CONF-800455--4

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Surface Composition and Erosion Yields for CVD TiB_2 Films Subjected to Low Energy Deuterium Ion Bombardment*

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ABSTRACT

The surface composition and low energy sputter yield of deuterium bombarded CVD TiB_2 films have been measured. The sputter yield increases with energy up to 1 keV where it reaches a maximum of 0.024 atoms/ion. Above 1 keV the yield decreases due to ion penetration effects. Surface composition measurements using Auger, x-ray photoelectron and secondary ion mass spectroscopies show that a surface layer about 200 Å thick is depleted in B during 2 keV deuterium bombardment. This effect is attributed to preferential sputtering. Oxides and deuterides of titanium are also observed on the deuterium bombarded TiB_2 surface.

* This work supported by the U. S. Department of Energy under contract DE-AC04-76-DP00789.

+ A U. S. Department of Energy facility.

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INTRODUCTION

The use of coatings to tailor the properties of the surface of interior components of a tokamak permits the bulk and surface material property requirements to be decoupled. Thus a coating material can be selected which has a high erosion resistance and low effective atomic number while retaining a substrate material with structural strength. One such coating which is undergoing development at Sandia Laboratories is TiB_2 deposited on graphite or Cu using chemical vapor deposition (CVD). We are studying the physical erosion and surface composition of these CVD TiB_2 films which have been bombarded with 500 eV to 10 keV deuterium ions. This paper reports the results of these measurements and compares them with the model developed by Bay et al. (1).

EXPERIMENTAL

The sputter yield measurements were made using a weight loss technique. The incident deuterium ion beams were provided with the low energy ion beam system shown schematically in Figure 1. It consists of a duoplasmatron ion source, a 30° magnetic mass analyzer, and an ultrahigh vacuum analysis chamber. The ions formed in the source are extracted at 10 keV, focused by an Einzel lens, mass analyzed, decelerated to the desired energy, and the refocused onto the target. Differential pumping is provided at both Einzel lenses in order to reduce charge exchange and to help maintain high vacuum conditions in the analysis chamber. The sample holder is mounted on an X-Y-Z plus rotation manipulator for sample alignment. A 0.64 cm mechanical aperture is used to define the irradiated area. The pressure in the analysis chamber during bombardment is approximately 10^{-5} Pa.

The analysis chamber is equipped with a secondary ion mass spectrometer for in situ surface analysis. The x-ray photoelectron and Auger electron spectrometers were located in another instrument and thus necessitated an air transfer for analysis. Surface composition data were obtained before, during and after ion bombardment. The details and capabilities of this instrument are described in reference 2.

The TiB_2 samples were made by chemical vapor deposition on graphite substrates by the hydrogen reduction of $TiCl_4$ and BCl_3 at 900°C and atmospheric pressure (3). Nominal coating thickness was 20 μm. The samples were 1.3 x 1.3 x .25 cm. They were mounted in the analysis chamber such that they were bombarded at normal incidence. The current to the sample was measured by biasing the sample to 45 volts to return the secondary electrons. The total deuterium fluence striking the sample was measured using a current integrator and was such that approximately 100 μg was lost during a measurement. The mass change measurements were made using a Mettler microbalance. The sputter yield was determined from

$$S = \frac{N_o \Delta M}{IA}$$

where N_o is Avogadro's number, ΔM is the mass change, I is the total deuterium fluence expressed as the number of incident ions, and A is the atomic weight of the target atoms. D_3^+ ions were used for the 500 eV, 1000 eV, 1500 eV, and 2000 eV measurements while D_1^+ was used for the 10 keV measurement. Appropriate adjustments were made for the number of atoms per ion and the energy per atom.

RESULTS AND DISCUSSION

The measured sputter yields are shown as a function of energy in Figure 2. The yields increase with energy up to about 1 keV where they reach a maximum of 0.024 atoms/ion. Above 1 keV the yield slowly decreases with energy. The data at energies below the maximum in the sputter yield curve can be interpreted in terms of the scaling law of Bay et al. (1). They have found that for a mass ratio of $M_1/M_2 \leq 0.4$ and a reduced energy of $1 < E' < 20$, the sputter yields can be represented by

$$S = 6.4 \times 10^{-3} M_2 \gamma^{5/3} E'^{1/4} \left(1 - \frac{1}{E'}\right)^{7/2} \quad (1)$$

when M_2 and M_1 are the target and incident ion masses in a.m.u., and

$$\gamma = \frac{4M_1M_2}{(M_1+M_2)^2}, \qquad E' = \frac{E}{E_{th}}.$$

E_{th} is the threshold energy for sputtering and can be calculated from $E_{th} = \frac{E_B}{\gamma(1 - \gamma)}$ where E_B is the surface binding energy.

