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THE USE OF $^{12}\text{C}(d,p)^{13}\text{C}$ AND $^{16}\text{O}(d,p)^{17}\text{O}$ REACTIONS
TO PROFILE CARBON AND OXYGEN IN SOLIDS*

J. A. Borders and J. H. Harris
Sandia Laboratories, Albuquerque, NM 87115

ABSTRACT

The use of nuclear reactions for depth profiling carbon and oxygen in solids is discussed. A general expression for the yield from a nuclear reaction is derived and used to extract depth profiles from the energy spectra by two methods. The first method compares data from a target of unknown composition with a target containing a known concentration of either carbon or oxygen. By dividing the yields from the samples for equal collision energies, a concentration profile within the analyzed sample can be obtained. The second method uses published reaction cross section data to obtain the profile. The (d,p) profiling is demonstrated for carbon in ScD_2 . A comparison between the two methods is made by extracting carbon profiles in the near surface region of ScD_2 samples. Effects due to inaccurate stopping cross section data are described. The technique is discussed for the $^{16}\text{O}(d,p)$ reactions used to profile oxygen along with the effect of interferences from the $^2\text{H}(d,p)^3\text{H}$ reaction and other reactions.

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1. INTRODUCTION

Rutherford backscattering analysis is an accepted technique for obtaining quantitative elemental analysis in the near surface region of a material. However, analysis for light elements such as carbon in a matrix of heavier elements is somewhat limited using this technique. Concentrations of less than a few percent are usually undetectable unless the material containing the light elements is thin and on a light substrate or is a self-supporting film.

Nuclear reaction analysis is an alternative to Rutherford backscattering when light elements are of interest. The principal advantage of using a nuclear reaction is that the detected reaction product usually has energy greater than that of projectiles elastically backscattered from the heavy matrix. The signal from the light element is thus in a region of the energy spectrum where the background is normally low. Detection sensitivity for a given element depends on the value of the reaction cross section, the background, and the geometry of the detection system. The background is caused by nuclear reaction products from species not being analyzed, the detector's response to light generated during the irradiation of insulators and pulse pile-up. Both the energy of the detected particles and the relative intensity of reaction yields are functions of the detection geometry. The angle between the projectile and the detector may be adjusted to take advantage of a large cross section or to locate the detected particle in an interference free region of the energy spectrum. The solid angle of the detector

can be adjusted to enhance the sensitivity or to obtain optimum depth resolution.

Nuclear reactions have been used in several laboratories for detection and depth profiling of light elements. Amiel and coworkers¹ have pioneered the use of nuclear reactions for detection of low-Z elements, particularly oxygen. Queglia² and Shulte³ have used the $^{12}\text{C}(d,p)^{13}\text{C}$ reaction for detecting carbon in metals. In the present work, the use of (d,p) reactions is discussed for profiling C and O in the near surface regions of solids. A general expression for the yield from nuclear reactions is derived. Depth profiles are calculated from the experimental data using both published reaction cross section data and a reference target method suggested by Shulte.³

II. EXPERIMENTAL

The apparatus necessary to perform nuclear reaction analysis is essentially the same as that used for Rutherford backscattering analysis. 1.4-1.6 MeV $^2\text{D}^+$ beams from a 2 MeV Van de Graaff accelerator at currents of 5-50 nA were used.

Protons from the $^{12}\text{C}(d,p)$ and $^{16}\text{O}(d,p)$ reactions were energy analyzed using a surface barrier detector similar to those used for backscattering analysis. The surface barrier detector responds to both the reaction product and the backscattered particles, so for a heavy matrix the backscattered particle intensity can be 10^3 times the intensity of reaction products so pulse pileup can be appreciable. The piled-up pulses occur in the same region of the spectrum as the reaction products and

therefore limit sensitivity. One method of reducing pileup is to use very low incident fluxes. However, this method may require excessive time to acquire spectra unless coupled with electronic pileup rejection systems which can reduce pileup by factors up to 40.⁴

