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Vacancy defects induced in sintered polished UO_2 disks by helium implantation

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Abstract. Vacancy defects have been investigated in sintered polished and annealed uranium oxide disks. Slow positron beam coupled with Doppler broadening spectrometer was used to probe the track region of 1 MeV ^{3}He ions implanted in UO_2 disks. The low and high momentum annihilation fractions, S and W respectively, were measured in the first µm near surface region of the disks as a function of positron energy. The S and W values indicate that the 1MeV He ions induce vacancy defects in the track region of their range. The vacancy defect depth distribution is heterogeneous. The positron trapping at these vacancy defects increases with the depth and with the implantation fluence indicating an increase of the vacancy defect concentration. The nature of the induced vacancy defects doesn't change with the fluence.

Keywords : Slow Positron Beam, uranium dioxide, vacancy defects, helium implantation, Doppler broadening

Introduction

A few experiments have been performed on the behavior of helium gas produced by alpha decay of actinides in spent fuel. Yet the amount of helium produced after irradiation are large in particular in the case of MOX (Pu, U mixed oxides) fuels : in MOX (burnup 47.5 Gwatt day /tons of Uranium), after a storage of 10,000 years the He amount is evaluated at 4 % He at/at_{iHM} (atoms per initial heavy metal atom). In CERI we are investigating the He migration process, bubble formation and He-vacancy defect interaction using Nuclear Reaction Analysis method to determine the helium depth profile in as-implanted UO_2 and positron annihilation spectroscopy to study vacancy defect properties.

The radiation damage in UO_2 has been already studied by using different techniques : Weber has used XRD [1] to measure the lattice parameter change as a function of the alpha decay dose. Matzke et al have studied the damage induced in UO_2 by heavy ion implantation by using channeling Rutherford Backscattering [2]. Soullard et al have shown with TEM the formation of interstitial clusters by irradiation with electrons (E> 1.6 MeV) at 300K [3]. While very few results have been published concerning the study of vacancy defects in UO_2 by using positron annihilation spectroscopy [4,5]. The annihilation characteristics (diffusion coefficient, lattice and defect lifetimes..) are not known in this UO_2 matrix. This work is a part of the study we have undertaken in CERI to determine these data and the defect properties.

In this work we have used slow positron beam coupled with Doppler broadening spectroscopy to study the vacancy defects induced in the track region of 1 MeV ^{3}He ions implanted in polished and 1700°C/24h/ArH_2 annealed sintered UO_2 disks.

Experimental.

Up to 15 disks cut from the same set of sintered uranium (0.2 at.% ^{235}U) dioxide pellets have been used for this study. After polishing of one side, the disks were annealed at 1700°C in a wet ArH_2 atmosphere to keep the samples at the stoichiometric composition. The mean grain size is about 18 µm and the mean O/U ratio is 2.0051±0.0001 as determined by polarography. The density of the material is 10.76 ± 0.03 g.cm^{-3}. The disks are 300 µm thick and 8.2 mm in diameter.

Ten UO_2 disks have been implanted with 1 MeV ^{3}He ions using the 3.5 MeV Van der Graaff accelerator at CERI Orléans. The implantation is performed by focusing the beam (1×1 mm^2) and by sweeping it over the disk surface to ensure a homogeneous fluence (see reference [6] for details). Seven different fluences have been performed in the range from 2×10^{14} cm^{-2} to 1×10^{17} cm^{-2}. For

each fluence, two UO_2 disks have been implanted during the same run. The flux were fixed from 1.6×10^{11} ^3He $cm^{-2}.s^{-1}$ for the implantations at the lowest fluences to 1.7×10^{12} ^3He $cm^{-2}.s^{-1}$ for the ones at the highest fluences. The temperature was below to 80°C during implantations.
The 1 MeV ^3He ion range in UO_2 calculated with SRIM program [7] has a value R_p=1.9 µm. The number of O and U vacancies induced per incident ion and per depth unit is calculated with SRIM as a function of depth, by using as displacement energies in the two sublattices : $E_d(U)$= 40eV and $E_d(O)$=20eV [8]. Let's notice that SRIM doesn't take into account the recombinations that could occur during implantation. In the track region of ^3He ions located between surface and approximately 1.5 µm depth, corresponding to the thickness of the ^3He implanted UO_2 disk which is probed with the slow positron beam, the total vacancy concentration $[V_{tot}]$ slightly varies as a function of depth (Fig.1) from 1×10^{21} cm^{-3} to 8×10^{21} cm^{-3} for the 1×10^{16} cm^{-2} ^3He fluence.

