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AND ION-INDUCED X-RAY EMISSION

P. G. Musket

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APPLICATIONS OF SIMULTANEOUS ION BACKSCATTERING
AND ION-INDUCED X-RAY EMISSION

R. G. Musket
Lawrence Livermore National Laboratory
Livermore, California 94550

Abstract

Simultaneous ion backscattering and ion-induced x-ray emission ($E_x > 300$ eV) analyses have been performed using helium ions as probes of the first few hundred nanometers of various materials. These studies serve as a demonstration of the complementary nature of the two types of information obtained. Uncertainties associated with each of the individual techniques were reduced by performing both analyses. The principal advantages of simultaneous analyses over sequential analyses have been delineated.

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EAB

1. INTRODUCTION

Although many applications of either Rutherford backscattering (RBS) or ion-induced X-ray emission (IIXE) have been reported in the literature, very few studies employed both techniques in the same study. In 1973, Bauer and Musket [1] contrasted proton-induced X-ray (PIXE) and backscattering results from oxide films on aluminum with those obtained using helium ions as probes; however, even though the same ion was used to produce both the PIXE and proton RBS (and HIXE and helium-ion RBS) data, they performed the experiments sequentially because they lacked the necessary electronics for simultaneous measurements. Svendsen et al [2] analyzed ash samples for trace elements by combining results from PIXE and helium-ion RBS measurements. Recently, I. V. Mitchell et al [3] reported simultaneous PIXE and proton RBS measurements of evaporated layers; they used the PIXE data to eliminate ambiguities in the identification of minor impurity components and to obtain semi-quantitative information on the amounts present.

Since the synergistic advantages of these two analysis techniques have been recognized for some time, it is surprising that they haven't been employed in more studies. The main advantage of combining these techniques is the complementary nature of the information obtained, which reduces the uncertainties associated with each of the individual techniques. RBS measurements provide depth distribution information for mainly the heavier elements in the surface layers of materials with depth resolutions of approximately 30 nm but with somewhat ambiguous elemental specificity for the heavier elements and the multi-isotope elements. In contrast, IIXE data yields only limited depth distribution information but essentially unambiguous

elemental identification. In addition, the relative elemental sensitivities, are complementary with IIXE having its greatest sensitivity for low atomic number Z elements (eg, oxygen) and RBS being most sensitive for high Z elements. Both techniques can be considered quantitative with RBS relying on the fundamental physics of the process and IIXE generally requiring appropriate standards. Although these techniques are essentially non-destructive, the total dose of ions (ie, ions/cm²) used to perform measurements must be as low as possible to minimize radiation damage, pyrolysis of surface hydrocarbons, and blistering (for ions insoluble in the sample material).

Since both X-rays and backscattered particles emanate from the sample surface during irradiation, simultaneous X-ray and particle spectroscopic measurements should be employed as a routine procedure. For general analytical applications, there are no requirements for the coincidental detection of an x-ray and a backscattered particle. Such coincidental measurements yield extremely low count rates and should be reserved for special analysis problems and fundamental physics studies. The principal advantages of simultaneous analyses with respect to sequential analyses are that (a) results from both techniques correspond to identical conditions over the same region of the sample, (b) ion-induced changes in the surface structure and composition are minimized by the reduced ion fluence (ie, dose), and (c) twice as many analyses can be performed in a given time. The main disadvantage is that the optimum ion and energy combination for one technique may not be the optimum for the other. For this reason, conditions should be optimized for the primary technique with the data from the secondary technique being auxilliary.

This paper describes studies employing simultaneous RBS and IIXE measurements as demonstrations of the advantages of such analyses. Helium ions have been used as probes of the surface layers of anodized tantalum, stainless steel implanted with aluminum, and stainless steel implanted with erbium. Backscattered particles were detected with a standard surface barrier detector, and x-ray analysis ($E_x > 300\text{eV}$) was performed with an ultra-thin-windowed (UTW) Si(Li) detector.