A more common method of reducing the effect of the back-scattered particles is to shield the detector with a thin foil. The foil thickness is chosen such that the backscattered particles are absorbed and the more energetic reaction products penetrate. The energy straggling in the foil reduces the energy resolution of the detection system and the corresponding depth resolution. Two spectra taken of a Ta₂O₅ target are shown in Fig. 1. The lower spectrum was taken with an electronic pileup rejection system but with no foil. The backscattering peak and the reaction products, as well as pileup, can be seen. The detector used has an energy resolution of approximately 20 keV corresponding to a depth resolution near the surface for the $^{16}\text{O}(d,p)^{17}\text{O}^*$ reaction of $\sim 1500 \text{ \AA}$ for 1400 keV $^2\text{D}^+$ at normal incidence. The upper spectrum was taken with a 19 μm mylar foil near the detector. The foil shifts the peaks to lower energy and contributes approximately 41 keV of straggling, degrading the near-surface depth resolution to about 3400 \AA . However, the pileup as well as the backscattering peak from Ta are absent, and their absence allows substantially increased sensitivity. The $^{16}\text{O}(d,\alpha)^{14}\text{N}$ reaction seen in the lower spectrum is also absent in the upper spectrum because the α particles produced by $^{16}\text{O}(d,\alpha)^{14}\text{N}$ cannot penetrate 19 μm of mylar.

The nuclear reaction cross sections are not known as accurately as are the Rutherford cross sections. Therefore referencing the signal from the analyzed specie to that of the substrate for absolute calibration is not as useful as in back-scattering. However, targets containing the specie of interest in a known concentration are quite useful references. Use of reference targets requires that the relative number of particles incident on the unknown sample and on the reference target be known. This implies that the charge integration system must be reproducible from target to target. If reaction cross sections are used to determine concentration profiles, the integration system must also be calibrated.

In addition to accurate charge integration, the fraction of the signal lost due to dead time of the electronics must be known. The fraction of the signal lost increases as the count rate increases. Techniques for dead-time determination are discussed elsewhere.⁵

III. THEORY AND DATA ANALYSIS

Expressions⁶ have been presented for evaluating depth profile data from nuclear reaction experiments which fail to properly treat the transformation of the yield from a depth interval δx at a depth x to the observed energy interval δE of the emergent particles. For a general nuclear reaction, the energy of the emitted light reaction product is given by

$$E_1 = K_1 E_0 \left\{ \cos \theta + \left[\frac{K_3}{E_0} + K_2 - \sin^2 \theta \right]^{1/2} \right\}^2 \quad (1)$$

where E_0 is the incident energy, θ is the laboratory scattering angle, and K_1 , K_2 and K_3 are constants defined as

$$K_1 = \frac{M_1 M_3}{(M_1 + M_2)(M_3 + M_4)}, \quad K_2 = \frac{M_2 M_4}{M_1 M_3}, \quad \text{and}$$

$$K_3 = \frac{M_2 M_4}{M_1 M_3} Q \left[1 + \frac{M_1}{M_2} \right]$$

M_1 and M_2 are the incident particle and target masses, respectively; M_3 and M_4 are the masses of the light and heavy products, respectively; and Q , the Q -value, is the excess of the sum of the energies of the reaction products over the incident energy, E_0 . The geometry is shown in Fig. 2 where the beam is incident at an angle θ_1 with respect to the sample normal and the product is detected at an angle θ_2 . The detected energy from a reaction with a target atom at a depth x is

$$E_{out} = K_1 \left[E_0 - \frac{x S_{in}(\bar{E}_{in})}{\cos \theta_1} \right] \quad (3)$$

$$\left\{ \cos \theta + \left[\frac{K_3}{E_0 - \frac{x S_{in}(\bar{E}_{in})}{\cos \theta_1}} + K_2 - \sin^2 \theta \right]^{1/2} \right\}^2 - \frac{x S_{out}(\bar{E}_{out})}{\cos \theta_2}$$

In Eq. 3, S_{in} and S_{out} refer to $\frac{dE}{dx}$ of the projectile and the light reaction product, respectively. \bar{E}_{in} and \bar{E}_{out} are average energies over the incoming and outgoing paths, respectively.

Brice⁷ has shown that the scattering yield from a general reaction at a depth x can be written

$$Y(E_0, E_3) dE_3 = \frac{I N(x) \frac{d\sigma}{d\Omega}(E_1, \theta) d\Omega dE_2}{\left[\frac{dE_2}{dE_1} \cdot S_{in}(E_1, x) + C S_{out}(E_2, x) \right]} \cdot \frac{\partial E_2}{\partial E_3}, \quad (4)$$

where E_1 is the energy before the reaction, E_2 the energy immediately after the reaction, E_3 the energy after leaving the target and dE_2/dE_1 is evaluated for E_1 at the depth of interest. I is the number of incident particles and $C = \cos \theta_1 / \cos \theta_2$. For a target in which the stoichiometry does not vary greatly with depth, we can approximate

$$\frac{\partial E_2}{\partial E_3} \approx \frac{S_{out}(E_2)}{S_{out}(E_3)}. \quad (5)$$

