RADIATION ENHANCED DIFFUSION OF NEODYMIUM IN SINGLE CRYSTAL THIN FILM UO₂

BY

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THESIS

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ABSTRACT

Radiation-enhanced diffusion (RED) of a Nd buried tracer layer in UO$_2$ thin films was measured with Secondary Ion Mass Spectrometry (SIMS). Samples were irradiated with 1.8 MeV Kr$^+$ over a temperature range from 400 °C to 800 °C. RED in UO$_2$ was found to be in the recombination limited regime with activation energy of $E_a = 0.41 \pm 0.04 \text{eV}$ and corresponding migration energy of $E_m = 0.82 \pm 0.08 \text{eV}$. The radiation enhanced diffusion in the temperature range above can be represented by the equation

$$D_{RED} = 1.62 \times 10^{-15} \exp\left(-\frac{0.41}{kT}\right) \text{cm}^2/\text{sec},$$

Dose rate dependence measurement showed $D_{RED}$ was proportional to the square root of the irradiation flux, further demonstrating that the diffusion mechanism in the temperature range could be characterized by the recombination limited kinetics. Mixing parameter measurements yielded $\xi = 1.65 \pm 0.13 \text{Å}^2/\text{eV}$ on the cation sublattice, which indicated that ballistic mixing was the dominant mechanism of ion mixing. Thermal diffusion was also measured in the temperature range above. A very small yet observable diffusivity on the order of $10^{-20} \text{cm}^2/\text{sec}$ was measured at 800 °C. A comparison of the diffusion properties between UO$_2$ and CeO$_2$ showed different behavior of the two materials, which indicated that the CeO$_2$ system might not be a good surrogate for the UO$_2$ system in terms of radiation enhanced diffusion.
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CHAPTER 1: INTRODUCTION

Atomic diffusion is a basic process that controls many phenomena during fabrication and irradiation of nuclear fuels, like sintering, creep, grain growth, fission gas bubble formation and migration, and fission gas release. In most ceramic nuclear fuels, cation diffusion is much slower than anion diffusion and the slower species is rate-controlling normally, so all the processes above are related to cation diffusion. The dependence of the cation mobility on temperature, on deviations from stoichiometry, on impurities, etc., should all be known to understand the diffusion processes.

Radiation enhanced diffusion (RED) occurs when materials are irradiated by energetic heavy ions at elevated temperature. Diffusion is enhanced because the concentration of defect population is increased and other diffusion channels may be opened up over thermal equilibrium mechanics by displacement cascade damage during heavy ion irradiation [1]. Fission products which create defects while travel in nuclear fuel represent such a scenario. Diffusion of transuranic actinides, the most long-lived irradiation by-products in $\text{UO}_2$, could be enhanced at elevated temperature. And these elements are removed from spent fuel and incorporated into fresh fuel for transmutation [2]. However, little is known about the behavior of the actinides in the $\text{UO}_2$ fuel during operation [3].

The transport of all chemical species in nuclear fuel results in dimensional instability, grain morphological changes, open pore volume/bubble formation and precipitation [4]. The effect of radiation enhanced diffusion on impurity transport is of special interest in a closed nuclear fuel
cycle. Since UO$_2$ is widely used as the fuel in nuclear reactors and the importance of understanding the underlying process of impurities, the present work studies the radiation enhanced diffusion in UO$_2$ in the elevated temperature, energetic heavy ion bombardment environment.

Single crystal UO$_2$ film with a tracer layer of neodymium in the film middle has been grown on YSZ substrates using a reactive-gas magnetron sputtering system. Neodymium is most commonly found in the Nd$^{3+}$ valence state and is therefore an attractive surrogate for americium which is difficult to oxidize beyond +3.

X-Ray Diffraction (XRD) has shown a single crystal property and the film thickness has been obtained from the X-Ray Reflectivity (XRR). Rutherford Backscattering Spectrometry (RBS) with 2 MeV He$^+$ and energetic heavy ion bombardment with 1.8 MeV Kr$^+$ has been performed by using HVE Van de Graaff accelerator in the University of Illinois. A set of thermal-only measurements has also been done to measure the thermal diffusion without irradiation. Secondary Ion Mass Spectrometry (SIMS) has been used to measure the depth profile of the film before and after thermal/irradiation treatments. The standard deviation from the Gaussian fitting of the Nd peak in the film has been converted to diffusivity. Three sets of experiments have been done using the experimental instruments and method above: room temperature, with variable doses to measure the mixing parameter, constant dose, irradiated at different temperature to measure the activation energy and constant temperature, constant dose with different dose rate measurement.