The positron-electron pair momentum distribution has been measured at 300 K by recording the Doppler broadening of the 511 keV annihilation line characterized by the low (S) and the high (W) momentum annihilation fraction in the momentum range (0-|2.80|) $x10^{-3}$ m_0c and (|10.61|-|26.35|)$x10^{-3}m_0c$ respectively. The energy resolution of the Ge detector is 1.76 keV at 1.28 MeV. To investigate the depth dependence of S and W, the curves S(E) and W(E) were recorded as a function of the positron energy E changed in 0.5 keV steps in the 0.5 to 25 keV range using the slow positron beam [9] at the CERI laboratory. The positron mean implantation depth in UO_2 varies from approximately 1 nm to 670 nm in this energy range [10]. The disk B23 polished and annealed at 1700°C during 24 hours in humid ArH_2 atmosphere has been measured regularly as a reference sample. In this disk, S and W values remain constant between 5 and 25 keV (S_{B23} = 0.3727(5); W_{B23} =.0.0783(2))

Results and discussion.

***As-received sintered UO_2 disks* :**

Five as-received sintered polished and 1700°C/24h/wet ArH_2 annealed UO_2 disks have given reproducible results which are shown for one disk in Fig.2. S(resp. W) decreases rapidly (increases) as a function of positron energy from 0.5 keV up to 2 keV and then more slowly up to 5 keV. Finally S and W remain constant from 5 keV to 25 keV. The S and W values measured on the plateaux between 5-25 keV are respectively (Sref, Wref)= (0.371 (1),0.079 (2)). The positronium fraction calculated from the 3 to 2 gamma annihilation rates reaches about 5% at 0.5 keV and becomes negligible from 1.5 keV. From 0.5 to 2 keV the S(E) and W(E) changes don't follow a diffusion law. *A modified version of VEPFIT [11] is used to consistently fit the S(E) and W(E) curves from 2.5 keV and the data below 2.5 keV are discarded* . The adjustment of the fit to the experimental data using one homogeneous layer model leads to a positron effective diffusion length L_+ = 11 nm and to the annihilation characteristics equal to the plateau values and considered as the reference values in this work : S_{ref} = 0.371(5), W_{ref} = 0.0785(2). It indicates that annihilation occurs in either two different states or two sets of annihilation states and the proportion of annihilation in each state remains constant as a function of depth. One of the set characterizes the annihilations at surface and the second one, the annihilations in the bulk of the disk These S_{ref}, W_{ref} values are respectively the lowest and the highest measured in the different sintered UO_2 sets that we have characterized up to now suggesting that they could correspond to the annihilation characteristics in the UO_2 lattice. But the effective positron diffusion length in the disks is very low compared to the ones that have been measured in other materials (100 – 300 nm) [11]. This L_+ value could be due either to an electrical field which could drive positrons towards the bulk of the disk, or to a high trapping rate at defects. We performed some positron lifetime measurements as a function of temperature with ^{22}Na fast positron source in a couple of UO_2 disks from the same set. It has shown a high trapping rate at negatively charged traps with a lifetime of 171ps [12]. The O/U ratio of 2.0051±0.0001 determined in the disks studied here indicates an oxygen excess. This stoechiometry deviation indicates that these UO_2 disks are p-type semiconductors [13]. It suggests that the negatively charged defects detected by positron could be related to oxygen interstitials. If that hypothesis is true, one can assume that this defect is ionic type and consequently the lifetime determined for this defect is also characteristic of annihilation in the UO_2 lattice. From the L_+ determined in as-received UO_2 it is possible to give an estimation of the trapping rate by assessing the positron diffusion coefficient -unknown in UO_2- is equal to the mean value determined in other solids 1.5 $cm^2\ s^{-1}$ [11]. It gives a trapping rate of about $10^{12}\ s^{-1}$ in the as-received sintered polished and 1700°C/24h/wet ArH_2 annealed UO_2 disks. If we assume a trapping coefficient of $3x10^{15}$ at. s^{-1} as determined at 300K for negatively charged Ga_{As} antisites in GaAs, the trap concentration in these UO_2 disks is $3x10^{19}\ cm^{-3}$. Assuming that one trap corresponds to one oxygen interstitial it leads to a stoechiometry deviation of about 10^{-3}. This value is in the same order of magnitude as the one determined with polarography.