Note that this expression contains no adjustable parameters. Following the suggestion of Bay et al. (1) we have used the sublimation energy for the surface binding energy. Using the data from the JANAF (4) tables we have calculated a binding energy of 7.4 eV for TiB_2. For the energy range criterion to be applicable, equation 1 should be good up to about 1 keV for deuterium on TiB_2. The solid curves in Figure 2 are a plot of equation 1 assuming the target mass is 1) boron, 2) titanium and 3) the average mass for TiB_2. As can be seen from the Figure, the best agreement between the data and

the formula of Bay et al. occurs when the mass of Ti is used for M_2. This observation is in agreement with data of Roth et al. (5) for carbides, i.e., one must use the mass of the heavier component as M_2 in order to obtain agreement between the experimental data and the formula of Bay. Roth has attributed this to the enrichment of the heavier component at the surface due to preferential sputtering of the light component. In compounds where preferential sputtering occurs, it is generally the heavier component which is enriched at the surface while the lighter element is sputtered away (6). The Bay formula is only valid for energies below the peak in the sputter yield. The dashed high energy portion of the curve is a smooth curve drawn through the data. The decrease in the sputter yield in this region is attributed to the increase of the ion penetration depth (7). The open circles are the recent data of Roth et al. (8) for TiB_2. As can be seen from the figure, there is good agreement between the two sets of data.

The assumption of preferential sputtering of B from the surface of TiB_2 before, during and after bombardment by the 2 keV deuterium ions has been studied by various surface analysis techniques. In Figure 3 are shown Auger spectra of TiB_2 obtained before and after deuterium bombardment. These spectra were obtained after a light Ar ion bombardment which removed the adsorbed hydrocarbon that had accumulated during air transfer to the Auger spectrometer. The continued presence of the carbon peak indicates that the samples contained a carbon impurity. As can be seen from the figure, the B/Ti ratio is lower after bombardment, again suggesting a B depletion in the surface region. This assumption is also confirmed by the depth profile of

Figure 4 where the B/Ti ratio is plotted as a function of sputter time (depth) into the sample. From the data and by estimating the sputter rate we find that the B is depleted in approximately the first 200 Å of the deuterium sputtered sample. This is about the range of a 2 keV D^+ ion on TiB_2 (9).

X-ray photoelectron data of TiB_2 after deuterium irradiation are shown in Figure 5. These data suggest that TiO_2 is formed near the bombarded surface. Due to the fact that the sample was transferred in air to the XPS spectrometer, the question of the oxides forming during the transfer was raised. While this is a possibility, the SIMS spectra shown in Figure 6 clearly indicate that TiO^+ and TiD^+ ions are being sputter removed from the sample during deuterium ion bombardment. These data are also consistent with the theory of preferential sputtering of B from the surface. They also indicate that the enriched Ti is reacting with the deuterium and oxygen in the analysis chamber to form TiD_x and TiO_y.

SUMMARY

The sputter yields for CVD TiB_2 have been determined for deuterium ions in the range of 500 eV to 10 keV. These results are in agreement with the formula of Bay et al. if preferential sputtering of the B is assumed. This assumption is supported by surface analysis data obtained from virgin and sputtered samples. The fact that this reduction in B content increases hydrogen and oxygen gettering must be considered when using TiB_2 in a tokamak.

ACKNOWLEDGEMENTS

The authors are indebted to A. Mullendore and H. Pierson for CVD preparation of TiB_2 samples and to M. C. Oborny for skilled technical assistance with the accelerator.

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FIGURE CAPTIONS

Figure 1. Schematic drawing of the low energy ion beam system used for the sputter yield measurement.

