Depth Profiling of Tritium by Neutron Time-of-Flight

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DEPTH PROFILING OF TRITIUM BY NEUTRON TIME-OF-FLIGHT

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ABSTRACT

We have developed a method to measure the depth profile of tritium implanted or absorbed in materials. The sample to be analyzed is bombarded with a pulsed proton beam and the energy of neutrons produced by the $^3$H$(p,n)$ reaction is measured by the time-of-flight technique. From the neutron energy the depth in the target of the $^3$H atoms may be inferred. A sensitivity of 0.1 at. % $^3$H or greater is possible. The technique is non-destructive and may be used with thick or radioactive host materials. Samples up to 20 μm in thickness may be profiled with resolution limited by straggling of the proton beam for depths greater than 1 μm. Deuterium depth profiling has been demonstrated using the $^2$H$(d,n)$ reaction. The technique has been used to observe the behavior of an implantation spike of $^3$H produced by a 400 keV $^3$H beam stopping at a depth of 3 μm in 11 μm thick layers of Ti and TiH. The presence of H in the Ti lattice is observed to inhibit the diffusion of $^3$H through the lattice. Effects of the total hydrogen concentration (H + $^3$H) being forced above stoichiometry at the implantation site are suggested by the shapes of the implantation spikes.

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INTRODUCTION

The processes of tritium diffusion and hydrogen isotope induced embrittlement pose severe radiological and materials problems for fusion reactor designers. A technique which we have developed to study the depth profiles of hydrogen isotopes in targets for 14 MeV neutron generators has applicability as a diagnostic tool for the study of these processes. While the initial measurements have been made on tritium and deuterium implanted in titanium and copper, the technique may be used with any solid sample.

To assay the tritium content of a sample, it is bombarded with a pulsed proton beam of fixed energy. The energy spectrum of neutrons produced by the T(p,n) reaction on tritium atoms in the sample is measured by time-of-flight (TOF) spectroscopy. From the reaction cross section and kinematics the number of tritium atoms present in the sample may be calculated as a function of depth below the surface of the sample. To assay for deuterium content, a pulsed deuteron beam is used and the neutron spectrum from the D(d,n) reaction is measured.

In the initial measurements, the behavior of tritium implanted in empty and hydrogen filled layers of titanium (H:Ti ~ 1.7-1.8:1) and in copper was observed. Relaxation of the implantation spikes in titanium shows the effects of the presence of hydrogen in the previously filled samples. The profiles of tritium retained in copper are consistent with the low solubility of hydrogen in copper, and suggest the presence of a surface barrier retarding tritium release or trapping of tritium on the surface.

Sensitivity of 0.1 at. % was obtained in these measurements. This can be readily improved to 1 ppm. For the proton energy used, resolution below 1 μm is limited by straggling and is better than that which can be obtained with light ion backscatter methods. Because the technique is non-destructive and allows profiles to be made rapidly, it allows the observation of the time history of tritium diffusion in materials.
SAMPLE PREPARATION

The titanium and titanium hydride host materials were prepared by the Isotopes Division of Oak Ridge National Laboratory. Titanium layers of nominal thickness 4.7 ng/cm² (11 μm) were vapor deposited on 1 mm thick copper backings. Half of the samples thus prepared were then loaded to near stoichiometry (2:1 hydrogen to titanium ratio) by heating in a hydrogen atmosphere. A loading ratio of 1.7 - 1.8:1 for these samples is inferred from the tritium concentration measured in similarly prepared samples containing tritium.

Tritium and deuterium implantaions were performed with a 400 keV beam from the Lawrence Livermore Laboratory ICT accelerator. To control sample heating, the beam current was limited to 10 μA and the samples were cooled with an air jet during implantation. Total quantities of tritium or deuterium implanted were calculated from the total charge deposited on each sample. Implantation doses were 4 x 10¹⁶, 4 x 10¹⁷, and 8 x 10¹⁷ ions on a 30 mm² beam spot. Since range straggling for these ions is ~ 0.2 μm, the highest doses should have produced tritium or deuterium concentrations exceeding the stoichiometric concentration (particularly for the TiH samples) at the end of the ion range. We were particularly interested in observing differences in the implantation profiles between the hydrogen loaded samples and in the pure titanium samples.

NEUTRON SPECTROMETRY

Neutron spectra from proton and deuteron bombardment of the samples were measured one month and seven months after implantation. Samples were stored at room temperature between measurements. The University of Oregon 5 MeV Van de Graaff accelerator and time-of-flight spectrometer were used for the measurements. The proton (or deuteron) beam from that accelerator is pulsed by sweeping the beam past an aperture in the high voltage terminal, and is bunched to produce a burst width of ~ 1.2 nsec FWHM at the target. The neutron detector for these measurements was a NE218 liquid scintillator*
11.4 cm dia x 2.5 cm thick mounted on an RCA 4522 photomultiplier tube*. The detector was 10.3 m from the target at 0° with respect to the direction of the incident beam. Detector bias was set to accept pulses larger than those from 410 keV recoil protons in the scintillator.

