



A NEW TECHNIQUE TO MEASURE FISSION-PRODUCT DIFFUSION COEFFICIENTS IN UO₂ FUEL

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Abstract

This paper describes a new out-reactor technique for the measurement of fission-product diffusion rates in UO₂. The technique accurately simulates in-reactor fission-fragment effects: athermal diffusion that is due to localized mixing in the fission track, radiation-enhanced diffusion that is due to point-defect creation by fission fragments, and bubble re-solution. The technique utilizes heavy-ion accelerators – low energy (40 keV to 1 MeV) for fission-product implantation, high energy (72 MeV) to create fission-fragment damage effects, and secondary ion mass spectrometry (SIMS) for measuring the depth profile of the implanted species. Preliminary results are presented from annealing tests (not in the 72 MeV ion flux) at 1465°C and 1650°C at low and high concentrations of fission products.

1. INTRODUCTION

Release of fission gas and other volatiles from fuel during irradiation is a critical performance factor because it can lead to sheath defects, and it contributes to the inventory available for immediate release during off-normal conditions and spent-fuel storage. One of the tasks of fuel-performance codes used throughout the nuclear industry is to predict the amount of gas released under various normal and off-normal operating conditions. After over 30 years, considerable work still is being applied to improving these computer codes. For example, the IAEA has sponsored a program over the last few years comparing fuel-performance codes to assess how they perform in a set of blind tests [1].

There are several steps between the formation of fission gas and its release to the fuel-sheath gap. The first is the diffusion of the gas atoms after their formation to grain boundaries where they coalesce into bubbles. This step can be a thermally activated process – normal diffusion by jumping from one lattice site to an adjacent one or from one interstitial site to an adjacent one (or by a more complicated neutral tri-vacancy mechanism as some propose [2]). But there is also a non-thermally activated process (termed *athermal* diffusion) that leads to the movement of gas atoms to grain boundaries – the passage of fission fragments through the matrix causes rearrangement of atoms in the *fission track*, and the result is similar to the random walk of diffusion. The passage of the fission fragments can be likened to a brief local heating or melting in the fission track (approximately 8 μm long). This is the important process at low temperatures where thermally activated diffusion is relatively slow.

In the process of diffusing from within the grains to grain boundaries, there is a complication – coalescence of gas atoms at defects in the matrix can produce tiny gas bubbles. These bubbles act as traps, effectively preventing the gas atoms from re-entering the fuel matrix. The bubbles migrate more slowly than the individual gas atoms, and thereby reduce the flux of gas atoms reaching the grain boundaries. Again, the fission fragments assist: as they pass through bubbles, they 'knock' gas atoms back into the UO₂ matrix, and can even totally eliminate small bubbles. This is termed *re-solution*. Taking into account the delay of gas atoms in these micro-bubbles, fuel-performance codes use an *effective* diffusion coefficient for the overall rate at which gas atoms move through grains. The diffusion rate strictly within the UO₂ matrix between bubbles, without considering trapping at bubbles, is termed *intrinsic* diffusion.

Measurements of diffusion rates of fission gas in nuclear fuels are difficult. First, the techniques usually rely on simple measurements of the rate at which the diffusing species are evolved from the samples. This is inaccurate – the best techniques for diffusion measurements, in general, measure profiles of the diffusion species (or of one particular isotope of that species) within the sample after diffusive spreading of a concentrated source, such as a deposited layer, has occurred. Also, in measuring the gas evolved from samples, all processes that contribute to movement of gas to the fuel surface are included, not just diffusion to the grain boundaries. While total gas evolution is an end-result that codes need to predict properly, this technique is not conducive to understanding or modelling individual processes so that the predictive capabilities being developed are applicable outside the specific conditions of the tests being done. Another reason for the difficulty of diffusion measurements is that out-reactor techniques do not include the effects of fission fragments — the athermal diffusion and re-resolution of bubbles, described above. In-reactor techniques, on the other hand, are difficult, expensive, and test parameters are not easily controlled or measured.

Dozens of papers describe diffusion of fission gases in UO_2 – see, for example, review articles by Catlow [2], Matzke [3], and Lawrence [4]. There is a large spread in reported diffusion rates; the new method described herein has the potential to be the most accurate and to be able to measure the effects of influences such as impurities, fission products and stoichiometry changes.