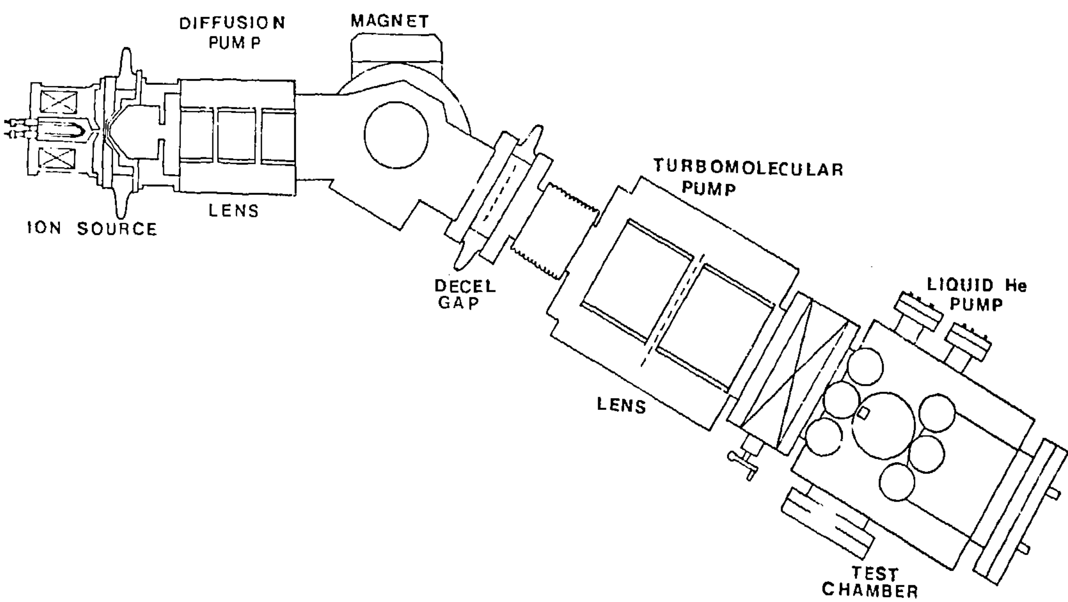
Figure 2. Sputter yield of TiB_2 irradiated by deuterium ions as a function of energy. The solid smooth curves were obtained from the formula of Bay et al. (1). The dashed curve is a guide to the eye.

Figure 3. Auger spectra from TiB_2 before and after exposure to $\sim 10^{20}$ 2 keV deuterium ions/cm^2.

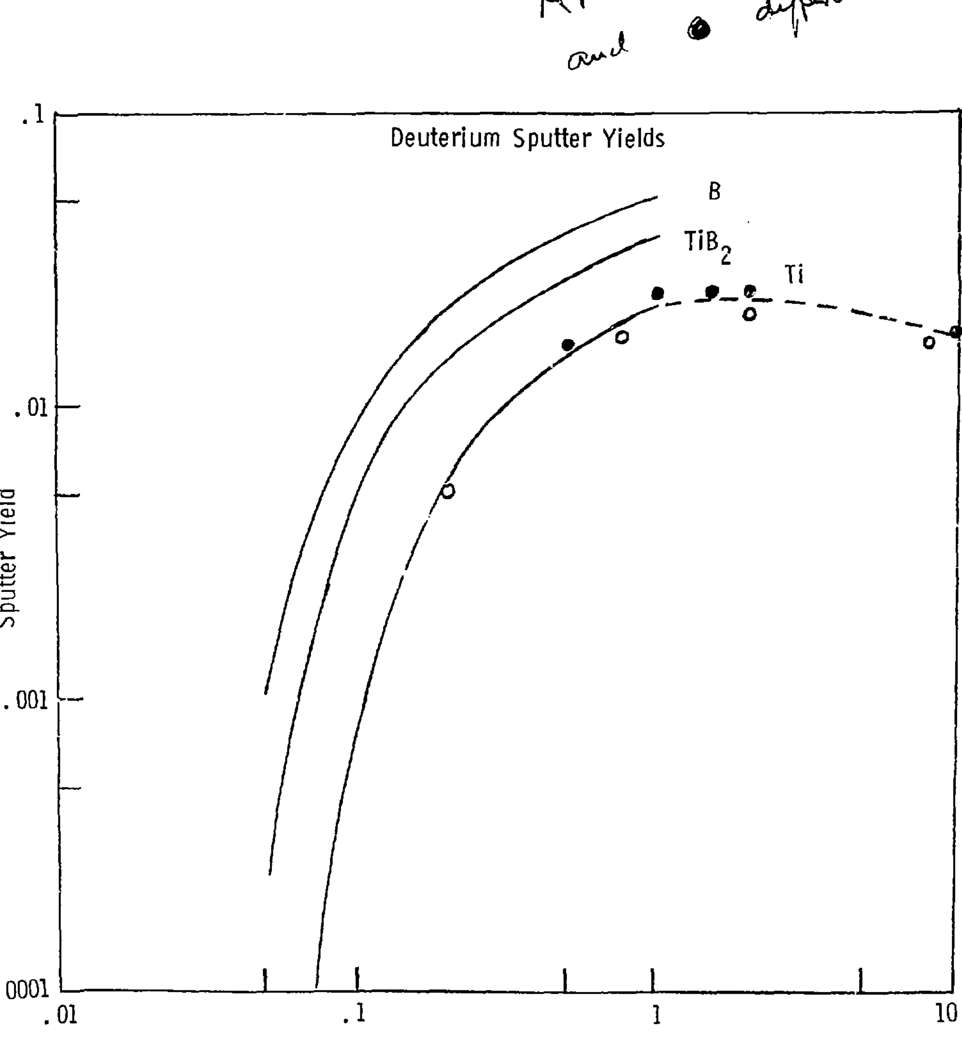
Figure 4. B/Ti as a function of sputter time (depth) of an as-received and deuterium sputtered TiD_2 sample.