Eq. (4) is the familiar equation for backscattering when $\frac{dE_2}{dE_1}$ is replaced by the kinematic scattering factor K . For nuclear reactions the proper expression is found by differentiating Eq. (1). In order to simplify the notation, we let

$$\tilde{S}_i(E) = \frac{dE_2}{dE_1}(E_1) \epsilon_{i_{in}}(E_1) + C \epsilon_{i_{out}}(E_2) \quad (6)$$

where i indicates the component of the target. The presence of both $\epsilon_{i_{in}}$ and $\epsilon_{i_{out}}$ arises from the fact that for most nuclear reactions, the incident particle and light reaction product are different species, requiring different stopping cross sections or an adjustment in the energy at which the stopping cross section is evaluated as for (d,p) reactions. $\tilde{S}(E)$ can be recognized as the well-known "backscattering factors" if $\frac{dE_2}{dE_1}$ is replaced by K . For more complex targets Bragg's rule is assumed and the energy loss parameter is expressed as a sum of atomic energy loss parameters. This is equivalent to a binary target with B-type atoms

responsible for the nuclear reaction yield and Λ -type atoms contributing to the stopping power but not to the reaction yield. Then

$$S(E, x) = N_A(x) \left\{ c_B(E) + R_{BA}(x) c_B(E) \right\} \quad (7)$$

where

$$R_{BA}(x) = \frac{N_B(x)}{N_A(x)}$$

Combining Eqs. (4) and (7) yields

$$Y(E_0, E_3) dE_3 = \frac{1}{S_A(E)} \frac{R_{BA}(x) \frac{d\sigma}{d\Omega}(E_1, E)}{S_A(E) + R_{BA}(x) S_B(E)} \cdot \left(\frac{\partial E_2}{\partial E_3} \right) \quad (8)$$

This expression can be used to directly calculate $R_{BA}(x)$ from the measured spectrum if the stopping powers are known.

Shulte³ has suggested that the yield from an unknown sample can be compared with that of a reference sample where the stoichiometry as a function of depth is known. This reference could be a pure sample, such as carbon, or a compound with a well-defined stoichiometry, such as TiO_2 or WO_3 , or other metal oxides. In these cases, the calculation is performed such that the yields in the two samples are compared for equal collision energies (E_1). The reaction cross section then cancels out, and the calculation is only dependent on the accuracy of the stopping cross sections. If the ratio of profiled atoms to all other matrix atoms is R_X in the unknown sample and R_R in the reference sample, Eq. (8) is solved for both cases and the results divided to yield

$$\frac{Y_X(E_0, E_3)}{Y_R(E_0, E_3)} = \frac{RX \left(\frac{\partial E_2}{\partial E_3} \right)}{RR \left(\frac{\partial E_2}{\partial E_3} \right)} \left[\frac{\tilde{S}_C + RR \cdot \tilde{S}_B}{\tilde{S}_A + RX \cdot \tilde{S}_B} \right] \quad (9)$$

The primed energies refer to energies in the reference target. If $Y = (Y_X/Y_R) \cdot \left(\frac{\partial E_2'}{\partial E_3'} / \frac{\partial E_2}{\partial E_3} \right)$, we can write

$$RX(x) = \frac{Y(x) \cdot RR \cdot \tilde{S}_A(E)}{\tilde{S}_C(E) + RR \cdot \tilde{S}_B(E)[1 - Y(x)]} \quad (10)$$

Programs have been written for a PD11-based multichannel analyzer which solve Eq. (8) or Eq. (10) and calculate $RX(x)$. Stopping powers are calculated using the Brice three-parameter fit⁸ to the data of Janni.⁹ Data for analysis using the reaction cross sections were obtained from the published literature^{10,11} and the program used linear extrapolations between the measured data points. The term $\partial E_2/\partial E_3$ was approximated by Eq. (5) for the reference targets, but was numerically calculated for the unknown targets.