The experimental procedures are presented in chapter 4, in which sample growth parameters, irradiation conditions, and SIMS measurement characteristics are all discussed. The film
characterization from the XRD measurement, depth profile of Nd for various irradiation conditions from SIMS measurement are shown in chapter 5. Calculation and analysis of diffusivities are presented in chapter 6. A comparison between the present work and the other related results (uranium self-diffusion, RED in CeO$_2$, RED in UO$_2$ during fission) is discussed in chapter 7.
2.1 Normalized Mixing Parameter

If a solid containing a buried marker is irradiated, the marker layer may become mixed with the matrix through one of the three displacement processes: direct recoil displacement, collision cascades and thermal spikes [6]. Mixing due to these prompt events should be temperature independent. It is convenient to characterize the mixing of a buried layer in terms of the normalized mixing parameter

\[ \xi = \frac{D t}{\Phi F_d} \]  

(2.1)

where \(D\) is the diffusion coefficient, \(t\) is the irradiation time, so that \(Dt\) represents the mean square displacement \(<r^2>\) associated with mixing. \(\Phi\) is the dose, \(F_d\) is the nuclear differential energy deposition, so that the product \(\Phi F_d\) represents the total nuclear differential energy deposition. So the mixing parameter is a constant of proportionality that equates the total nuclear differential energy deposition to the total mean square displacement induced by displacement cascade damage [14].

The mixing parameter normalizes for the various irradiation conditions of ion energy and mass through the damage energy, thereby allows comparisons of mixing in different systems. If only direct recoil and cascade mixing are present, transport calculations predict a mixing parameter of approximately 1.0 to 2.0 \(\text{Å}^2/\text{eV}\) which is roughly independent of the material [6].
2.2 Radiation Enhanced Diffusion (RED)

When materials are irradiated by energetic heavy ions at elevated temperature, enhanced diffusion occurs because the concentration of defect population is increased and other diffusion channels may be opened up over thermally activated processes by displacement cascade damage [1, 5]. Supersaturation of interstitial and vacancy point defects remain in the lattice at the completion of a collision cascade or thermal spike phases of a cascade. These point defects are immobile and do not contribute to additional mixing at low temperatures (T/Tm<0.4 for UO₂ approximately, Tm is the melting point). However, at higher temperatures, the point defects become mobile, and then add to the mixing as they undergo long range migration. Mobile point defects migrate until they recombine with their anti-defect (vacancy–interstitial recombination), or become trapped or annihilated at a defect sink. These different reactions limit the amount of mixing and control all the high temperature radiation effects such as void swelling, segregation, embrittlement, etc. [6]

Lomer [7], Dienes and Damask [5] first presented the fundamentals of RED theory for metals and later reviewed by Sizmann [1].

The very basis for the radiation enhanced diffusion effects is given by the equation:

\[ D_a = f_v D_v C_v + f_{2v} D_{2v} C_{2v} + f_i D_i C_i + ... \]  \( (2.2) \)

where \( D_a \) is the diffusion coefficient of a particular lattice atom. \( f \) values are the correlation factors [8] and are usually <1, \( D \) values are the diffusion coefficients, \( C \) values are the concentration. Subscript \( v \) means vacancies, \( 2v \) means di-vacancies, \( i \) means interstitials, etc.
This equation shows two aspects for increasing $D_a$ by radiation. One is by increasing the concentration of those defect species, e.g. vacancies. The other is by opening up other diffusion channels, e.g. di-vacancies, tri-vacancies [1].

The kinetics was treated by employing chemical rate equations. Three assumptions are made for analytical solutions for the rate equations by Lomer, Dienes and Damask, and Sizmann:

1. Production of point defects is homogeneous;
2. Only vacancy-interstitial recombination, interstitial-sink annihilation and vacancy-sink annihilation reactions are included. Di-vacancies and di-interstitials or other higher order complexes formation is ignored;
3. No concentration gradient of defects is present in the sample.

It should be noted that this is a simplified model and was done for a pure single atom system.