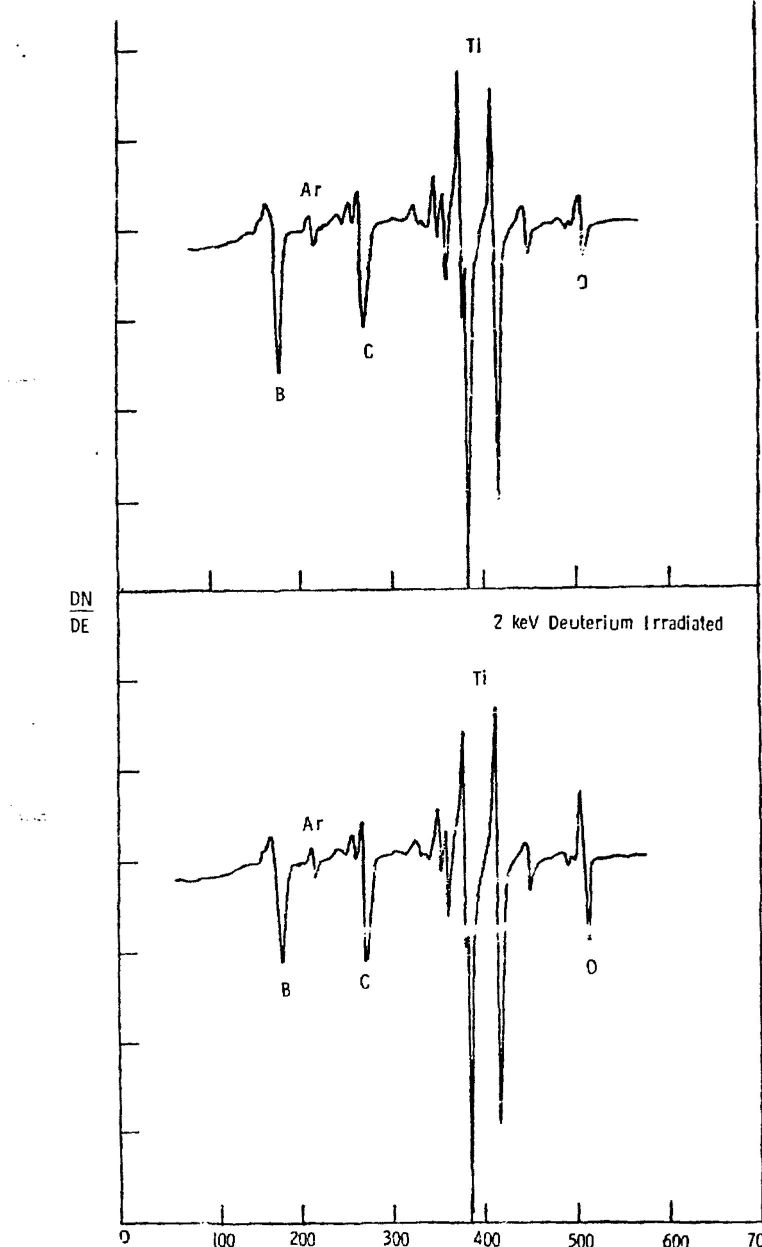
Figure 5. High resolution x-ray photoelectron spectra of Ti from a deuterium bombarded sample.

