL^5 is decreased because the probability that the $n = 5$ vacancy has been filled has increased.

In order to correlate the observed spectral variations to changes in the local chemical environment, a parameter which describes the intensity profile, called the average L-shell vacancy fraction, P_L is required. It is defined as the apparent number of L-shell vacancies as determined by the weighted sum of the relative satellite configuration-line intensities divided by eight; the total number of electrons in the closed L-shell. A plot of the variation of P_L with sulfur dose for one suite of samples is shown in the top curve (S) of fig. 3. The positive slope indicates that as sulfur is added to the quartz matrix the higher-order satellites increase in intensity relative to the lower-order lines, i.e. the addition of more sulfur effectively reduces the refilling rate because sulfur has a lower valence electron density than the quartz matrix [1]. In contrast, the addition of atomic oxygen to a sulfur implant distribution reduces the higher-order sulfur KL^n satellite lines relative to the lower-order lines and reduces the P_L value as shown in fig 2 and the lower curve of fig. 3 (S/O), respectively. Thus atomic oxygen increases the local valence electron density relative to sulfur. Similar results for three additional suites of quartz samples implanted with sulfur and sulfur and oxygen at equal depths were also found (data not shown here).

4. Summary

We have shown that high-resolution HIXSE measurements of sulfur implanted in quartz glass can be used to probe the presence of oxygen co-implanted to equal depths and doses. These results are significant because they demonstrate the sensitivity of HIXSE to small changes in the subsurface local chemical environment and because they show that HIXSE

can detect small, localized changes in the subsurface concentration profile of a major species in a complex matrix. One potential application is the detection of small changes in the oxygen concentration of thin film superconductors. These results also suggest that, with an appropriate choice of an implanted probe ion, high-resolution HIXSE measurements may be capable of detecting not only the addition of atomic oxygen in an oxide matrix, but any impurity ion in any matrix, including matrices that normally mask the impurity.

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FIGURE CAPTIONS:

Fig 1. The profiles of equal doses of 70 keV sulfur and 35 keV oxygen implanted in quartz as determined by a TRIM calculation.

Fig 2. The corrected, normalized and smoothed high-resolution sulfur $K_{\alpha}L^{\alpha}$ satellite spectra produced by the collision of 24 MeV Si^{q+} ions with quartz glass implanted with a dose of $8 \times 10^{16}/cm^2$ (a) sulfur at 70 keV and (b) sulfur at 70 keV and oxygen at 35 keV. The dashed lines highlight the change in the relative intensity distribution of the KL^{α} satellite lines.

Fig 3. The variation of sulfur P_L with dose of sulfur (top curve) and with equal doses of sulfur and oxygen (bottom curve).

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