This technique is an out-reactor technique that gives in-reactor-equivalent results. That is, the effects of fission fragments are properly simulated. The method determines both intrinsic and effective diffusion rates, and is not based on measuring the rate or amount of gas evolution from test samples. Rather, it is a technique based on profiling of the diffusing species after spreading of a concentrated layer has occurred.

2. METHOD

The basics of the method are (subsections provide details):

- Preparing fuel samples
- Implanting a stable isotope of a fission product into a thin layer near the surface of the samples. A small fluence¹ means that the concentrations are low enough that bubbles have a low probability of formation. Larger fluences will favor the formation of bubbles. Measurements from the former provide intrinsic diffusion rates; measurements from the latter provide effective diffusion rates.
- Diffusive spreading of this implanted layer either by heating or by a second process akin to athermal diffusion – the implanted sample surface is bombarded by iodine ions of energy 72 MeV, typical of fission-fragment energies. Because this energy is much higher than that used in the implantation step, these ions pass completely through the implanted layer and cause diffusion almost exactly as fission fragments do.
- Measurement of the concentration of the implanted ions, as a function of depth, before and after diffusion broadening, by secondary ion mass spectrometry (SIMS).

2.1. Sample Preparation

One surface of each sample of sintered UO_2 , simulated extended burnup fuel (SIMFUEL) and single crystal UO_2 was mechanically polished and annealed at 1500°C in flowing Ar-4% H_2 . The anneal removes the effects of polishing damage near the surface.

¹ The term *fluence* is used to indicate the total number of implanted atoms (or ions) per unit area of sample in the beam.

2.2. *Implantation*

Samples were implanted with iodine or xenon using an accelerator at an ion-implantation energy of approximately 1 MeV. This gave a mean range of about 150 nm. Other samples were implanted with krypton, rubidium or iodine at about 40 keV, which gave a mean range of 10 to 20 nm. The implantation fluence was varied to achieve a wide range in concentrations of the implanted species. The lowest fluence used was 1×10^{13} ions/cm², and the highest was 1×10^{16} ions/cm². New samples are being prepared, some with europium implantation, to fluences even lower than those previously used to ensure that bubbles do not form.

2.3. *Diffusive spreading of the implanted layer*

As indicated previously, two methods of broadening the implanted layer have been used: thermal anneals and re-bombardment with high-energy ions to simulate fission fragments. For the latter, iodine at 72 MeV was used because this represents a typical fission-fragment element at a typical fission-fragment energy. These ions have a range of about 6 μ m, and thus pass through the implanted layer and cause localized diffusion within the volume of their 'tracks'. The only differences to in-reactor fission-fragment effects are

- (a) all the ions move essentially in the same direction, compared with all directions for fission fragments;
- (b) all accelerator ions are iodine, whereas, in-reactor, there are many fission-fragment elements; and
- (c) the energies of the ions as they pass through the implanted layer all have approximately the same energy, whereas fission-fragments in-reactor would have a complete distribution of energies representative of fission fragments at all points along their paths.

Points (a) and (b) will not likely have much effect on diffusion; in point (b) because ions slowing to rest from 72 MeV occur mainly by electronic interactions between the ion and the matrix, this process is independent of ion species. Nuclear interactions occur only at the end of the implantation track because the ion is nearly at rest. However, point (c) could potentially have an effect on diffusion rate – this could be tested and corrected for by using different energies or by using a range of energies in one test. This has not yet been done. Also, all the accelerator tests have been at ambient temperature (<150°C) to effectively eliminate thermal diffusion and observe effects that are totally attributable to the accelerator bombardment. Tests at elevated temperatures should be performed because the fission fragments will also affect the diffusion rates through much of the thermal regime. This effect occurs because the fission fragments induce point defects, additional to those that are naturally present. In other words, the concentration of point defects that contribute to thermal diffusion is not the thermodynamic equilibrium concentration but a higher concentration that is due to those created by the passage of fission fragments through the fuel matrix. This is termed *radiation-enhanced diffusion (RED)*; only at sufficiently high temperatures, above about 1400 to 2000 K, depending on many factors such as the fuel power, is the equilibrium concentration of point defects sufficiently high that the extra defects that are due to fission fragments are largely inconsequential.