IV. RESULTS

The computer programs described above were used with spectra taken from bulk TaC, TiC and graphite with 1600 keV D^+ to extract the concentration profile of C in the TaC. Shulte's method was used with TiC or graphite as the reference. The purpose of this exercise was to check the program and the sensitivity of the computational method to small variations in external parameters such as the stopping power. The results are shown in Fig. 3. Ideally, the profile should be intersecting the vertical axis

at 50 at.f. The apparent bump in the concentration at 1.5×10^{19} atoms/cm² occurs near a narrow resonance in the $^{12}\text{C}(d,p)$ cross section at ≈ 1430 keV. This technique relies on taking the yield ratio of the unknown and reference spectra for equal deuteron energies. Small uncertainties in the calculated deuteron reaction energies (due to uncertainties in the stopping cross sections) can thus lead to relatively large errors if the reaction cross section is rapidly changing. The calculated deviations from actual stoichiometry probably result from the uncertainty in the relative shapes of the stopping power curves for protons and deuterons in carbon and titanium. An increase by 10% in the carbon stopping power for the 1400 keV D^+ ion significantly reduces the size of this bump. Using a reference spectrum taken on TiC rather than graphite also reduces the bump as shown in Fig. 3. These results suggest that proton stopping cross sections for Ti and Ta may be more accurate than for C. Use of the stopping powers tabulated by Northcliffe and Schilling¹² gave larger stoichiometry deviations than those obtained using Janni's data.

Samples of 3 μm films ScO_2 and bulk Kovar containing small amounts of carbon and oxygen were analyzed with 1400 keV D^+ . The $^{12}\text{C}(d,p)^{13}\text{C}$ spectra for TiC and ScO_2 reference samples are shown in Figs. 4a and 4b, respectively. The general shape of the $^{12}\text{C}(d,p)^{13}\text{C}$ reaction cross section below 1400 keV can be seen in the spectrum from the TiC sample seen in Fig. 4a. The carbon profile from the ScO_2 spectrum was calculated both by Shulte's method and by direct use of the available cross section data. The results are shown in Fig. 5. The method using cross section

values on the average gives 10 to 20% lower concentrations than does the method using reference materials; however, the shape of the profile obtained from the two methods is quite similar. The lower values using the cross section method could be the result of systematic errors, probably in the values of cross sections. The accuracy of the profile is somewhat difficult to assess; however, based on the data collected by profiling bulk TiC, the profile is probably within $\pm 20\%$ of the true concentration profile.

The oxygen profiles in Kovar and ScD_2 were similar to the carbon profiles. The $^{16}O(d,p_0)^{17}O$ was used for profiling because of the large $^2H(d,p)^3H$ background in the region of the $^{16}O(d,p_1)^{17}O^*$ reaction. The $^{16}O(d,p_0)^{17}O$ was not background-free because of the interference from the $^{16}O(d,\alpha)^{14}K$ reaction. Both the reference method using WO_3 as the reference material and the cross section method were used to obtain profiles which are not shown here due to space limitations. As with the carbon profiles, the two methods gave similar shapes, which is consistent with the above results. Considering the interferences, the oxygen profiles obtained are probably within $\pm 25\%$ of the true profile.

The depth resolution using (d,p) nuclear reactions is not high. Where possible, (d, α) reactions and sample tilting are methods to obtain better depth resolution. But the (d,p) technique is very useful for profiling over a few μm of depth. Profiles of up to 5 μm deep have been analyzed for both ^{12}C and ^{16}O .

V. CONCLUSIONS

Carbon and oxygen have been profiled in Kovar and ScD_2 using the $^{12}\text{C}(d,p)^{13}\text{C}$, $^{16}\text{O}(d,p_0)^{17}\text{O}$ and $^{16}\text{O}(d,p)^{17}\text{O}^*$ nuclear reactions. The formalism given can be used to extract concentration profiles using either published values for the reaction cross sections or reference spectra taken from targets containing known concentrations of the profiled element. The accuracy of the method using cross sections is limited primarily by the uncertainties in the values of the cross sections and the stopping power data; whereas, the method using reference targets is usually limited in accuracy only by uncertainty in the values of the stopping power.