Time intervals were measured with a time-to-amplitude converter followed by an analog to digital converter. Time-of-flight spectra were stored with an on-line PDP-7 computer. For each target, data were collected until a preset amount of charge - typically 400 μC - had been delivered to the target. As time averaged beam current was ~ 2 μA during the spectrum measurements, measurement time was typically 3.5 minutes for each sample. Proton beam energy for the profiling measurements was 2.3 MeV. Typical spectra have been shown in previous publications.1,2

DEPTH RESOLUTION

Processes which cause uncertainty in or broaden the energy spread of the incident ion beam or of the outgoing neutrons limit the depth resolution obtained. There are three contributions to the overall resolution: the energy spread of the ion beam from the accelerator, the increase in energy spread of this beam with depth due to straggling, and the energy resolution of the neutron spectrometer.

These energy uncertainties were evaluated and were converted to depth resolution using the values of dE/dx for protons in titanium tabulated by Janni.3 The individual contributions to depth resolution, and the overall depth resolution obtained by quadratic combination are shown in Fig. 1. One sees from Fig. 1 that for the present proton energy (2.3 MeV) the resolution is dominated by straggling at depths greater than 1 μm. At such depths, resolution of this technique exceeds that which can be obtained by light ion backscattering as the straggling of the backscattered ion contributes additional energy spread, hence depth uncertainty. Figure 2 shows depth resolution for deuterium profiling in titanium using the D(d,n) reaction with the same spectrometer.
ANALYSIS - DATA TRANSFORMATION

The neutron energy spectrum from a thick target may be expressed in absolute form as:

\[
S(E_n) = \frac{n_n(E_n \sigma(\theta))}{n_p} = \frac{\sigma(\theta)}{\varepsilon} = \frac{dE_p}{dE_n} \frac{\text{neutrons}}{\text{proton MeV sr}}
\]  

(1)

where \( \sigma(\theta) \) is the differential reaction cross section for protons of energy \( E_p \), and \( \varepsilon \) is the compound stopping cross section per reactive atom in the target. All quantities except \( \varepsilon \) are characteristic of the nuclear reaction while \( \varepsilon \) is characteristic of the atomic composition of the target.

The apparent stopping cross section per tritium atom is the compound stopping cross section given by:

\[
\varepsilon = \frac{n_T \varepsilon_T + n_H \varepsilon_H}{n_T}
\]  

(2)

where \( n_T \) and \( n_H \) are number densities of tritium and host atoms respectively, and \( \varepsilon_T \) and \( \varepsilon_H \) are the corresponding atomic stopping cross sections. The stopping cross sections are known to several percent for most elements. If the host substance consists of several different types of atoms one should replace \( n_H \varepsilon_H \) by a summation over all constituents of the host.

In order to obtain the tritium content, the ratio of the neutron spectrum from the sample to that calculated for a pure tritium target is determined. From Eqs. (1) and (2) then one obtains:

\[
\frac{S_u(E_n)}{S_T(E_n)} = \frac{n_T \varepsilon_T}{n_T \varepsilon_T + n_H \varepsilon_H}
\]  

(3)

The atomic percentage of tritium is then:

\[
100 \times \frac{n_T(x)}{n_T(x) + n_H(x)} = 100 \left[ 1 + \left( \frac{S_u(E_n)}{S_T(E_n)} - 1 \right) \frac{\varepsilon_T}{\varepsilon_H} \right]^{-1}
\]  

(4)
This expression does not depend explicitly on nuclear reaction parameters since they cancel in the ratio given by Eq. (3). In order to evaluate Eq. (4), $S_n(E_n)$ must be calculated from Eq. (1), and $S_u(E_u)$ must be obtained from the experimental spectrum by correcting it for detector efficiency and other experimental parameters.

When Eq. (4) is evaluated at a neutron energy $E_n$, the concentration is determined at a specific depth $x$ in the sample. This depth is:

$$x = -\int \frac{1}{n_L \varepsilon_L + n_H \varepsilon_H} \frac{dE_p}{dE_n} \ dE_n$$

(5)

We do not evaluate Eqs. (4) and (5) directly but approximate them numerically. A depth increment is arbitrarily chosen and the corresponding neutron flight time interval is calculated assuming pure host material. The average tritium concentration is determined for this interval. This first order tritium content is then added to the host material to calculate revised flight time intervals. The procedure is iterated until self-consistency is achieved. We start at the front surface of the target and step through it by the chosen depth increment. The number density of host atoms is held constant for the calculations presented here. As titanium expands when hydrided, this latter assumption introduces a 7-10% uncertainty in the depth scale. A more sophisticated approach such as keeping the number density of atoms constant or maintaining constant total atomic volume would reduce this uncertainty. In this experiment, the maximum possible error from this source is less than other errors and has thus been neglected.