2. EXPERIMENTAL CONSIDERATIONS

One of the first considerations for obtaining, simultaneously, useful statistics from IIXE and RBS is the selection of an appropriate combination of detector solid angles and efficiencies. For the RBS analysis, a standard silicon surface barrier detector was employed at a scattering angle of 168° in the vertical plane of the horizontal ion beam. The 100 percent efficient detector was collimated to eliminate edge effects and subtended a solid angle of approximately 2 mstr. A pulser resolution of 7.5 keV was typical for the measurements reported. X-ray spectroscopy was performed with an ultra-thin-windowed (UTW) Si(Li) detector at 90° from the incident beam. Properties of such detectors have been previously detailed [4]. In the present arrangement, the 30 mm^2 Si(Li) detector subtended a solid angle of approximately 0.3 mstr with a resolution for Al(K) x-rays of $\sim 150\text{ eV}$. The actual efficiency of the detector/UTW combination has not been determined but the efficiency for O(K) x-rays is expected to be between 1 and 10 percent. Since the UTW consisted of 200 nm of aluminum deposited on 150 nm of parylene,

scattered particles could penetrate (and damage) the window giving rise to large current pulses and radiation damage in the Si(Li) detector. To preclude ionic bombardment of the window and detector, a permanent-magnet deflection unit, consisting of magnets, yokes, and collimators, was installed on the x-ray axis. The overall size of this compact unit was 3.44 mm dia x 4.85 mm; it was sized to fit inside a standard 3.81 mm O.D. tube. Although no deflection system precludes bombardment by neutral particles, the neutral fraction is expected to be small for the energies employed. This expectation was supported by brief x-ray measurements taken with and without the deflection unit installed. Calculations predicted that He^+ with energies up to 2 MeV would be precluded from bombarding the UTW; measurements to date confirm this expectation.

A schematic top-view of the experimental arrangement is given in Fig. 1. Magnetically analyzed ions from a 3 MV van de Graaff accelerator were collimated initially by a four-plate assembly and finally to a 2 mm diameter by the electron strippers held at +300V. The samples were mounted on a vertically movable ladder that was biased at +90V to suppress secondary electron emission. Although this is not the optimum scheme for correct current integration with solid samples [5], it has proven adequate for the present studies. In the measurements reported here the sample normals were rotated 30° from the horizontal beam axis about a vertical axis as shown. The turbo-pumped chamber was isolated from the accelerator beam line vacuum by a differentially ion-pumped section on the accelerator side of the electron strippers. Typically, the measurements were made at pressures in the 10^{-7} Torr range, which has proven adequate for minimizing the rate of hydrocarbon pyrolysis.

Separate preamplifiers, amplifiers, and analog-to-digital converters (ADC) were employed for each of the two techniques. The ADC outputs were simultaneously processed by a computerized multichannel analyzer system with 1024 channels for each technique. Conversion gains used gave ~ 3 keV/channel for RBS and ~ 10 eV/channel for IIXE. Sample currents were integrated electronically to permit calculation of the fluence used in each measurement.

3. DISCUSSION OF APPLICATIONS

The surface layers of anodized tantalum, stainless steel implanted with erbium, and stainless steel implanted with aluminum have been studied using simultaneous helium-ion RBS and HIXE analyses. Results from these analyses demonstrate some of the advantages of such measurements.

3.1 Anodized Tantalum

High purity tantalum that had been anodized to form a uniform planar oxide layer ($18.7 \pm 0.3 \mu\text{g oxygen/cm}^2$ [6]) has been analyzed as a standard to verify the validity of the RBS and HIXE results and to demonstrate the value of IIXE for elimination of ambiguities of RBS results from high-Z materials with surface layers containing low-Z elements.

Fig. 2 gives the results from simultaneous RBS and HIXE analyses of the anodized tantalum. Since only two edges and one plateau are apparent in the RBS spectrum, it could represent either a uniform surface compound on a high-Z material (ie, tantalum in this case) or a uniform alloy of the high-Z element with a lower-Z element (ie, rhodium in this case). The absence of any definitive indication of the presence of oxygen is simply a consequence of the

small relative cross-section for scattering from oxygen (cross-section approximately 1% that for tantalum) and the statistics of the data ($\pm 1\%$). Examination of the x-ray results immediately leads to the conclusion that the surface region of the sample contains only tantalum and oxygen but does not provide any depth distribution information. Although only the x-ray spectrum for the 0-4 keV region is shown, data was taken for 0-10 keV, with all observed peaks characteristic of either oxygen (K x-rays) or tantalum (L and M x-rays). Thus, the HIXE results provided unequivocal elemental identification, and the RBS results were, in fact, indicative of a surface layer with uniform composition. With the ambiguity removed, standard RBS techniques [7] were applied to the results for the oxidized tantalum surface. Assuming the uniform layer to be Ta_2O_5 , these computations yielded an oxide thickness of 1190 Å, which is equivalent to $18.8 \mu\text{g oxygen/cm}^2$ and agrees very well with the known oxygen surface density ($18.7 \pm 0.3 \mu\text{g oxygen/cm}^2$).