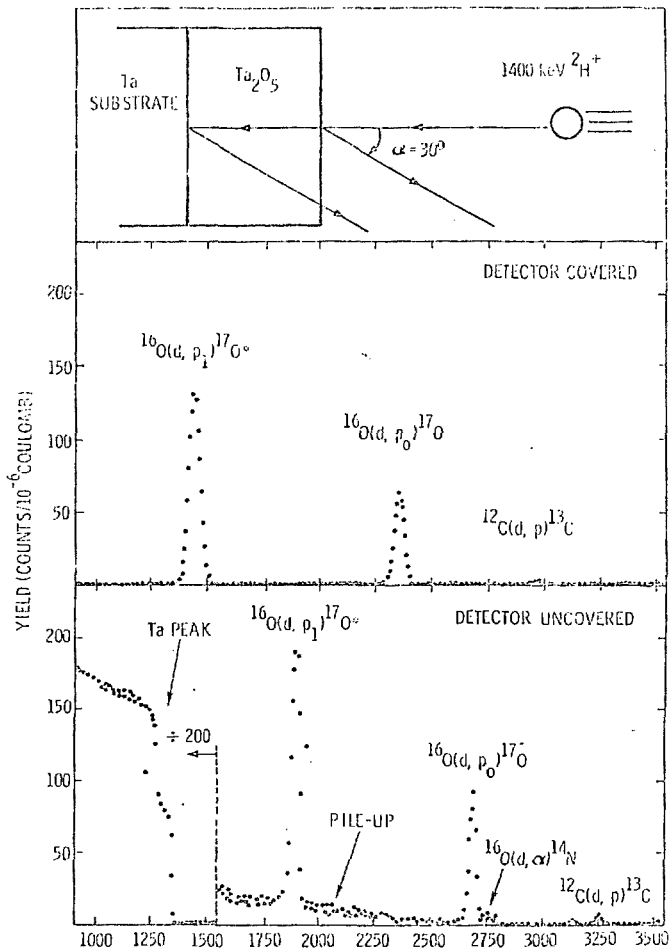
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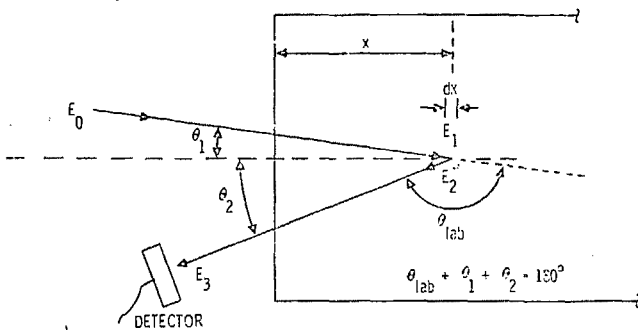
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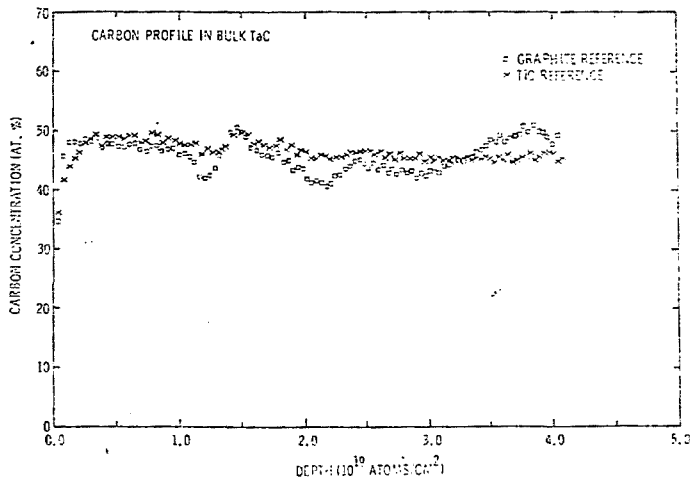
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FIGURE CAPTIONS

- (Upper). Spectra taken from 3300 Å of anodized Ta₂O₅ on Ta with a 1600 keV D⁺ beam using a detector covered with a 19 μm mylar foil.
 - (Lower). Spectra taken under the same conditions and with the sample as in Figure 1a, except detector was not covered. Both spectra shown were taken using an electronic pile-up rejection system.
- Diagram depicting a nuclear reaction occurring at depth x within a target.
- Depth profile of carbon in bulk TaC using reference samples of graphite and TiC. Approximately 10^{19} atoms/cm² corresponds to 1.1 μm in bulk TaC.
- (Upper). Spectrum of the $^{12}\text{C}(d,p)^{13}\text{C}$ reaction from a bulk target of TiC with 10 μC of 1400 keV D⁺.
 - (Lower). Spectrum of the $^{12}\text{C}(d,p)^{13}\text{C}$ reaction from ScD₂ target with 10 μC of 1400 keV D⁺. Both spectra shown were taken with an uncovered detector.
- Depth profile of carbon in the ScD₂ sample described in Figure 4b using the spectrum in Figure 4a as a reference. Depth profile using published cross section data also shown.







$^{12}\text{C}(\alpha, p)^{13}\text{C}$ USING 1400 keV D^+