In the following, only the relative values of the S and W characteristics will be given, determined as the ratios S/S_{ref} and W/W_{ref} respectively.

1 MeV ^3He implanted sintered UO_2 disks

The S and W positron annihilation characteristics in the ten ^3He implanted sintered UO_2 disks differ strongly from the ones measured in the as-received UO_2 disks. Whatever the fluence, all

the S(E) values are higher in the implanted disks than in the as-received ones when all the W(E) values are respectively lower. This indicates that ^{3}He ions have induced vacancy-related defects in their track region. Except for the highest fluence 1×10^{17} cm^{-2}, the S(E) and W(E) curves have the same general look as it is shown in Figure 2a and 2b for the 5×10^{15} ^{3}He cm^{-2} fluence. S is high at the surface and decreases very fast as E increases up to 1.5 or 2 keV depending on the ion fluence. Then S(E) increases more or less fast also depending on the ion implanted fluence. W(E) behaves in a reverse way. S(E) and W(E) reach plateau values when the fluence is sufficiently high ($\geq1\times10^{16}$ ^{3}He cm^{-2}) for positron energy value which depends on the ^{3}He fluence. This provides evidence that the spatial distribution of defects seen by positrons is heterogeneous in concentration and, or, in type as a function of depth, and that this spatial distribution changes with the implantation fluence.
For the 5×10^{15} ^{3}He cm^{-2} implanted UO_2 disk, the S(W) plot above 1.5 keV consists of a segment of straight line denoted D running over the total energy range (Fig. 2c) where S globally increases and W decreases as the positron incident energy increases. This indicates that positrons annihilate, at least, into two different states. If more than two different states are detected these states are grouped into two different sets : one set is characteristic of the near surface and the second one of the bulk. Only the proportions of the both state sets change as a function of the depth. This D segment of straight line goes through the (Sref,Wref) point - characteristic of annihilation in as-received UO_2 - indicating that, whatever the positron incident energy, a fraction of the positrons annihilate at the negatively charged traps detected in the as-received UO_2. This fraction decreases with the depth. A good fitting of the S(E) and W(E) data measured in the 5×10^{15} ^{3}He cm^{-2} implanted disk is obtained when using a three homogeneous layer model. The (S ;W) values are (1.051 ; 0.92) in the first layer. S increases and W decreases in the second layer to reach (1.063 ; 0.90) in the third one. The effective diffusion length L_+ decreases from approximately 5.5 nm in the first layer down to 3.5 nm in the last one. It remains lower than the one determined in the as-received UO_2 and decreases as S increases. It indicates that the trapping at vacancy defects increases with the depth, and suggests that, as it is expected from the SRIM calculations, a continuous gradient would be more correct to describe the vacancy depth profile than the model with 3 homogeneous layers.
The same conclusions can be driven also for all 1 MeV ^{3}He implanted UO_2 disks with a fluence $\leq 10^{17}$ cm^{-2} as it can be observed in the figure 3. S and W saturations are observed at high positron energy (about 18 keV) for the 5.10^{16} ^{3}He.cm^{-2} fluence and from 2 keV for the highest fluence of 10^{17} cm^{-2}. This saturation phenomenon is due to the saturation of positron trapping at the different defects detected in UO_2 that means the vacancy defects induced by the implantation but also the negatively charged ones present in the UO_2 disks before implantation and which can be still detected after implantation.

