Recovery Stages in UO_2 at Low Temperatures

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Formation of radiation damage and its recovery in UO_2 single crystals were investigated in the temperature range from 5 to 293 K. The samples were implanted with Xe ions at 5 K and subsequently *in situ* analyzed using the ion-channeling technique. Successive measurements were performed during the warming-up of the sample to 293 K. Two recovery stages in the U sublattice were revealed: the first one in the vicinity of 77 K and the second one at 110 ± 5 K.

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Radiation damage effects are of primary concern in materials for nuclear energy production. The slowing down of high-energy heavy ions (fission products with mass numbers between about 75 and 160 and energies of about 70 to 100 MeV) is the main source of nuclear energy in reactors for large-scale electricity production. The fuel of today's power stations is UO_2, a fluorite-type ceramic oxide with a melting point of 3150 K. Many investigations[1-5] have been done on UO_2 reactor irradiated at "reactor ambient" temperatures (often ~400-500 K). In addition to the not well defined and rather high temperature during damage production, a further drawback of most of these previous studies on damage ingrowth and recovery in UO_2 consists of the fact that the physical properties used to detect the damage (mainly lattice parameter, density, and electrical—or thermal—conductivity) do not uniquely indicate in which sublattice (oxygen or uranium sublattice) defects are created or anneal. Changes or stages in ingrowth or recovery curves can therefore not be uniquely attributed to oxygen or uranium defects. The Rutherford backscattering (channeling) technique[6] avoids this ambiguity. Because of the great mass difference between U and O, the radiation damage in the U sublattice can easily be studied separately. Such measurements have recently been reported for UO_2 damaged by ion bombardment at room temperature.[7] During subsequent anneals, recovery stages were observed between 670 and 1070 K. The present investigation completes this study by measuring damage formation at 5 K and following damage recovery up to room temperature. Previous work on the isostructural dioxide PuO_2 has shown a large recovery stage[8] at 54 ± 2 K. One would therefore expect a recovery stage in UO_2 below room temperature as well.

The samples used were single-crystalline UO_2 disks of ⟨100⟩ orientation. The samples were polished down to $\frac{1}{4}$-μm diamond paste and subsequently annealed at 1700 K in Ar-8% H_2 for 30 min to recover the polishing damage.[9]

The experiment to be reported was performed using the two-axis cryostatic goniometer at Institut für Nukleare Festkörperphysik (INFP), Kernforschungszentrum Karlsruhe (KfK). This setup is connected to an ion implanter and to a 2-MeV Van de Graaff accelerator which makes it possible to perform both ion implantation and Rutherford backscattering analysis without changing the temperature or the vacuum.[10]

The experiment was performed in three stages: The UO_2 single crystal mounted in a cryogenic goniometer was cooled down to 5 K, it was then implanted with 100-keV Xe ions to a fluence of 1×10^{15} atom/cm^2, and subsequently slowly warmed up to room temperature. During the warming-up, the aligned spectra were measured. The measurement time was 10 min, and the corresponding temperature change did not exceed 4 K.

Figure 1 shows the comparison of random and channeling spectra obtained for an unimplanted UO_2 single crystal and for the same crystal after implantation with 100-keV Xe ions at 5 K. The implantation fluence was low enough to avoid important cascade overlap; on the other hand, the dose was high enough to produce a damage peak of an intensity allowing an accurate determination of the damage evolution. Two well distinguished damage peaks are present for the aligned crystal: a surface peak (SP) and damage peak (DP) at larger depth. The inset shows the evolution of the damage ingrowth as a function of the implantation fluence. The SP grows rapidly and reaches its saturation value already at 0.5×10^{15} Xe ions/cm^2. On the other hand, a steady growth of DP is observed.