2.4. *SIMS measurements of the distributions*

A CAMECA IMS 6f SIMS is being used to profile the iodine distributions. This instrument is extremely sensitive to iodine – concentrations ranging from less than 10^{14} atoms/cm³ to greater than 10^{20} atoms/cm³ have been measured. To calibrate the SIMS sputtering rate, depths of all craters were measured with a stylus profilometer. Results of these depth measurements are given in the next section. Figure 1 shows an example of the distribution directly after implantation of a low fluence of iodine, and after a thermal anneal at 1650°C for 2 h, showing the broadening that has occurred. In contrast, Figure 2 shows the results after a similar heat treatment for a sample with a high-fluence implant. Little broadening of the distribution has occurred. The implanted iodine has formed bubbles, which, without

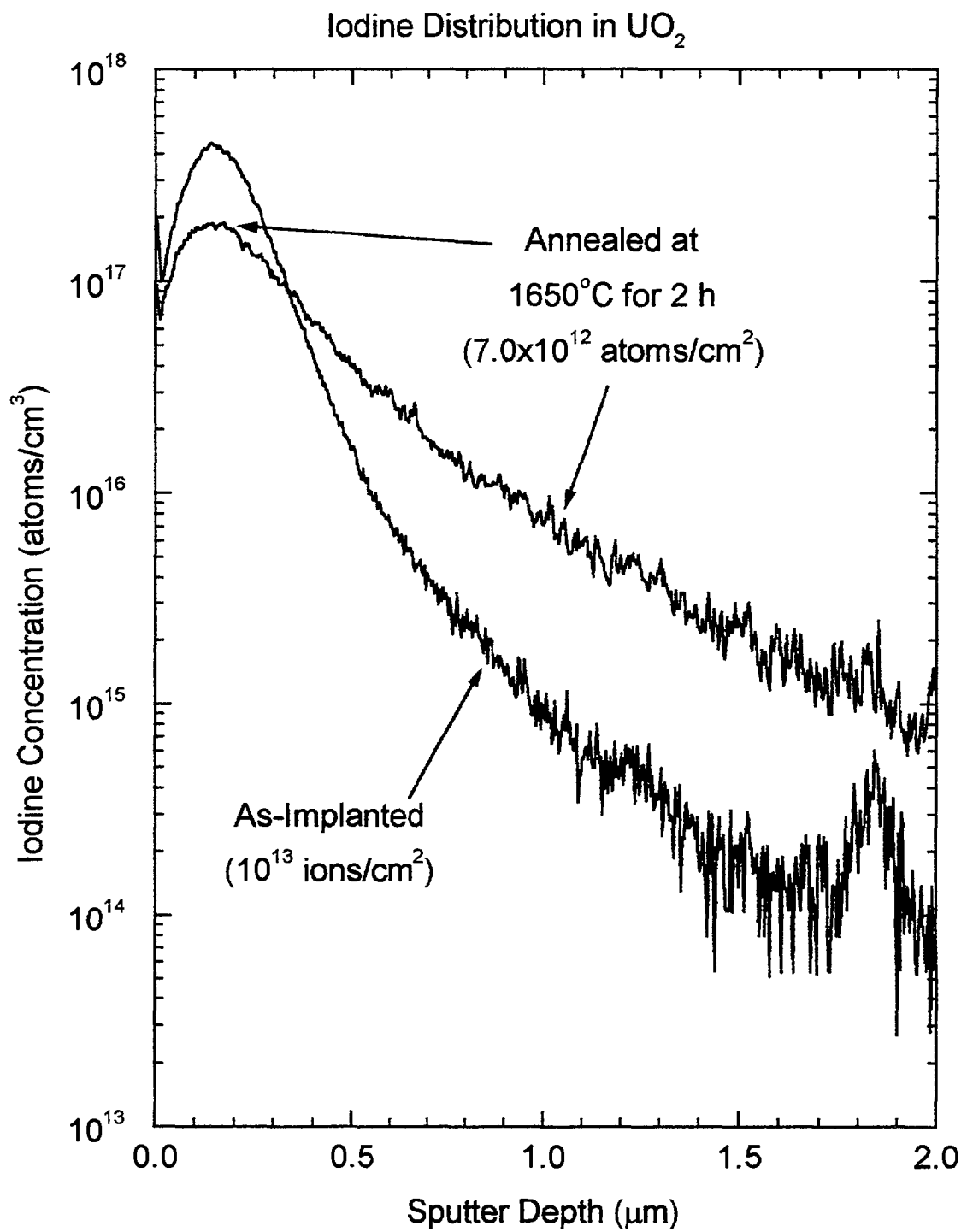


FIGURE 1 SIMS depth profile of a low fluence of iodine implanted at 1 MeV before and after an anneal at 1650°C for 2 h.