The S(W) points with positron energy and ^{3}He fluence as the running parameters -plotted in figure 3b- follow the same straight line which goes through the (Sref, Wref) point. It indicates that the nature of the detected vacancy defects doesn't depend on the ^{3}He fluence. This straight line has a slope R = ΔS/ΔW = 0.64. It is the same slope as the one measured in as-polished UO_2 disks [5], indicating that the same defects are detected in the near surface after polishing and in the track region of 1 MeV ^{3}He ions. Matzke et al have demonstrated that polishing induces disorder in the U sublattice by using channeling RBS in monocristalline UO_2 [14]. Evans et al have also observed polishing damage with slow positron beam and by comparing their results with Matzke and his coworkers studies they have attributed the increase of the low momentum fraction S near the surface to the positron detection of uranium vacancies V_U [4]. Even if one can expect that V_U are detected in the track region of 1MeV ^{3}He implanted UO_2, it doesn't exclude the detection of V_O Oxygen vacancy related defects. Indeed C/RBS is much less sensitive to the disorder in the O sublattice and also because O interstitial recombination with V_O should be difficult during implantation due to the high migration energy (about 1 and 1.7-2.8 eV respectively) that have been determined [15].

Summary

The momentum distribution of annihilating electron-positron pairs has been measured by Doppler broadening spectroscopy with a slow positron beam in polished and 1700°C/24h/ArH_2 annealed sintered UO_2 disks. A high positron trapping rate has been found in these as-received disks and has been attributed to acceptor defects. After implantation with 1 MeV ^{3}He at different fluences in the range from 2×10^{14} to 1×10^{17} ^{3}He cm^{-2}, vacancy defects have been detected in the ion track region (0-1.5µm deep zone). The nature of these vacancy defects is the same whatever the depth in the ion track region and whatever the ion fluence, fixed in the investigated range. Positron trapping at these track region vacancy defects has been shown to increase with the ^{3}He fluence up to reach saturation from 1×10^{16} ^{3}He cm^{-2} deeper in the track region and at 1×10^{17} ^{3}He cm^{-2} for its whole thickness.

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References

[1] W. J. Weber, Journal of Nuclear Materials **98** (1981) 206.

[2] H. Matzke and A. Turos, Nuclear Instruments & Methods in Physics Research, Section B Beam Interactions with Materials and Atoms **46** (1990) 117.

[3] J. Soullard, Journal of Nuclear Materials **135** (1985) 190.

[4] H. E. Evans, J. H. Evans, P. Rice-Evans, et al., Journal of Nuclear Materials **199** (1992) 79.

[5] M.-F. Barthe, S. Guilbert, H. Labrim, P. Desgardin, T. Sauvage, G. Blondiaux, G. Carlot, P. Garcia and J.P. Piron, Mat. Science Forum, Vols 445-446(2004) 48

[6] S. Guilbert, T. Sauvage, P. Garcia, et al., Journal of Nuclear Materials **327** (2004) 88.

[7] J. F. Ziegler and J. P. Biersack , *The stopping and range of ions in solids*, (Pergamon press, New York, 1985)

[8] J. Soullard and A. Alamo, Radiation Effects **38** (1978) 133.

[9] P. Desgardin, L. Liszkay, M.-F. Barthe, et al: Mater. Sci. Forum Vol.363-365 (2001) 523.

[10] E. Soininen, J. Mäkinen, D. Beyer and P. Hautojärvi, Phys. Rev. B 46 (1992) 13104

[**Erreur ! Signet non défini.**~~**Erreur ! Signet non défini.**~~] A. Van Veen, H Schut, J. de Vries, et al AIP Conf. Proc. **218** (1990) 171.

[11] "Positron spectroscopy of defects in metals and semiconductors" P. Hautojärvi and C. Corbel in Positron spectroscopy of solids edited by A. Dupasquier and A. P. Mills jr (1995) 511

[12] MF Barthe, H. Labrim, P. Desgardin to be published

[13] R. K. Willardson, J. W. Moody, and H. L. Goering, J. Inorg. Nucl. Chem. **6** (1958) 19.

[14] H. Matzke and A. Turos, Journal of Nuclear Materials **113** (1983) 249.