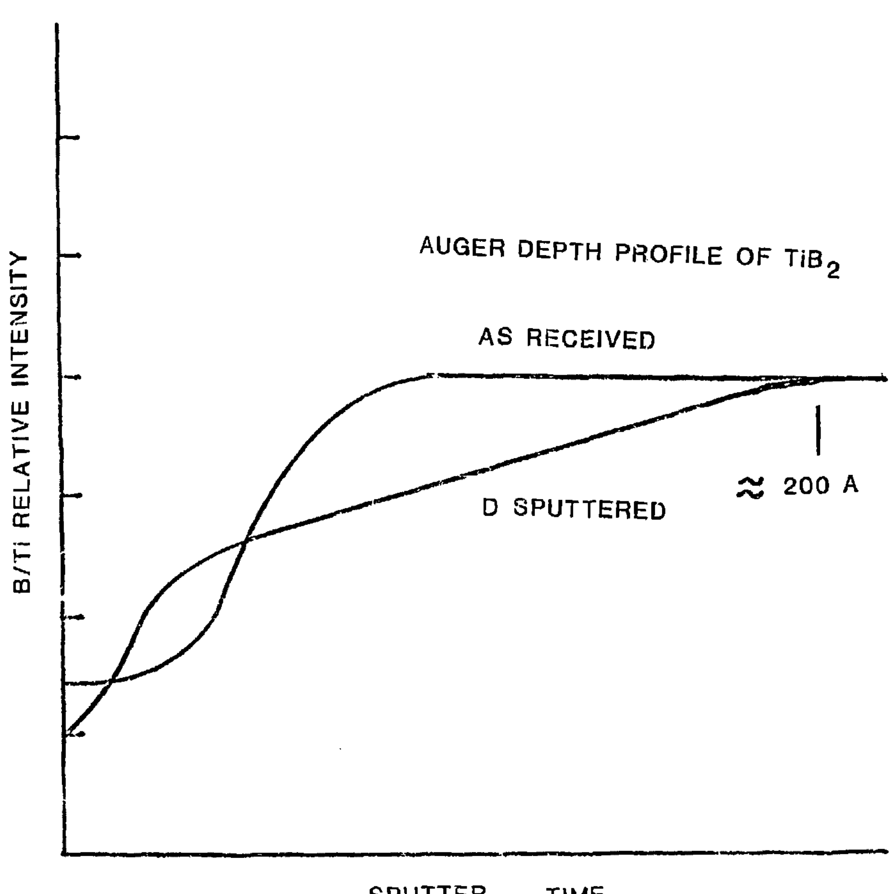
Figure 6. Positive secondary ion mass spectra obtained during deuterium ion bombardment.


DIFFUSION PUMP
MAGNET
ION SOURCE
LENS
TURBOMOLECULAR PUMP
DECEL GAP
LIQUID He PUMP
LENS
TEST CHAMBER

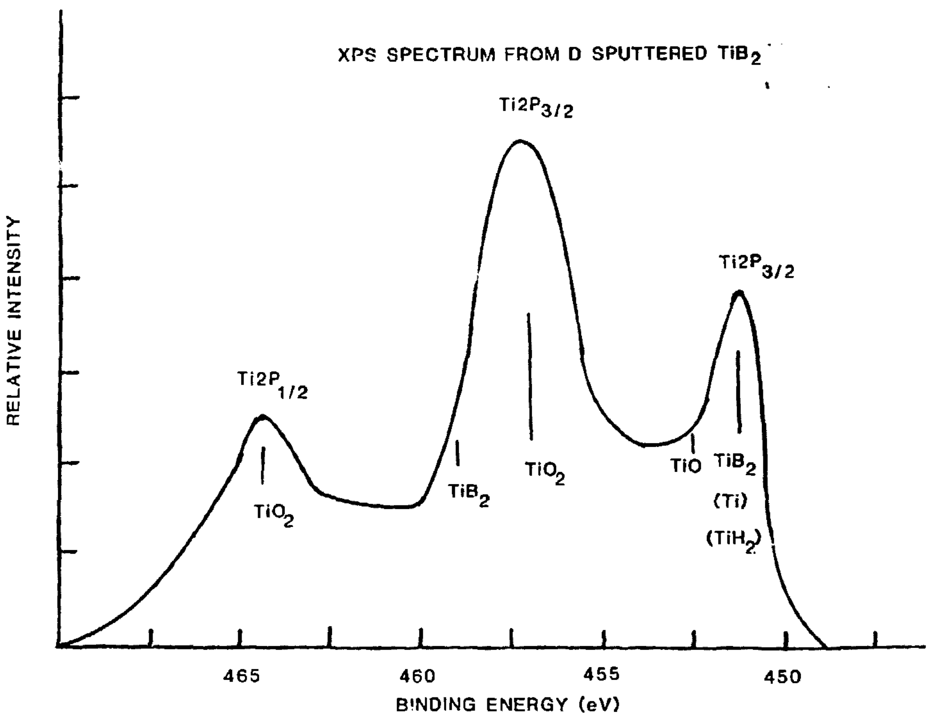
Are ○ and ● different?