3.2 304L Stainless Steel Implanted with Erbium

Implantation of a high-Z element (eg, Er) into stainless steel is normally thought to be the ideal case for RBS analysis; this is correct assuming existence of independent evidence for the identity of the high-Z element. Fig. 3 shows the RBS and HIXE spectra for 304L stainless steel implanted with $5 \times 10^{16} \text{ Er/cm}^2$ and oxidized in 5×10^{-6} Torr of air at 700°C for 8 hr. The RBS spectrum can be interpreted as a high-Z element (eg, erbium) implanted into stainless steel or stainless steel with a thin surface layer of a different high-Z element (ie, neodymium in this case). Comparison of the HIXE spectrum of the present sample with a plain 304L stainless steel sample under the same conditions showed that the only additional x-ray peak was the one at 1.42 keV which matches that of the $Er(M_{\alpha, \beta})$ x-ray lines.

Adjacent Z elements holmium and thulium were eliminated from consideration because their $M_{\alpha, \beta}$ peaks occur at 1.36 and 1.48 keV, respectively, which are well outside the measured x-ray energy calibration error of ± 1 percent. Since no $Nd(L_{\alpha})$ x-ray peak (5.2 keV) was observed on a log display, neodymium was not present at any significant surface concentration. Thus, a combination of RBS and HIXE results lead to the conclusion that the erbium distribution was centered below the surface, as expected for an implantation. The amount of erbium present, as calculated directly from the RBS data, was within ten percent of the implanted dose of 5×10^{16} Er/cm². This could also be calculated from the HIXE data provided a suitable standard was available. In fact, this sample could be used to standardize the $Er(M_{\alpha, \beta})$ x-ray yield and to predict detection (peak/bkgd=1) of $< 5 \times 10^{15}$ Er/cm² in stainless steel surfaces using HIXE.

3.3 304L Stainless Steel Implanted with Aluminum

As shown in Fig. 4, RBS results for aluminum implanted into stainless steel are difficult to analyze with any reasonable precision. In fact, both unequivocal identification and quantitative evaluation of the aluminum is virtually impossible for the level of aluminum implanted (ie, 2×10^{17} Al/cm²). Since the dip at energies below the transition metal edges is a function of the stopping cross-section, which depends of the relative concentrations of the implanted and host species near the implanted depth [8], determination of the level of implanted aluminum can be made only by an iterative procedure with low precision. Moreover, the weak aluminum scattering edge results in ambiguities with regard to the identification of the implanted species.

The identification uncertainty is removed by reference to the HIXE results, which clearly indicate that the only significant change from the non-implanted sample was the addition of aluminum at levels at least ten times greater than the detection limit using HIXE. Such x-ray measurements can permit evaluation of the uniformity of low dose implantations with much greater precision than could be obtained from the RBS results. Appropriate thin film and/or implanted standards would permit absolute quantitative determination of the implanted concentration of aluminum. Once again, the combination of the two techniques gives an essentially complete analysis of the sample with the X-ray data providing the implanted element's identity and quantity and the RBS results defining the depth distribution of the implantation.

CONCLUDING REMARKS

The applications discussed above clearly demonstrated the enhanced ion-beam analysis capability achievable with simultaneous RBS and IIXE analyses. Such combinations of results often allow incontrovertible conclusions to be drawn from only one ion bombardment without the need for auxiliary experiments or information. Certainly such capabilities are needed for ion beam analysis to yield, consistently, quantitative results and to provide analysis of poorly defined samples.

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Fig. 1: Schematic of experimental arrangement (top view).

Fig. 2A

Fig. 2B

Fig. 2: Spectra from simultaneous analyses of anodized tantalum. (A) Helium-ion backscattering spectrum and (B) helium-ion induced X-ray spectrum. (fluence = 1.5×10^{15} He⁺/cm²)

64ER64

Fig. 3A

X4ER03

Fig. 3B

Fig. 3: Spectra from simultaneous analyses of 304L stainless steel implanted with erbium. (A) Helium-ion backscattering spectrum and (B) helium-ion induced X-ray spectrum. (fluence = 6.7×10^{15} He⁺/cm²)

64AL41

Fig. 4A

X4AL34

Fig. 4B

Fig. 4: Spectra from simultaneous analyses of 304L stainless steel implanted with aluminum. (A) Helium-ion backscattering spectrum and (B) helium-ion induced X-ray spectrum. (fluence = 1.2×10^{16} He⁺/cm²)