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INTERACTION OF IMPLANTED DEUTERIUM AND HELIUM WITH BERYLLIUM: RADIATION ENHANCED OXIDATION*

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The interaction of implanted deuterium and helium with beryllium is of significant interest in the application of first wall coatings and other components of fusion reactors. Electropolished polycrystalline beryllium was first implanted with a Xe backscatter marker at 1.98 MeV followed by either implantation with 5 keV diatomic deuterium or helium. A 2.0 MeV He beam was used to analyze for impurity buildup; namely oxygen. The oxide layer thickness was found to increase linearly with increasing implant fluence. A 2.5 MeV H^+ beam was used to depth profile the D and He by ion backscattering. In addition the retention of the implant was measured as a function of the implant fluence. The mean depth of the implant was found to agree with theoretical range calculations. Scanning electron microscopy was used to observe blister formation. No blisters were observed for implanted D but for implanted He blisters occurred at $\sim 1.75 \times 10^{17}$ He$\cdot$cm^{-2}. The blister diameter increased with increasing implant fluence from about 0.8 μm at 10^{18} He$\cdot$cm^{-2} to 5.5 μm at 3×10^{18} He$\cdot$cm^{-2}.

1. INTRODUCTION

Low Z elements and compounds are being considered for materials for use in fusion reactors since D/T plasmas can tolerate much higher concentrations of low Z impurity atoms than of high Z. [1] Beryllium (Z = 4) is one of the elements being considered because it has the capabilities of being coated onto structural materials to form a low Z inner surface in fusion reactors. [2,3] The response of Be and its compounds to implanted high doses of low energy hydrogen and helium is important for the selection of first wall materials.

In this experiment depth profiles and trapping of 2.5 keV deuterium and 5 keV helium in polycrystalline beryllium is reported for a temperature of 25°C. In addition, measurements of radiation enhanced oxide growth and blister formation were made.

2. EXPERIMENT

The implantations were carried out using an acceleration-deceleration system with a turbo-pumped target chamber. In addition the target chamber had a liquid nitrogen trap surrounding the target which was cooled during implantation.

The pressure in the target region was 5×10^{-6} Torr during implantation but was composed mainly of the working gas, i.e. D_2 or He/Ar. Partial pressures of the major gaseous impurities, as measured by residual gas analysis, were H_2O-6×10^{-8} Torr, CO-3.5×10^{-8} Torr, CO_2-0.25×10^{-8} Torr and O_2-0.2×10^{-8} Torr. The implant dose rate was 3×10^{16} D$\cdot$cm$^{-2}\cdot$min^{-1} and 1×10^{16}He$\cdot$cm$^{-2}\cdot$min^{-1}.

Depth profiles of implanted D and He were made using elastically backscattered 2.5 MeV H ions and the oxide layer thickness was measured using elastically backscattered 2.0 MeV He ions. These analysis techniques have been fully explained in the literature [4] and will not be discussed further here. Both optical and scanning electron spectroscopy were used to analyze the surfaces before and after implantation for deformation.

The polycrystalline beryllium used for this experiment was obtained from Kawecki Berylco Industries, Inc. It had been prepared by cold isostatic pressing, followed by hot isostatic pressing and the average grain size was given as 10 μm. The principal metallic impurities reported by the manufacturer were Fe (165 ppm by weight), Ni(105), Si(82), Al(60), Mg(44), and Cu(40), with others totaling less than 50 ppm. Beryllium oxide was present in much larger quantities (about 9000 ppm by weight). Sample discs 10 mm in diameter and 1 mm thick were cut, mechanically polished and finally electropolished to remove about 5 μm from the surface. It was anticipated that this procedure would leave a clean damage-free surface. Subsequent backscattering analysis yielded an impurity content which was consistent with that given above, but with a surface oxide layer less than 1×10^{17} O atoms/cm^2. Photomicrographs showed that the mean grain size was ≈ 10 μm.

3. RESULTS

The initial goal of the experiment was to measure the sputtering coefficients for low

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energy D and He on beryllium using an implanted high Z marker [5]. After completion of the first measurements it became obvious that beam induced oxide growth precluded the achievement of the initial goal using the existing target chamber and implant fluence rates, since the oxide growth rate was substantially larger than the sputter rate. Subsequent sputter measurements were made for He on thermally grown BeO and are give in Reference 6.

