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**Analysis of Coatings and Thin Films
Using Energetic Ions***

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ABSTRACT

Energetic ion analysis techniques provide non-destructive information on the depth distribution of atomic composition in the near-surface (1-10 μm) region of a solid sample. The techniques are quantitative and are not complicated by the presence of chemical or matrix effects. Generalized nuclear reaction analysis is described and its application to the measurement of the stoichiometry of Ta_2O_5 films and BeO coatings on Cu-Be is briefly discussed.

Metallurgical coatings and thin films on the surfaces of materials can be used to tailor the response of that material to outside environmental influences. For example, hard oxide layers can be formed on the surface of certain steel alloys to inhibit corrosive attack. The physical or chemical properties of interest are generally very dependent upon the processing parameters used in the formation of the coating. These coatings or films generally have thicknesses

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in the range of .01-100 μm and thus may not be conducive to study using bulk analytical techniques. Methods such as Auger electron spectroscopy and glancing incidence x-ray diffraction have been commonly used to study coatings and new methods are constantly being developed. Energetic nuclear scattering techniques, including elastic backscattering and nuclear reaction analysis are methods suited to the study of surface layers in the thickness range commonly found in metallurgical coatings. The techniques provide nondestructive quantitative measurements of the depth distributions of atomic composition in the first 1-10 μm of a solid. Because of the equipment requirements, these methods have not as yet found general usage in most laboratories.

Energetic ion analysis methods rely on detection of the products of scattering events between energetic (usually 500 keV - 2 MeV) light ions (H or He isotopes) and target nuclei to measure the number and species of target nuclei present in a sample. These methods can be understood by reference to the upper part of Fig. 1. An energetic particle of Mass M_1 and Energy E_1 is incident on a nucleus (mass M_2) of an atom in the target. After scattering, the energy of one of the reaction products (usually the lighter) is measured. If the sum of the energies of the two particles after reaction is equal to the energy of the incident particle before reaction, the event is called elastic scattering. Rutherford scattering is one type of elastic scattering which

is a very useful method for analyzing the near-surface layers of solids, and the literature on this subject is extensive so the method will not be discussed in detail in this paper (1).

If a nuclear reaction occurs, the sum of the energies of the reaction products can be greater or less than the incident particle energy E_i . This energy difference is accounted for in the reaction Q -value which can be either positive or negative. Generally speaking, only reactions with positive Q -values are useful for materials analysis, because the products of these reactions usually have energies greater than the energies of the elastically scattered particles and can be detected in an energy region where there is little or no background.

If the equations governing the conservations of momentum and mass-energy are solved in the general case, expressions can be derived for the energy of the emitted reaction products in terms of the incident energy, the reaction Q -value, the laboratory scattering angle and the masses of the four particles (2,3). In the absence of energy-loss mechanisms, the detected product has a well-defined energy for each reaction, at a fixed incident energy and laboratory scattering angle. When an ion is incident on a solid material the probability (cross-section) of a nuclear collision (elastic or inelastic) is very small. Most of the ions penetrate into the target and lose energy by excitation of various electronic processes. This energy loss is directly related

to the depth of penetration. Small numbers of incident particles will continue to react with the target nuclei, but at greater depths and lower incident energies. When this energy loss mechanism is considered, expressions can be derived for determining the depth distribution of atomic composition from the energy distribution of the nuclear reaction products (3).

Inelastic nuclear reaction analysis is most useful for low atomic number nuclei, because the higher the atomic number, the higher the Coulomb barrier that the incident particle must penetrate and the higher the incident energy must be. Typically, with incident ions of 2 MeV, nuclei up to atomic number 14 can be detected. These are elements which are often very difficult to quantitatively measure using other analysis methods. Energetic ion techniques are absolute quantitative methods because the reaction cross sections do not depend on the chemical state of the atoms within the target. The cross sections can be very complicated functions of energy and scattering angle, however, and must be known in order to perform quantitative work (4).

The experimental apparatus used in nuclear reaction analysis is shown schematically in the lower portion of Figure 1. Ions are produced and accelerated to an energy of 0.5 to 2.0 MeV by an ion accelerator. A beam of ions of a well-defined mass and energy is directed onto a target by a magnet. Energetic reaction products and elastically scattered ions from the target are detected in a silicon

surface barrier detector. The pulses from the detector are amplified and sorted according to their amplitudes. The result is a plot called a pulse height spectrum of the number of particles detected at a given energy versus the energy of the detected particles. For nuclear reaction analysis it is often important to provide a foil in front of the detector to absorb elastically scattered particles which are much more numerous than reaction products. Rejection techniques are often used to eliminate pile-up pulses which result from high count rates (5).

Examples of two spectra are shown in Figure 2, which illustrate the detection of carbon and oxygen on anodically oxidized tantalum. The top spectrum was taken with a 19 μm mylar foil in front of the detector. Very little carbon is present, but large amounts of oxygen are detected. The two peaks correspond to protons emitted by decay of the ^{18}F nucleus to the ground state and the first excited state of the ^{17}O nucleus. The shift in energy between the two spectra is due to the energy lost by the protons passing through the mylar film. The bottom spectrum also shows the scattering due to elastically scattered deuterons, particles from the $^{16}\text{O}(\text{d},\text{c})^{14}\text{N}$ reaction and a background due to pulse pile-up. These data indicate that there are $1.9 \times 10^{18} \text{O/cm}^2$ in the oxide layer. Rutherford backscattering was used to measure the areal density of Ta atoms and the combined results give a stoichiometry of Ta_2O_5 . The areal density of carbon is about $4 \times 10^{15} \text{C/cm}^2$. The spectra illustrate the

ability to measure oxygen and carbon in surface layers of solids. These data are used to calibrate our sensitivity to oxygen since the amount of oxygen in this sample can be determined in other ways (backscattering, weight gain, color).

A study of the formation of BeO on the surface of a Cu-Be alloy also illustrates the power of the nuclear reaction method for measuring low-Z species. The stoichiometry of the film was measured using nuclear reaction methods and found to be 1:1 with an uncertainty of about 10%. The data are illustrated in Figure 3 which shows two spectra of BeO film on bulk Cu-Be taken with (top) and without (bottom) a detector foil. The bottom spectrum illustrates the plethora of reaction products which can be seen in complicated situations. In the upper spectrum, where signals due to pile-up, backscattered deuterons and $^9\text{Be}(d,\alpha)$ reactions are absent, the Be signals from the surface (in the BeO layer) and in the bulk Cu-Be under the BeO layer can be visually distinguished.

These examples illustrate the power of the nuclear reaction technique for measuring and profiling low-Z atoms in the surface layers of solids. For further information the reader is referred to Ref. 3 and 4. The author would like to acknowledge J. M. Harris for collaboration in obtaining the data illustrated in this paper.

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FIGURE CAPTIONS

- Figure 1. Schematic diagram of nuclear reaction events (top) and experimental apparatus (bottom).
- Figure 2. Spectra of anodized Ta O on Ta using 1400 keV $^2\text{D}^+$. The upper spectrum was taken with a detector covered with a 19 μm mylar foil and the lower spectrum was taken with an uncovered detector.
- Figure 3. 1400 keV $^2\text{D}^+$ spectra of a Cu-Be permeation barrier taken with a detector covered with a 19 μm mylar foil (top) and with an uncovered detector (bottom).

REACTION KINEMATICS

EXPERIMENTAL APPARATUS

Fig 1