Under these assumptions, the kinetics can be written in simultaneous and consecutive chemical rate equations, e.g.

$$\frac{dC_v}{dt} = K_o - K_{iv}C_iC_v - K_{vs}C_vC_s$$  \hspace{1cm} (2.3) \\
$$\frac{dC_i}{dt} = K_o - K_{iv}C_iC_v - K_{is}C_s$$  \hspace{1cm} (2.4)

where $C_v$, $C_i$ and $C_s$ are the concentrations of vacancies, interstitials and sinks respectively, $K_o$ is the production rate of Frenkel pair in displacements-per-atom/sec (dpa/sec). $K_{iv}$, $K_{is}$ and $K_{vs}$
are rate constants for the reactions of interstitial-vacancy recombination, interstitial-sink annihilation and vacancy-sink annihilation respectively.

For the case of vacancy-interstitial recombination and point defect annihilation at a spherical sink the rate constants are given as [1]:

\[ K_{iv} = \frac{4\pi r_{iv} (D_i + D_v)}{\Omega} \]  \hspace{1cm} (2.5)

\[ K_{vi} = \frac{4\pi r_{vi} D_i}{\Omega} \]  \hspace{1cm} (2.6)

\[ K_{vs} = \frac{4\pi r_{vs} D_v}{\Omega} \]  \hspace{1cm} (2.7)

where the \( r_{iv} \) are the respective radii, \( D_i \) and \( D_v \) are the diffusivities of interstitials and vacancies, \( \Omega \) is the atomic volume. At steady state, the solutions for the vacancy and interstitial concentration are:

\[ C_v = \frac{K_{vi} C_i}{2K_{iv}} + \left[ \frac{K_{vi} K_{iv} + K_{iv}^2 C_i^2}{K_{i} K_{vs} + 4K_{iv}^2} \right]^{1/2} \]  \hspace{1cm} (2.8)

\[ C_i = \frac{K_{vi} C_v}{2K_{iv}} + \left[ \frac{K_{vi} K_{iv} + K_{iv}^2 C_v^2}{K_{i} K_{vs} + 4K_{iv}^2} \right]^{1/2} \]  \hspace{1cm} (2.9)

The radiation enhanced diffusion coefficient (\( D_{RED} \)) is given by:

\[ D_{RED} = D_v C_v + D_i C_i \]  \hspace{1cm} (2.10)

With the assumption that the interaction radius of the sinks for both vacancies and interstitials is the same, it is found from the symmetry of the equations that at steady state:

\[ D_v C_v = D_i C_i \]  \hspace{1cm} (2.11)
So,

\[ D_{\text{RED}} = 2D_v \bar{C}_v \]  \hspace{1cm} (2.12)

Interstitials will migrate to sinks much faster than vacancies because the mobility of interstitial is generally much higher than the vacancy. \( C_i \) would be much lower than \( C_v \):

\[ \frac{C_i}{C_v} = \frac{D_i}{D_v} \]  \hspace{1cm} (2.13)

The expression for \( D_{\text{RED}} \) can be simplified in two limiting kinetics regimes, namely recombination limited kinetics and sink limited kinetics.

Recombination between vacancies and interstitials is the dominate kinetics at low temperatures and low sink concentration, resulting in recombination limited kinetics. \( D_{\text{RED}} \) is reduced to:

\[ D_{\text{RED}} = 2D_v \bar{C}_v = 2D_v \left[ \frac{K_v K_o}{K_v K_o} \right]^{1/2} \]

\[ = AK_{o}^{1/2} \exp(-E_{m} / 2kT) \]  \hspace{1cm} (2.14)

where \( A \) is a constant and \( E_{m} \) is the migration enthalpy of the less mobile of the two species (interstitials and vacancies). Two characteristic features of this regime should be noticed: \( D_{\text{RED}} \) is proportional to the square root of the defect production rate, \( K_o \), and the apparent measured activation enthalpy is \( 1/2 \) of migration enthalpy of the slower moving defect, which can be expressed as:

\[ D_{\text{RED}} \propto K_o^{1/2} \]  \hspace{1cm} (2.15)
\[ E_a = \frac{1}{2} E_m \]  

(2.16)

where \( E_a \) is the migration enthalpy of the less mobile of the two species.

The expression for \( K_o \) can be written in the formula below:

\[ K_o = \sigma_{FP} \phi \]  

(2.17)

Where \( \sigma_{FP} \) is the production cross section of the Frenkel pairs, \( \phi \) is the ion flux.