[15] H. Matzke, J. Chem. Soc. Faraday Trans. 2 **83** (1987) 1121

Figure 1 : SRIM Calculations of the vacancy and helium concentrations as a function of the depth in 1MeV ^{3}He implanted UO_2 at the $1x10^{16}$ cm^{-2} fluence

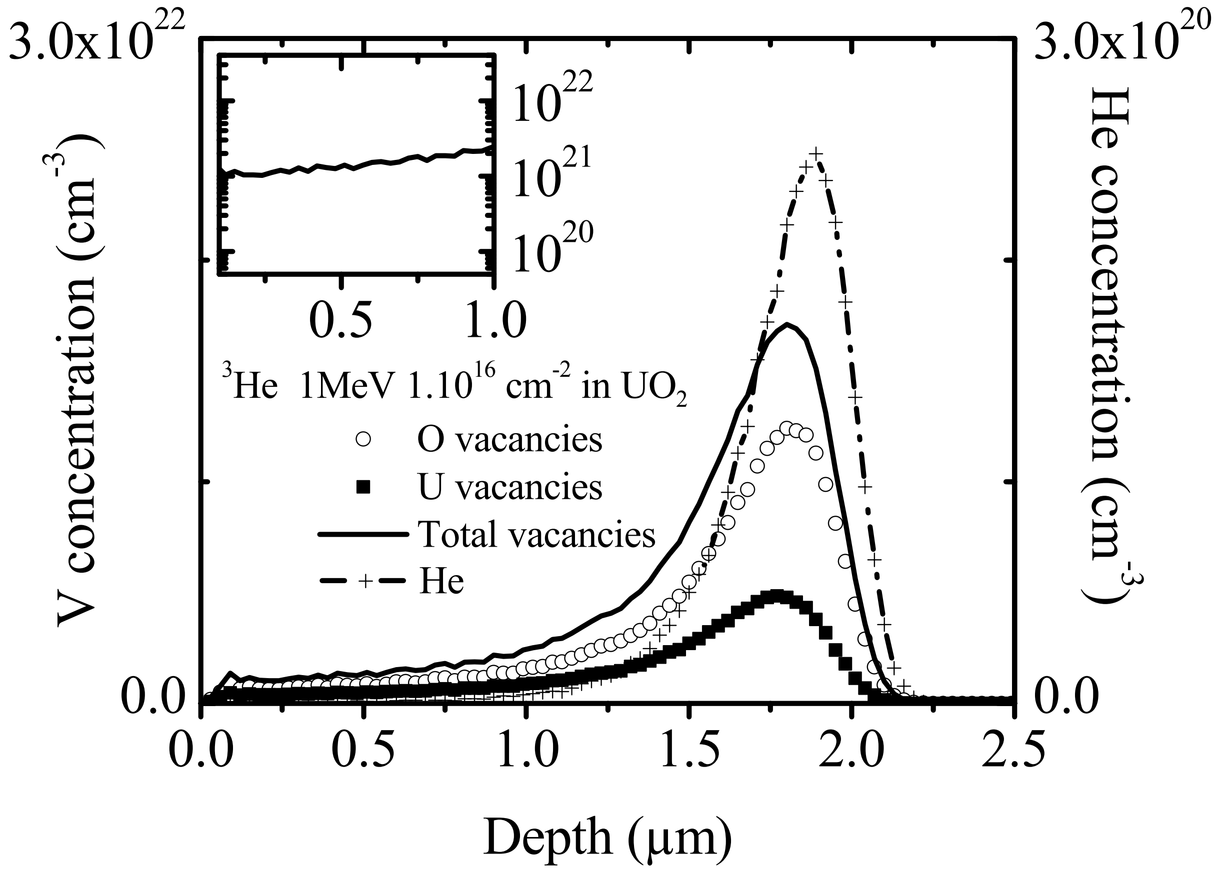


Figure 2: Relative low momentum fraction S/S_{ref} and relative high momentum fraction W/W_{ref} as a function of positron energy (a,b respectively) and S/S_{ref} as a function of W/W_{ref} (c) in *UO_2 disks before* (○) *and after 1 MeV ^3He implantation at the $5x10^{15}$ cm^{-2} fluence* (■). A modified version of VEPFIT is used to consistently fit (solid lines) the S, W curves with a model of homogeneous layers.