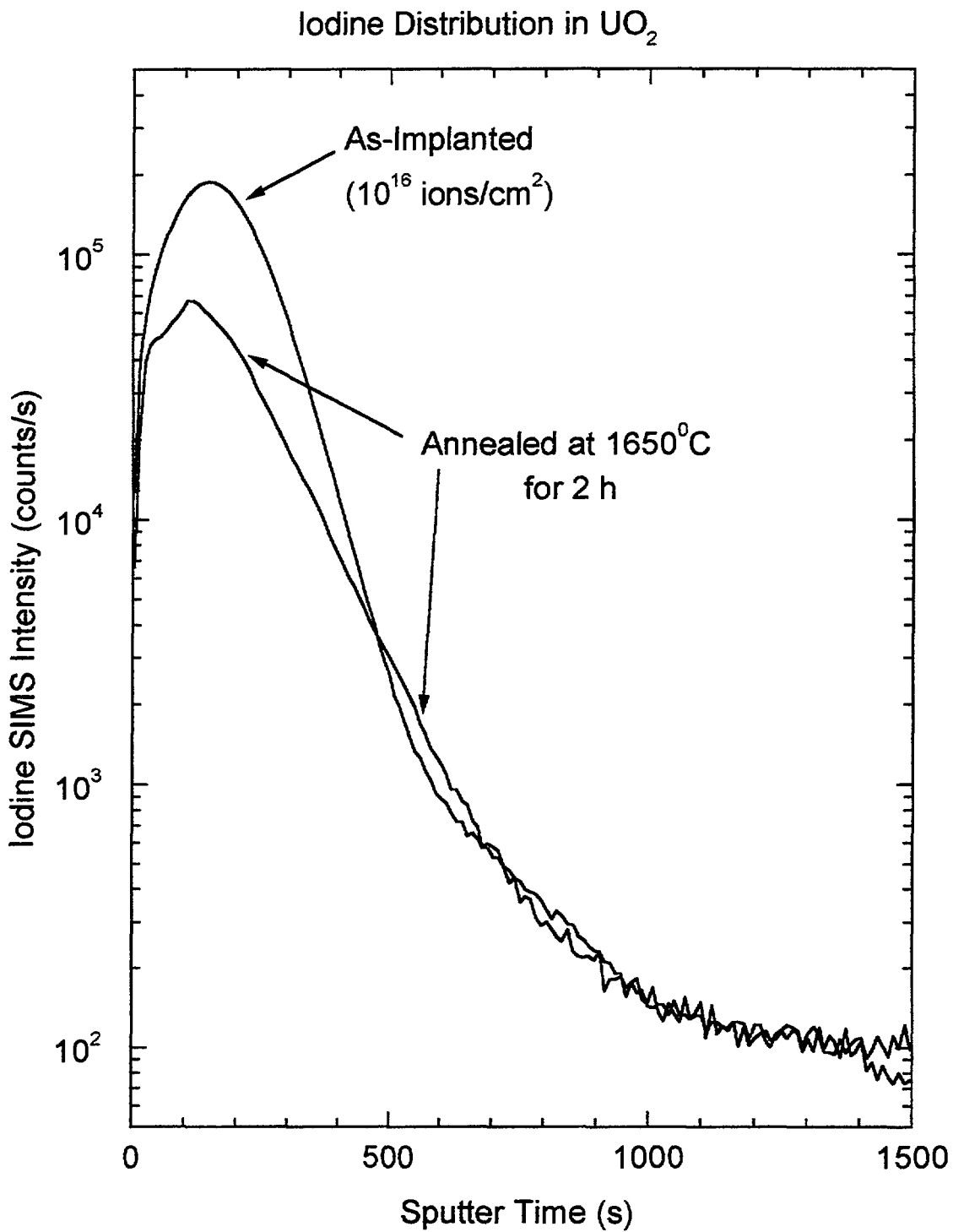


FIGURE 2 SIMS depth profile of a high fluence of iodine implanted at 1 MeV before and after an anneal at 1650°C for 2 h.