Therefore, \( E_m \) can be determined by measuring \( D_{RED} \) as a function of temperature with a constant irradiation flux. Recombination limited regime can be further characterized by the flux dependence, which means measuring \( D_{RED} \) as a function of \( \phi \) with constant temperature.

Sink limited kinetics happens at high temperatures or high sink concentrations, where annihilation of vacancies and interstitials at their respective sinks is the dominate defect reaction.

In the sink limited regime, \( D_{RED} \) is given as:

\[
D_{RED} = 2D_v C_v = 2D_v \left[ \frac{K_o}{K_{vs} C_s} \right] = B K_o
\]  

(2.18)

where \( B \) is a constant. \( D_{RED} \) now is linear proportional to the irradiation flux:

\[ D_{RED} \propto K_o \]  

(2.19)
$D_{RED}$ will be independent of temperature because a fixed sink concentration does not vary with temperature and the diffusion length is also fixed in the sink limited regime.
CHAPTER 3: REVIEW OF RED AND DIFFUSION PROCESSES OF UO₂

3.1 RED Literature Review

Diffusion in crystalline solids proceeds via lattice defects. The concentration of defects increases steeply with increasing temperature. Excess point defects concentration is produced by irradiation, thereby not only the usual diffusion path is enhanced but also channels can be opened by way of defect species which are not available in normal thermally activated diffusion [1]. Chemical rate equations are employed to formulate the problem in terms of mean field theory firstly by Lomer [7], Dienes and Damask [5].

Lomer presented solutions for the steady state conditions and for the kinetics of defect build-up under irradiation in 1954 for the chemical rate equations as mentioned in chapter 2, Eq. 2.2, and Eq. 2.3.

In 1958, Dienes and Damask worked out a simple theory of RED which describes the dependence of the enhancement on flux and temperature under steady-state conditions. Alpha-brass was chosen for their experimental work and agree excellent with the theoretical predictions. Vacancies and interstitials are created at a constant rate during irradiation. They are annealed out at temperatures where the vacancies and interstitials are mobile. The anneal mechanisms could be migration to internal or external surfaces, direct annihilation of vacancies and interstitials, etc. A steady-state concentration of defects is created by the opposing processes (defect creation versus annealing out). The authors characterize the annealing process in three cases: (I) linear annealing of defects, (II) annealing of defects by direct recombination and (III) linear anneal
plus recombination. In the case (I), it is assumed that the defects disappear by migration to sinks. Enormous enhancement can occur at low temperatures and $D_{RED}$ becomes independent of temperature. In the case (II), $D_{RED}$ depends on $(\phi)^{1/2}$ in contrast to the linearity in flux of case (I). In the case (III), both annealing to surfaces and recombination are occurring. Experimental work was done by irradiating alpha-brass with neutron. The results fully support the conclusion that local or microdiffusion can be greatly enhanced by the presence of extra defects produced by fast particle irradiation. Linear anneal, which is temperature independent, dominates the enhanced diffusion of alpha-brass. The authors finally came to the conclusion that neutron radiation enhanced diffusion coefficient is expected to be temperature independent in a wide class of alloys.

Sizmann [1] reviewed the basic kinetic equations and their solutions for homogeneous systems and in systems with extended sinks, producing local defect concentration gradients in 1968. All these work were mostly about diffusion in metals.

The first measurement of RED in an oxide system was done by Sambeek and Averback [9]. They did a complete study of radiation enhanced diffusion in MgO in 1998. Thin film of MgO with buried tracer layers of $^{18}$O, Ca, Zn grown by molecular beam epitaxy (MBE) was irradiated by 2.0 MeV $Kr^+$ and 1.0 MeV $Ne^+$, $He^+$, and $H^+$ from 30 to 1500 °C. The experimental results showed a recombination limited kinetics on the aion sublattice between 1350 and 1500 °C, and a transition to sink limited kinetics as the temperature is decreased. This result was opposite to the RED theory in chapter 2. A simple RED model based on the assumption of temperature dependence of net defects production was formed to demonstrate how the different kinetic behaviors evolve in MgO. The ratio of two types of defects, namely freely
migrating defects and immobile defects, is temperature dependent. The model obtained a recombination limited kinetics in the highest temperature region (1500-1350 °C), a transition from recombination limited kinetics to sink limited kinetics in the intermediate temperature region (1350-1100 °C), and sink limited kinetics in the lowest temperature region (1100-900 °C) on the anion sublattice. Experiment yields a normalized mixing parameter of 2.0-5.0 Å³/eV on the anion sublattice and 1.0-3.0 Å³/eV on the cation sublattice, which indicates that ballistic mixing is the dominant mechanism of ion mixing and that thermal spike activity is negligible. The activation enthalpy was 1.2 eV in the recombination limited regime. This value was very close to one-half the predicted migration enthalpy of anion vacancies in MgO, 2.1-2.4 eV. However, the activation enthalpy in the sink limited regime is as high as 4.1 eV. This can be explained by temperature dependence in the net production of freely migrating defects.