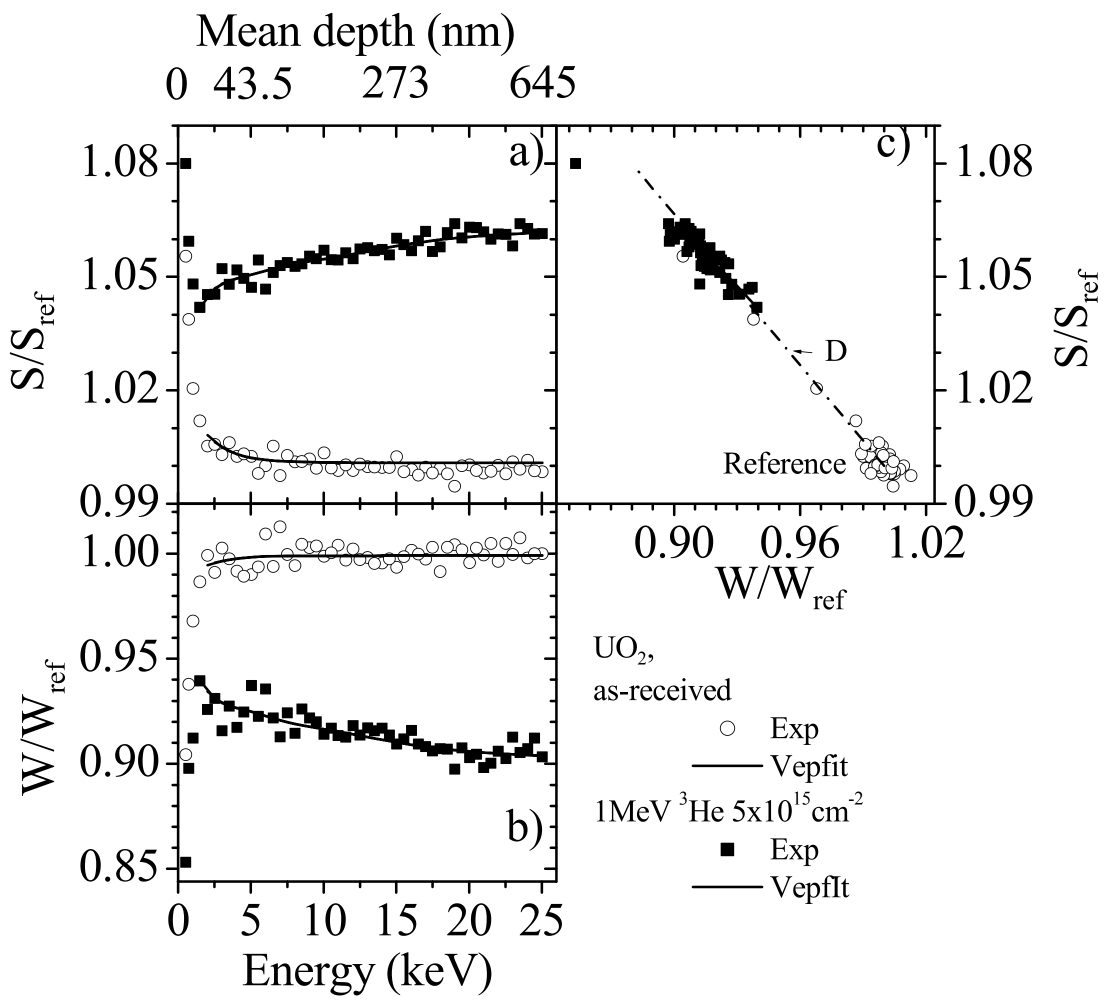
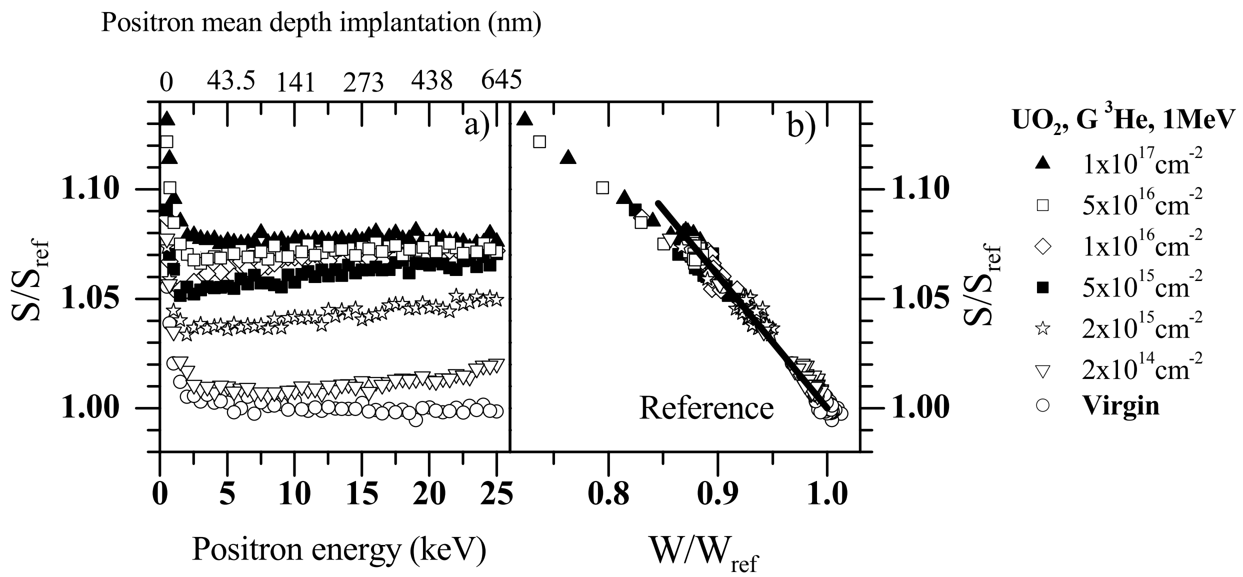