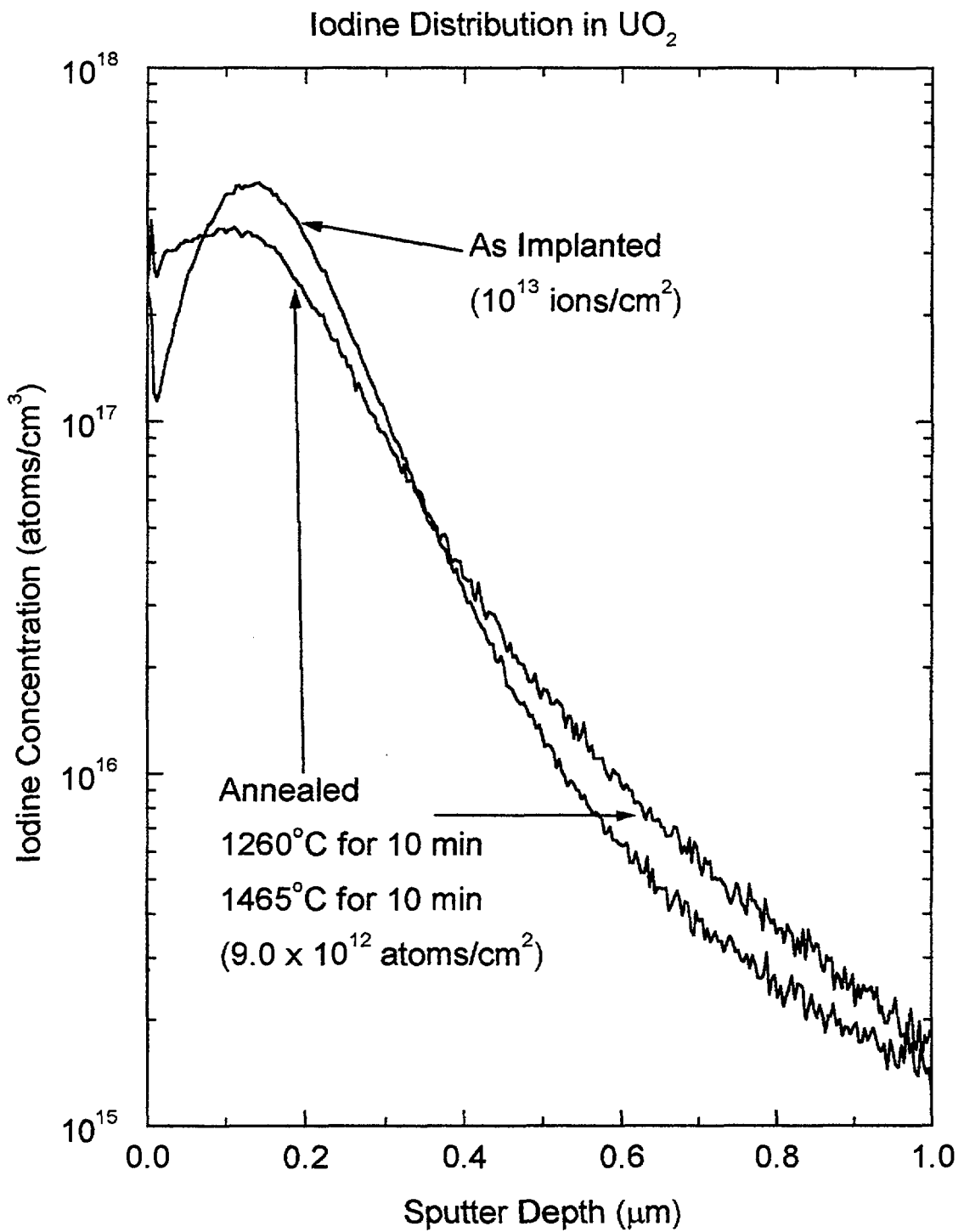


FIGURE 3 SIMS depth profile of a low fluence of iodine implanted at 1 MeV before and after anneals at 1260°C for 10 min, and 1465°C for 10 min.