3.1 Mean Ranges and Profile Spread

Accurate determination of the mean range of the implanted D and He must include analysis of the energy loss in surface oxide layer since it is a substantial fraction of the total energy loss. The oxide layer was observed to increase with increasing implant fluence so that the range varied with fluence. A unique range could be calculated since the oxide layer thickness was experimentally measured. For D implants the oxide thickness rate of increase with fluence was small and, to within experimental error, a single range could be calculated; the results are given in Table 1 for an oxide thickness of 10^{17} O·cm^{-2}. From the shape of the Be edge and oxygen peak in the He backscatter spectra it was determined that the ratio of O to Be in the surface layer was 1:1 and it was assumed that the oxygen is chemically combined with Be to form BeO. For He implants the oxide layer increased substantially with implant fluence and two ranges are given in Table 1; one for a measured oxide thickness of 10^{17} BeO·cm^{-2} and the other for an oxide thickness of 2.5×10^{17} BeO·cm^{-2}. For all fluences the mean range of the implanted D and He agreed with theoretically determined values using stopping cross sections obtained from Brice [7] and Anderson and Ziegler [8,9].

The depth profiles of the implanted D and He had normal distributions for all implant fluences. The measured spread of the distribution was dominated by the energy resolution of the detection system but the deconvolved spread was not inconsistent with the theoretical values, [7] i.e., σ(2.5 keV D) = 3.3×10^{17} Be·cm^{-2} and σ(5 keV He) = 2.9×10^{17} Be·cm^{-2}.

3.2 Trapping

Trapping of the implanted species as a function of fluence is shown in Figure 1. A trapping coefficient of 100% is observed for implanted D up to a fluence of 2×10^{18} D·cm^{-2} with saturation occurring 5×10^{18} D·cm^{-2}; this behavior is similar to previous results in other metals [10] and non-metals [11]. For implanted He 100% trapping is observed to a fluence of 2×10^{18} He·cm^{-2} but decreases above this fluence. This loss of He with increasing fluence is indicative of blistering [12].

3.3 Radiation Enhanced Oxidation

Beryllium has a high free energy of formation

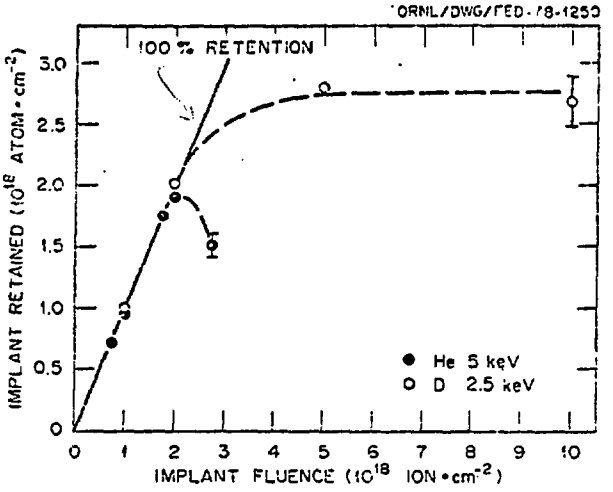

Fig. 1. Amount of deuterium and helium trapped in surface layer as a function of primary ion fluence.

of the oxide BeO (0.58 J/kg-mole) [13] and will form a thin limiting oxide surface layer on exposure to air. The thickness of this layer can be minimized to less than 10^{17} O·cm^{-2} by treatment of the surface with a chemical etch as was done for this experiment. For room temperature implants of both D and He, the oxide layer thickness was observed to increase with increasing implant fluence; see Fig. 2. This oxide growth is probably due to radiation enhanced diffusion of Be from the bulk through the oxide surface layer which combines with oxygen at the surface. This atomic oxygen is probably produced by beam breakup of CO and H_2O, the main contaminants in the vacuum system. Radiation enhanced oxide growth has been previously reported for GaAs [14] as has radiation enhanced diffusion [15]. The rate of oxide growth is linear with fluence which is contraindicative of diffusion being the rate limiting mechanism. If diffusion were the rate limiting mechanism, a square root dependence with fluence would be expected. The measured rate of oxide growth for 5 keV He was 0.09 ± 0.01 O/He and for 2.5 keV D it was 0.007 O/D for the implant conditions given in Section 2. This large difference in rate observed between He and D implantation, a factor of 13, cannot be simply explained by either damage production or electronic excitation.