Figure 2 shows the spectra as measured at 5, 77, and 293 K illustrating the most important transformations which took place in the crystal. Only very small changes were observed in the spectra in the temperature range

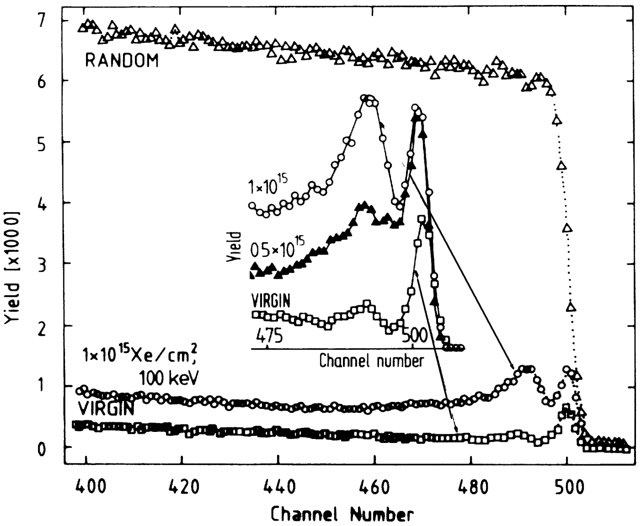

FIG. 1. Random and aligned backscattering spectra for a ⟨100⟩ UO_2 single crystal implanted with Xe ions at 5 K. The aligned spectrum for the unimplanted crystal is also shown. Inset: Aligned spectra for UO_2 single crystals implanted with different doses of Xe ions at 5 K.

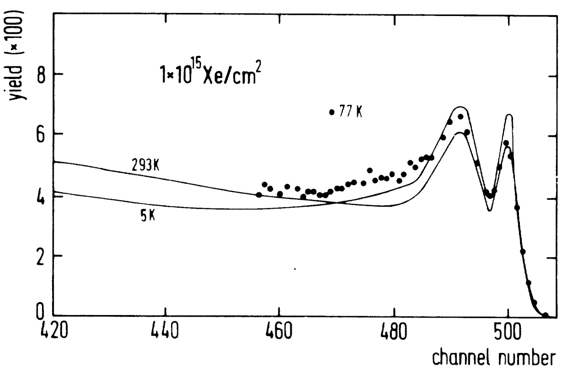

FIG. 2. Evolution with the annealing temperature of aligned spectra for a UO_2 single crystal implanted with Xe ions at 5 K.

from 5 and 70 K. Once the temperature of 77 K was reached, the warming-up was stopped and the sample was stored at this temperature for 48 h. Somewhat surprisingly, an important change of the SP was noticed after the prolonged storage at 77 K. In contrast to the SP, the changes in DP were apparently smaller. Changes in both damage peaks were noticed in the temperature interval 100–120 K: At these temperatures, both SP and DP decreased. In the course of the subsequent temperature increase up to 293 K, a small but continuous increase of both peaks was observed.

The *analysis* of the presented spectra is by no means straightforward. First of all, the changes in the spectra induced by the changes in amplitudes of thermal vibrations of crystal atoms due to different crystal temperatures have to be separated from the changes in the crystal damage. In addition, the two types of damage represented by SP and DP should be separated. The amplitudes of thermal vibrations of U and O atoms increase with increasing temperature, producing higher dechanneling levels and larger surface peaks in the aligned channeling spectra. For virgin UO_2 single crystals, the minimum yield amounted to 0.01 at 5 K, 0.02 at 77 K, and 0.03 at 293 K. The surface peak also grows and is about 25% larger at 293 K than at 5 K. Thus, the first step of the evaluation consists of the subtraction of the corresponding aligned spectra for virgin crystals from the aligned spectra for the implanted crystal. This procedure was performed for each temperature of interest.

As a next step, the dechanneling background under the damage peaks was calculated using the "linear increase model,"[11] and was subtracted from the spectra. The typical damage-depth distributions for different temperatures are shown in Fig. 3. Two characteristic portions of the damage distributions can be distinguished which correspond to SP and DP in aligned spectra.

Let us first discuss the nature of the surface peak. Ion bombardment of a binary or multicomponent material results in the modification of its surface composition due to preferential sputtering. This leads to the formation of a so-called altered surface layer.[12] Compositional changes can occur at much larger depths than that from which sputtered atoms are emitted. This effect can be attributed to ballistic processes like recoil implantation or cascade mixing, or to atomic migration phenomena such as thermal and radiation-enhanced diffusion and/or segregation. Since at 5 K the second kind of phenomena is ineffective, the formation of an altered layer at this low temperature can only be attributed to ballistic effects.