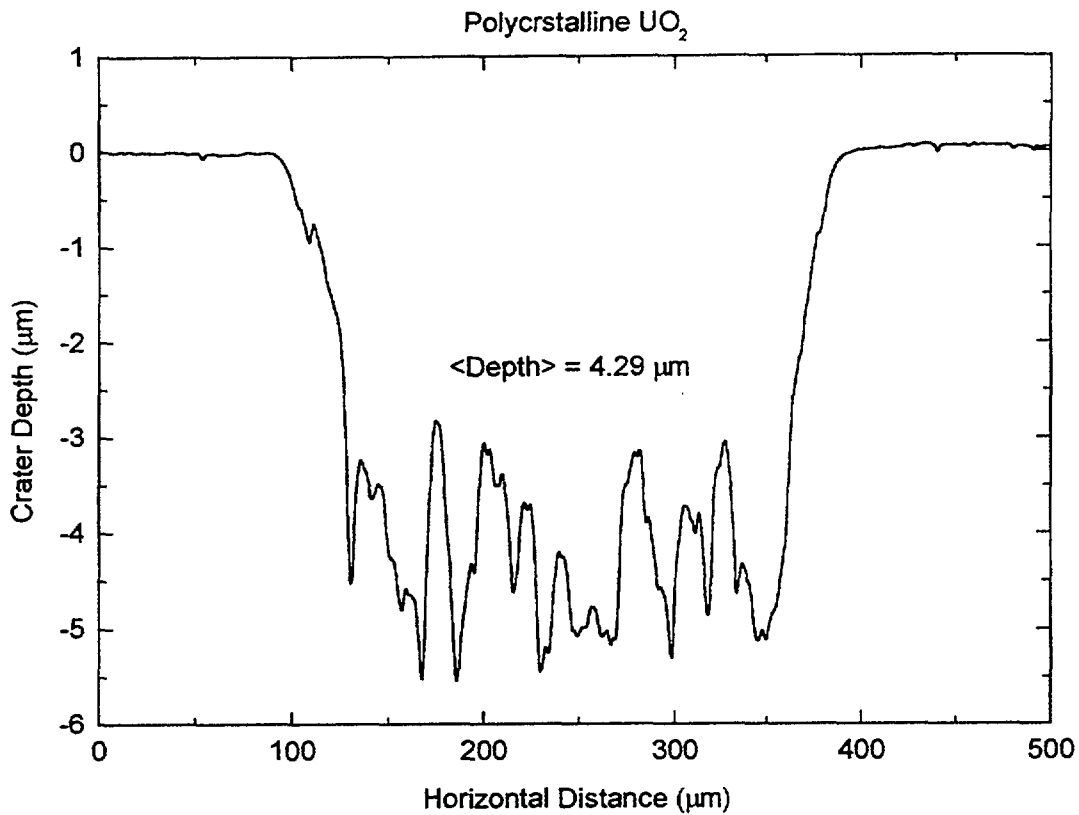


FIGURE 4 Stylus profilometer trace across a representative sputter crater in a sintered UO_2 sample implanted with a low fluence of iodine.