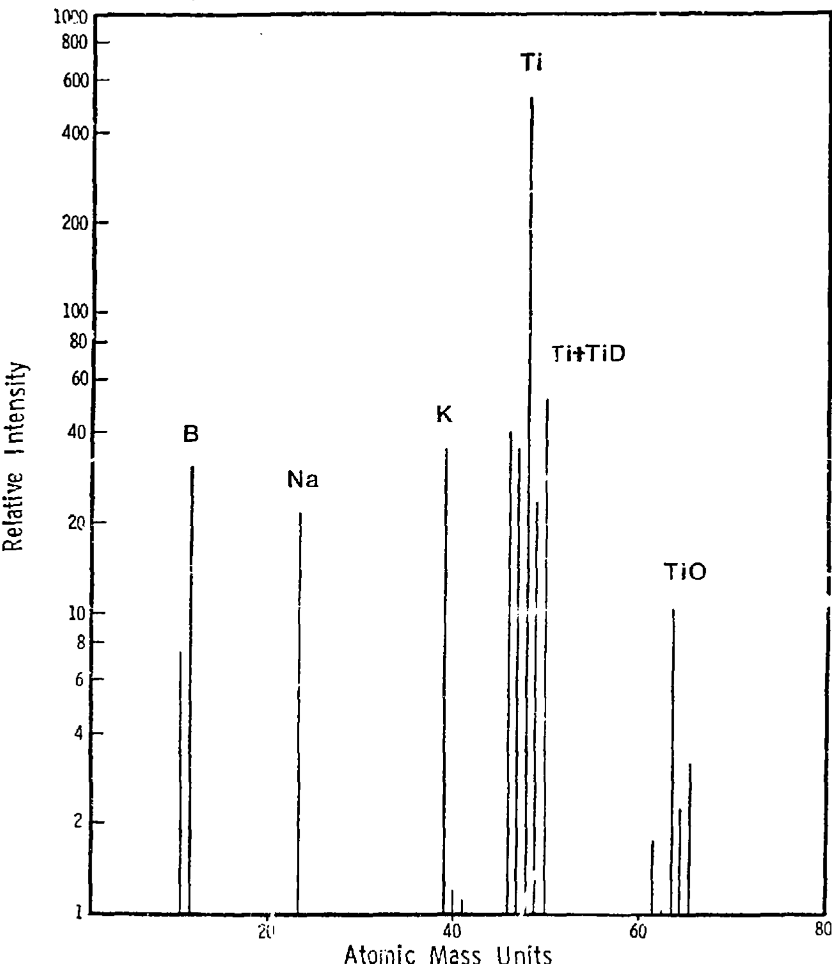

Ti
Ar
B
C
O
DN
DE
2 keV Deuterium Irradiated
Ti
Ar
B
C
O
0
100
200
300
400
500
600
700



AUGER DEPTH PROFILE OF TiB_2
AS RECEIVED
D SPUTTERED
≈ 200 A
B/Ti RELATIVE INTENSITY
SPUTTER TIME



XPS SPECTRUM FROM D SPUTTERED TiB2
Ti2P3/2
Ti2P3/2
Ti2P1/2
TiO2
TiB2
TiO2
TiO
TiB2
(Ti)
(TiH2)
RELATIVE INTENSITY
465
460
455
450
BINDING ENERGY (eV)



Relative Intensity
Atomic Mass Units
Ti
TiH+TiD
K
B
Na
TiO
1000
800
600
400
200
100
80
60
40
20
10
8
6
4
2
1
20
40
60
80