Theoretical values of the energy loss rates were determined by using calculations of Brice [16] and are given in Table 2. Brice's calculations accounted for backscattered beam particles and change of direction of the incident particle.

It would be purely conjecture to assess what the enhancement effect would be if the incident particle expended all of its energy in the oxide layer, i.e., is the enhanced oxide growth self limiting.

Table 1

	Calculated Projected Range	Experimental Mean Range
2.5 keV D → Be(10^{17}BeO·cm^{-2})	1.0 x 10^{17}BeO·cm^{-2} +3.9 x 10^{17}Be·cm^{-2}	1.0 ± 0.2 x 10^{17}BeO·cm^{-2} +4.0 ± 2.0 x 10^{17}Be·cm^{-2}
5.0 keV He → Be(10^{17}BeO·cm^{-2})	1.0 x 10^{17}BeO·cm^{-2} +6.78 x 10^{17}Be·cm^{-2}	1.0 ± 0.2 x 10^{17}BeO·cm^{-2} +7.1 ± 2.0 x 10^{17}Be·cm^{-2}
5.0 keV He → Be (2.5 x 10^{17}BeO·cm^{-2})	2.5 x 10^{17}BeO·cm^{-2} +4.45 x 10^{17}Be·cm^{-2}	2.5 x 10^{17}BeO·cm^{-2} +6.3 ± 2.0 x 10^{17}Be·cm^{-2}

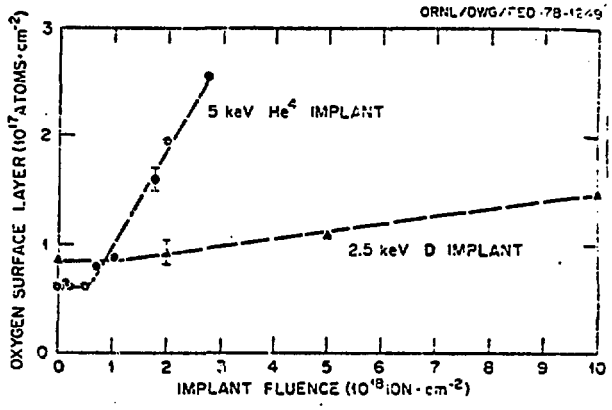

Fig. 2. Growth of oxide surface layer as a function of primary ion fluence.

3.4 Blister formation and growth

No surface deformation was observed for any fluence of implanted D but for implanted He blister formation was observed starting at a fluence of 7.5 x 10^{17} He·cm^{-2}. The mean diameter of the blisters increased with increasing fluence starting at ∿0.8 μm and growing to ∿5.5 μm at 2.75 x 10^{18} He·cm^{-2} as shown in Figure 3. Cracking of the blister lids was first observed at a fluence of 2 x 10^{18} He·cm^{-2} (see Fig. 4) and correlates well with the loss of implanted He as shown in Figure 1. No exfolication was observed for any fluence as has been previously reported for other materials [17].

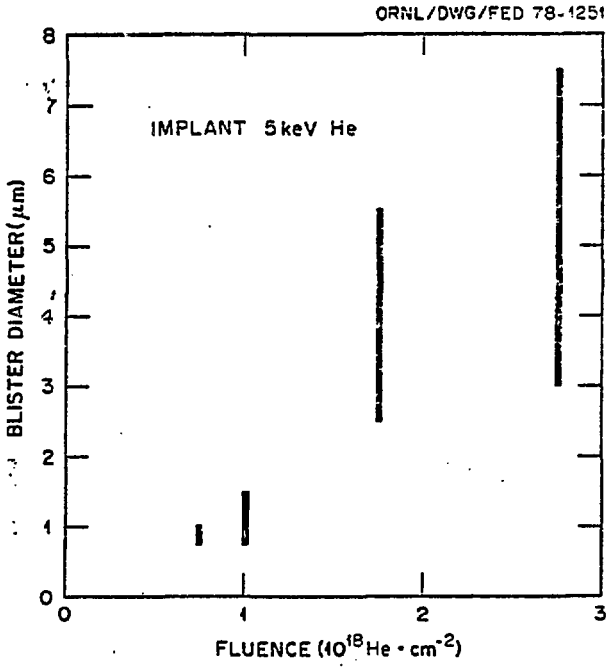

Fig. 3. Blister diameter as a function of primary ion fluence. The vertical bars represent the range of blister diameters with the mean diameter at the mid point.