Figure 4 shows the results of calculations of the

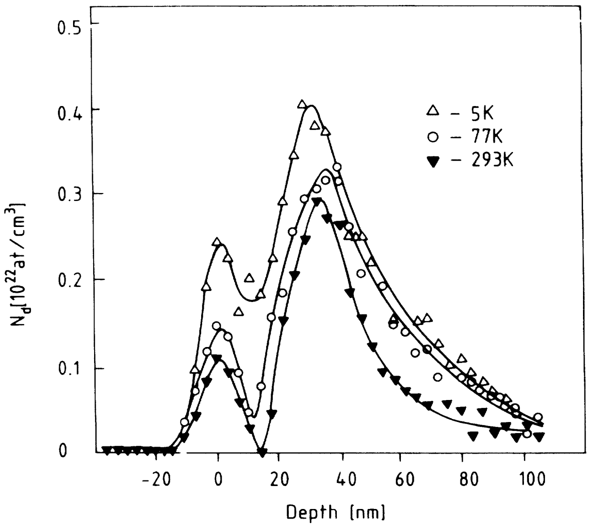

FIG. 3. Damage-depth distributions obtained from the spectra shown in Fig. 2.

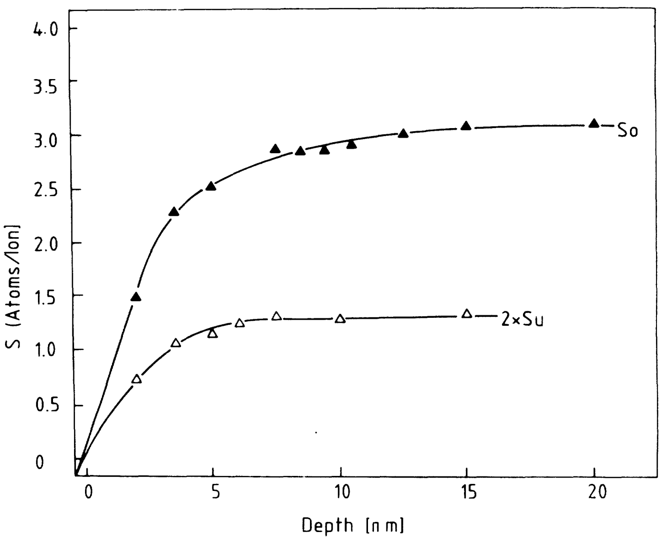

FIG. 4. Dependence of the sputtering yield on the target thickness as calculated with the TRIM.SP code. The solid lines are drawn to guide the eye.

sputtering coefficient using the TRIM.SP code.[13] The calculations were performed with surface binding energies of 9 eV for O and 30 eV for U.[14] The saturation sputtering coefficients amount to $S_O=3.1$ and $S_U=0.65$. This implies a strong depletion of the surface in oxygen creating an extremely unstable atomic configuration causing rapid, athermal rearrangements of surface atoms. The second important conclusion from Fig. 4 is that the maximum depth which contributes to sputtering amounts to approximately 7 nm. Therefore, the width of the SP is limited by the depth resolution of the experimental system which is 20 nm. Consequently, Gaussian peaks of full width at half maximum FWHM of 20 nm were fitted to the SPs and subsequently subtracted from the damage-depth distributions.

In such a way the damage due to displacement cascades (DP) can be extracted. One notes that the maximum of this distribution is located at approximately 30 nm. This value is larger than the median depth of the U-recoil distribution which according to the TRIM calculations amounts to 13 nm. This is a clear indication that some channeling of the implanted Xe ions occurs. Although this was not made purposely, it enables us to easily separate SP from DP. Also, the defect concentration is smaller which reduces the probability of defect clustering already in the collision cascade. It should also be pointed out that because of the large critical angles for channeling of 100-keV Xe ions, it is practically impossible to avoid at least partial channeling during bombardment of UO_2 single crystals with heavy ions.

The results of the warming-up experiment are summarized in Fig. 5. Two recovery stages are clearly visible. The first one, located at 77 K, appeared only after prolonged (48 h) storage at this temperature. Its location at 77 K is somewhat ambiguous because of the very slow kinetics of defect transformation. It cannot be excluded that this transformation could have taken place at somewhat lower temperatures. However, it is impossible for our experimental setup to maintain the temperature for a long time between 5 and 77 K. The second recovery stage is located at 110 ± 5 K.