Figure 3: Relative low momentum fraction S/S_{ref} as a function of positron energy (3a) and as a function of relative high momentum fraction W/W_{ref} (3b) in *UO_2 disks before* (○) *and after 1 MeV ^3He implantation at different fluences in the range from $2x10^{14}$ to $1x10^{17}$ cm^{-2}.*



References :

[1] W. J. Weber, Journal of Nuclear Materials **98**, 206 (1981).

[2] H. Matzke and A. Turos, Nuclear Instruments & Methods in Physics Research, Section B Beam Interactions with Materials and Atoms **46**, 117 (1990).

[3] J. Soullard, Journal of Nuclear Materials **135**, 190 (1985).

[4] H. E. Evans, J. H. Evans, P. Rice-Evans, et al., Journal of Nuclear Materials **199**, 79 (1992).

[5] M.-F. Barthe, S. Guilbert, H. Labrim, P. Desgardin, T. Sauvage, G. Blondiaux, G. Carlot, P. Garcia and J.P. Piron, Mat. Science Forum, Vols 445-446, 2004, p. 48

[6] S. Guilbert, T. Sauvage, P. Garcia, et al., Journal of Nuclear Materials **327**, 88 (2004).

[7] J. F. Ziegler and J. P. Biersack , *The stopping and range of ions in solids*, (Pergamon press, New York, 1985)

[8] J. Soullard and A. Alamo, Radiation Effects **38**, 133 (1978).

[9] P. Desgardin, L. Liszkay, M.-F. Barthe, et al: Mater. Sci. Forum Vol.363-365 (2001), p. 523.

[10] E. Soininen, J. Mäkinen, D. Beyer and P. Hautojärvi, Phys. Rev. B 46 (1992), p. 13104

[11] "Positron spectroscopy of defects in metals and semiconductors" P. Hautojarvi and C. Corbel in Positron spectroscopy of solids edited by A. Dupasquier and A. P. Mills jr 1995, p 511

[12] MF Barthe, H. Labrim, P. Desgardin to be published

[13] R. K. Willardson, J. W. Moody, and H. L. Goering, J. Inorg. Nucl. Chem. **6**, 19 (1958).

[14] H. Matzke and A. Turos, Journal of Nuclear Materials **113**, 249 (1983).

[15] H. Matzke, J. Chem. Soc. Faraday Trans. 2 **83**, 1121 (1987)