Table 2

Comparison of Calculated Energy Loss Rates (10^{-15} eV·cm^2·(BeO)$^{-1}$)

	Damage Production	Electronic Excitation
5 keV He→ BeO	1.3	1.7
2.2 keV D→ BeO	0.25	0.9

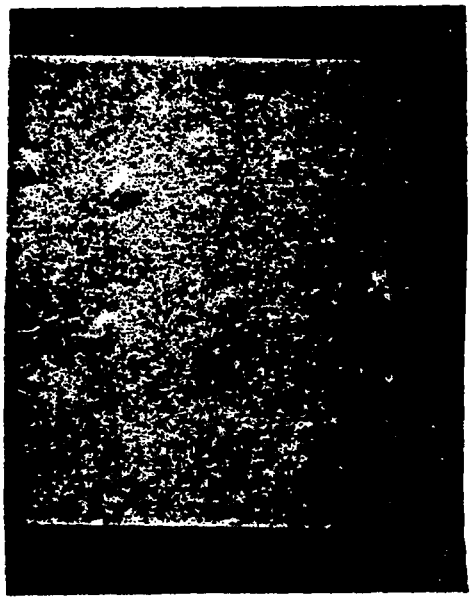

Fig. 4. Scanning electron microscopy picture of the surface of Be after implantation of 2.75×10^{18} He·cm^{-2}.

4. CONCLUSIONS

These measurements demonstrate that radiation enhanced oxidation can be important in irradiation studies involving beryllium. The results are applicable to the use of beryllium as a first wall material of a fusion reactor. It would getter oxygen impurities continuously from the plasma during operation since significant fluxes of energetic hydrogen and helium are expected to bombard the first wall. Mean energies of 1-4 keV and fluxes of 10^{17}cm^{-2}·sec^{-1} of hydrogen and 10^{15}cm^{-2}·sec^{-1} of helium are expected. [18] Using these parameters and the results obtained in this experiment gettering rates for oxygen of 8×10^{14}O·cm^{-2}·sec^{-1} would be expected.

Further experiments are indicated before use of beryllium as a first wall material; in particular it should be determined if the oxide thickness is dependent upon the range of the incident particles and the effect of elevated temperatures during implantation.

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REFERENCES

[1] D. M. Meade, Nucl. Fus., 14 (1974) 289.
[2] J. Norem and D. A. Bowers, Argonne National Laboratory Report ANL/FPP/TM-108 (1978).
[3] R. A. Langley and T. S. Prevender, Thin Solid Films, 45 (1977) 235.
[4] R. A. Langley, Ion Beam Surface Layer Analysis, (Plenum Press, 1976), Vol. 1, 201.
[5] P. Blank and K. Wittmack, Rad. Eff. 27 (1975) 29.
[6] J. A. Borders, R. A. Langley and K. L. Wilson, J. Nucl. Mat. 76 (1978) 168.
[7] For computational procedure see: D. K. Brice, Rad. Eff. 11 (1971) 227 and D. K. Brice, Sandia Research Report, SAND75-0622 (July 1977).
[8] H. H. Anderson and J. F. Ziegler, Hydrogen Stopping Powers and Ranges in All Elements, (Pergamon Press, 1977).
[9] J. F. Ziegler, Helium Stopping Powers and Ranges in All Elements, (Pergamon Press, 1977).
[10] R. A. Langley, R. S. Blewer and J. Roth, J. Nucl. Mat. 76 (1978) 313.
[11] R. Behrisch, R. S. Blewer, J. Borders, R. A. Langley, J. Roth, B. M. U. Scherzer and R. Schulz, To be published in Budapest Proceedings, 1978.
[12] R. A. Langley, R. S. Blewer, and P. S. Peercy, J. Nucl. Mat. 76 (1978) 261.
[13] G. V. Samsonov, The Oxide Handbook, (Plenum Press, 1973).
[14] C. W. Arnold, R. E. Whan, J. K. Maurin, and J. A. Borders, Ion Implantation in Semiconductors-Physics and Technology, Thousand Oaks, California May 4-7, 1970, Abstract.
[15] S. M. Myers, J. of Vac. Sci. Tech., 15 (1978) 1650.
[16] Private communication, D. K. Brice, Dec. 1978.
[17] See for example, W. Bauer, J. Nucl. Mat. 76 (1978) 3.
[18] Private communication, A. T. Mense, Jan. 1979.