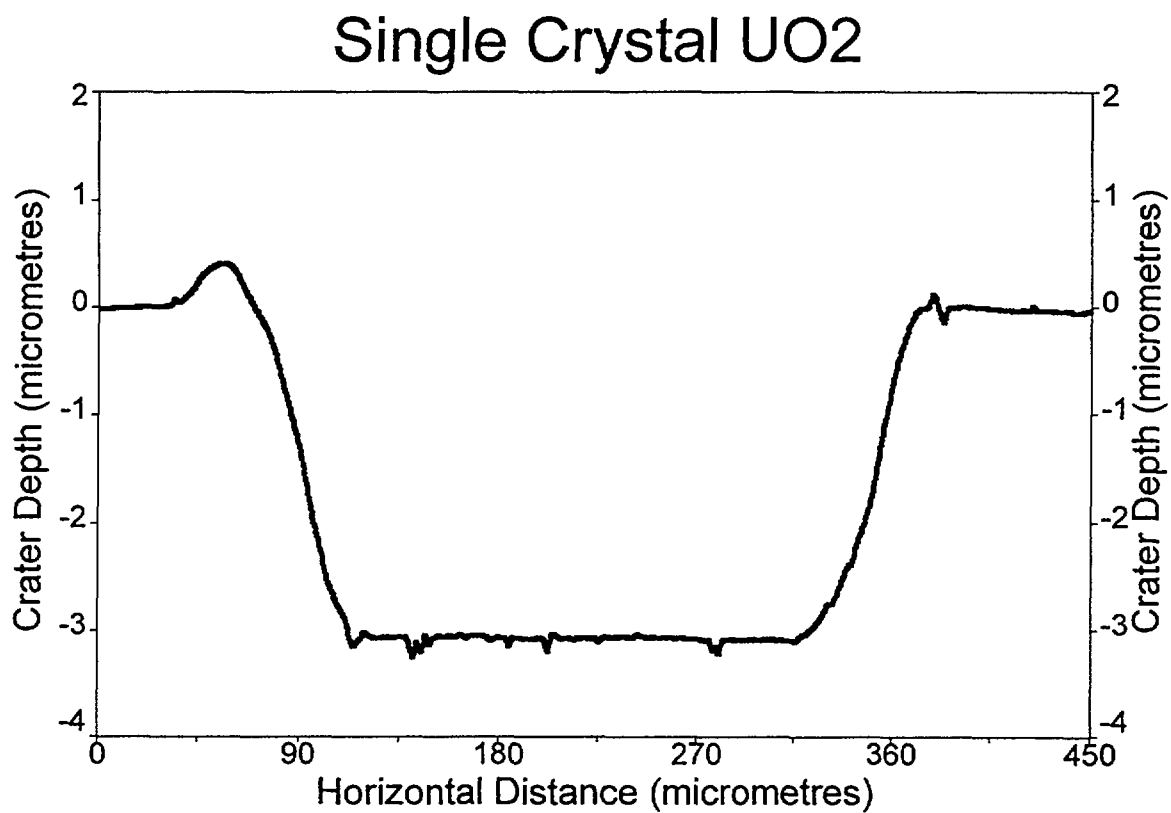


FIGURE 5. Stylus profilometer trace across a representative sputter crater in a single-crystal UO_2 sample implanted with a low fluence of iodine.

re-resolution because of fission fragments, has largely immobilized the iodine² and inhibited diffusion into the bulk.

Figure 3 show the results for a low-fluence implantation at lower temperatures – 1465°C. The main observation is that, without fission-fragment effects, the temperature was too low for diffusion into the body of the sample. A second observation is that iodine has migrated towards the sample surface – note the relatively higher concentrations near the surface and the shift of the peak maximum toward the surface. We interpret this as evidence that the damage to the lattice, caused by the ion implantation, enhanced diffusion within the damaged zone. From the sample surface to the peak maximum, the lattice was heavily damaged during the implantation, and diffusion occurred there. On the other side of the peak maximum, however, there was much less damage and little diffusion.

2.5. Depth profiling of SIMS craters

As stated above, the craters produced by the SIMS distribution measurements are all depth-profiled to calibrate the sputtering rate for each SIMS run. Profiles of the crater floors from the sintered samples were rough (Fig. 4). Because similar profiles for single crystal samples (Fig. 5) are smooth, and the horizontal scale of roughness is approximately that of the grain size, this roughness was attributed to different sputtering rates for different crystal orientations. For the rough craters, an average depth was used to determine the sputtering rate. Because the SIMS analysis is over a sample area 60 µm across, 50 to 100 grains are included in the analysis, and this number provides sufficient averaging to use an average depth in the SIMS calibration.

3. SUMMARY

Accelerators and SIMS have been used to develop a new technique for measuring fission-product diffusion rates, both intrinsic and effective (includes holdup at bubbles). Although the methods are out-reactor, in-reactor effects of fission fragments are included. Preliminary results show that at 1650°C, iodine at high concentrations is held up at bubbles if re-resolution of the bubbles is not included. At low concentrations, fewer bubbles form at 1650°C and diffusion of iodine is seen. At 1465°C, movement of iodine into the bulk UO₂ was not observed in anneals without fission-fragment effects, even at low iodine concentrations, but movement towards the surface through the layer heavily damaged by the implantation was observed. Analysis of samples prepared using a high-energy accelerator to simulate in-reactor behaviour that is due to fission fragments will be undertaken in the near future.

The results obtained to date in this study are promising. It appears that a more complete understanding of diffusion rates can be established, and we expect to be able to determine bounding limits on intrinsic and effective diffusion coefficients for specific fission products in UO₂ in the near future.

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²The reduction of iodine peak intensity and the slight asymmetry towards the sample surface is evidence that iodine diffusion through the damaged zone near the surface did occur, possibly during the temperature rise 1650°C before bubble formation was advanced.