RESULTS

The profile of tritium absorbed in a 0.35 μm thick titanium layer on copper is shown in Fig. 3. This thin target was used for calibration purposes to check resolution. When the calculated resolution is combined with the target thickness, the apparent thickness should be 0.45 μm. This result is in good agreement with the measured width of 0.48 μm determined from Fig. 3.
Depth profiles resulting from implantation doses of $4 \times 10^{16}$ tritons in titanium and titanium hydride are shown in Fig. 4. This dose corresponds to a loading of 9 at. % (in empty titanium) if all the tritium stays at the implantation site. Depth profiles from implantation doses of $4 \times 10^{17}$ tritons (50 at. %) and $8 \times 10^{17}$ tritons (67 at. %) in both titanium and titanium hydride are shown in Figs. 5 and 6. Several interesting trends are apparent depending upon dose and whether or not the titanium is filled with hydrogen. First, in no case is the implantation peak centered about the nominal 3.7 μm range of the tritons. Rather, the peak of the distribution is about 2.7 μm below the front surface. This displacement may result from radiation enhanced diffusion and trapping or simple beam heating effects during tritium implantation. At the lower doses (9 at. % and 50 at. %) the tritium has diffused well beyond the implantation peak in the titanium samples, producing secondary peaks at a depth of about 9 μm. For the same doses in the titanium hydride there has been much less diffusion to deeper in the target. Virtually all diffusion of tritium appears to have occurred during or shortly after implantation as no significant changes in the profiles occurred during the six month interval between the two sets of measurements.

At the largest dose (67 at. % in empty titanium) the results are somewhat different. Surprisingly, there is less diffusion beyond the ion range in the empty titanium sample than at lower dose. However, the implantation spike in the empty sample is higher and narrower than that in the hydrogen filled sample. Also, in the hydrogen filled sample, there is now significant displacement of tritium to greater depths in the sample. Both these effects suggest that diffusion is enhanced as the lattice nears the stoichiometric hydrogen content. This is consistent with the FWHM of the implantation peak being greater at 67 at. % dose than at 50 at. % dose in both empty (1.4 μm vs. 1 μm) and hydrogen filled (2.4 μm vs. 1.4 μm) samples. Results obtained by profiling deuterium implanted in similar substrates were the same.
Finally, the absolute tritium content determined by this technique is qualitatively correct, i.e., the amount of tritium calculated by integrating these depth profiles and multiplying by the area of the beam spot is within 10% of that calculated by integrating the beam current. As no special effort was made to ensure uniformity of the tritium beam across the spot during implantation, this agreement is quite satisfactory.

For comparison, the depth profile resulting from implantation of $4 \times 10^{17}$ ions in copper is shown in Fig. 7. This profile should be compared with those of Fig. 5. Only $\sim 20\%$ of the tritium remains in the sample. A clear surface peak is obvious, suggesting a barrier retarding tritium release or some surface trapping.

CONCLUSIONS

The results obtained to date demonstrate that the time-of-flight profiling method is a powerful technique for the study of tritium and deuterium diffusion in solid hosts. The somewhat confusing results of the present observation of tritium diffusion in empty and hydrogen filled titanium suggest that an experiment with better controls is required, however. We plan to load tritium in samples held at liquid nitrogen temperature and then observe the behavior of the implantation spikes as the sample temperature is increased. Such an experiment would decouple beam-induced and temperature-induced transport processes.

The sensitivity and resolution of this profiling technique can be further improved. Examination of Fig. 4 shows that a sensitivity of 0.1 at. % was obtained in the present experiments with only a proton charge of 0.4 mC - a 3.5 minute run at 2 $\mu$A average beam current. If the time resolution of the spectrometer were reduced to below 1 ns and the neutron flight path shortened until spectrometer resolution was $\sim 70\%$ of the beam straggling limit, then a sensitivity of $10^{-4}$ at. % or 1 ppm could be obtained with the same resolution but would require an hour long run. The effects of the amount of hydrogen injected into the sample by the proton beam might not be negligible, however.
Improvements in resolution depend upon selecting operating parameters to optimize resolution at the depth region of interest and reducing spectrometer resolving time. In particular, to assay near the front surface of a material a much lower proton energy is preferred. This reduces the neutron energy, increases the time-of-flight, and reduces the limitation imposed by spectrometer resolution.

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REFERENCES


*Reference to a company or product name, here or elsewhere in this report, does not imply approval or recommendation of the product by the University of California or the U. S. Energy Research and Development Administration to the exclusion of others that may be suitable.
ATOMIC CONCENTRATION (%)
FIGURE LIST

Caption

Fig. 1: Resolution vs depth curve for tritium in titanium. The calculations are for an incident proton energy of 2.3 MeV, flight path of 10 m, and spectrometer time resolution of 1.5 ns.

Fig. 2: Resolution vs depth curve for deuterium in titanium. Spectrometer parameters are the same as Fig. 1. Incident deuteron energy is 1.5 MeV.

Fig. 3: Depth profile of tritium in 0.35 μm thick Ti target on a 1 mm Cu backing.

Fig. 4: Depth profiles of 9 at. % tritium doses (at end of tritium range) in titanium and titanium hydride. Samples 11 μm thick.

Fig. 5: Depth profiles of 50 at. % tritium doses in titanium and titanium hydride.

Fig. 6: Depth profiles of 67 at. % tritium doses in titanium and titanium hydride.

Fig. 7: Depth profile of tritium in Cu. The dose was the same as that given the samples in Fig. 5.