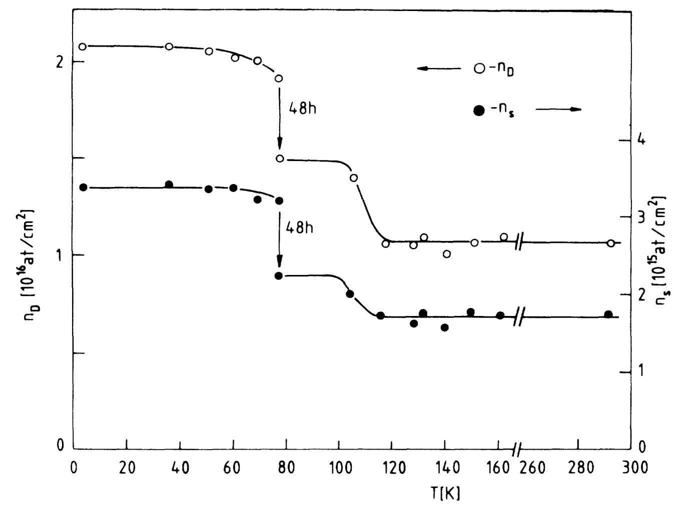

FIG. 5. Variation of the damage content in SP, n_S, and in DP, n_D, with the annealing temperature.

Recovery stages in radiation-damaged solids are usually assigned to different defect reactions, the simplest being annihilation of vacancies and interstitials by recombination. In this manner the mobility of different kinds of defects can be revealed. The presently accepted values for the onset tempertures T_m for defect mobility, and for the migration enthalpies ΔH_m for UO_2 are summarized in Table I.[15]

Up to now only one low-temperature experiment[8] was performed with a fluorite-type ceramic oxide (PuO_2) and it revealed important changes in the lattice parameter at 54 ± 2 K. The results presented in Fig. 5 are actually the first ones reported for UO_2.

The first recovery stage located in the vicinity of 70 K can be attributed to the mobility of U interstitials. Such a stage is usually rather broad.[16] It begins with so-called correlated recombinations where the close Frenkel pairs recombine. To achieve this, an interstitial atom needs to

TABLE I. Presently accepted values for the onset temperatures T_m, for defect mobility, and for the migration enthalpies ΔH_m for UO_2 (Ref. 15).

Defect	T_m (K)	ΔH_m (eV)
O interstitial	420–520	~1
O vacancy	970–1070	1.7–2.8
U interstitial	? (low)	? (0.2)
U vacancy	870–1020	2.4

make only a few jumps before it reaches its own vacancy. With increasing temperature, long-range migration of interstitials starts. During the migration, the interstitial can recombine with an alien vacancy (uncorrelated recombination). At the end of this stage, interstitials survive only in the form of small clusters.

Accordingly, the recovery stage at 110 K can be due to the migration and dissociation of small interstitial clusters (e.g., di-interstitials) and the release of interstitials from shallow traps. These processes can lead to the growth of large interstitial clusters and dislocation loops.

Previous indications of low-temperature mobilities of uranium interstitials were the observations of loops in UO_2 irradiated at room temperature with 1.8-MeV electrons[17] or in UO_2 irradiated in nuclear reactors[18] at temperatures between 50 and 100 °C, as well as results of radiation-enhanced U diffusion[19,20] in UO_2 at low temperatures. In contrast, an analysis[21] of high-temperature diffusion data[22] yielded a rather high activation enthalpy for U interstitials, i.e., 2.0 eV, which, however, is still lower than the corresponding value for U vacancies (2.4 eV). Theoretical calculations,[23] finally, had predicted U interstitials to be less mobile than U vacancies. The present data do not support such values, but are rather helpful in explaining the rather high measured coefficients of fission-enhanced U diffusion.[19,20] The present results confirm the picture of a temperature-independent mobility of U interstitials away from the center of the fission spikes, due to the biasing force of the connected presure effects as postulated previously.[19,20]

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