Pappas, Heuser and Strehle [14] had done the RED measurements on cation diffusion in CeO₂ thin film, which is quite related to the present work. CeO₂ is often considered to be a UO₂ fuel surrogate because they have the same crystal structure, and similar lattice parameters: 5.464 Å for UO₂, and 5.411 Å for CeO₂. Thin film of CeO₂ was grown in the MBE system with a tracer layer of La at the film half thickness. Samples were irradiated by 1.8 MeV Kr⁺ from 400-933 °C. Thermal diffusivity of La in the same system was measured also over a temperature range of 500-800 °C. A shift of diffusion mechanism from recombination-limited kinetics to sink-limited kinetics and ultimately to thermal vacancy self-diffusion (VSD) was found in the experiments. RED measurements showed recombination limited kinetics below ~530 °C with a activation enthalpy of $E_a \sim 0.2$ eV and migration enthalpy of $E_m \sim 0.4$ eV. Thermal diffusivity
resulted in an activation enthalpy of $E_a \sim 1.4\text{eV}$. Finally the formation enthalpy was determined to be $E_f \sim 1.0\text{eV}$. The mixing parameter was also measured and found to be $\sim 4\text{Å}^3/\text{eV}$, which means that ballistic mixing is the dominate mechanism of ion mixing.
3.2 Diffusion Processes of UO₂ Literature Review

Uranium dioxide (UO₂) is the most frequently used fuel in water cooled reactors, e.g. pressurized water reactor (PWR). Several studies of diffusion mechanism had been done from 1950s to 1980s, e.g. uranium self-diffusion, oxygen self-diffusion and diffusion process in (U, Pu)O₂, etc. Very little work can be found for the radiation enhanced diffusion in UO₂. Here, we mainly make a brief review for the uranium self-diffusion in UO₂, as a comparison for the present work. And the very limited study on radiation enhanced diffusion in UO₂ in the past would also be reviewed.

To the best of our knowledge, the first study on uranium self-diffusion in UO₂ was done by Auskern and Belle [10] in 1960. In their experiment, diffusion coefficients were measured by using the technique of surface activity decrease. Uranium diffusion in the temperature range 1450 – 1785 °C was done and the resulting activation energy was \( E_a \approx 3.8 \) eV, pre-exponential \( D_o \approx 4.3 \times 10^{-4} \text{ cm}^2/\text{sec} \), diffusion coefficients was of the order of \( 10^{-15} - 10^{-13} \text{ cm}^2/\text{sec} \) in this temperature range.

Lindner and Schmitz [11] also used the \( \alpha \)-radiation absorption surface activity decrease method to measure the diffusion coefficients. They gave a comparison of the cation diffusion coefficient in samples heated in hydrogen and argon. Uranium diffusion in the temperature range 1300 – 1600 °C was done and the resulting activation energy was \( E_a \approx 4.5 \) eV, pre-exponential \( D_o \approx 0.23 \text{ cm}^2/\text{sec} \), diffusion coefficients was of the order of \( 10^{-15} - 10^{-13} \text{ cm}^2/\text{sec} \) in this
temperature range. However, the stoichiometry of the samples was not controlled, hence this study did not provide detailed information.

Since the variations of diffusion coefficient in $\text{UO}_2$ appeared, grain boundary diffusion was mainly considered to be the reason. However, Lidiard [12] pointed out that, although grain boundary diffusion may be important in polycrystalline material, the influence of impurities and of slight departures from stoichiometric composition upon volume diffusion should be adequately considered as a reason for the variable results. He worked out a theory for the non-stoichiometric, $\text{UO}_{2+x}$, in which the diffusion coefficient is proportional to $(\pm x)^2$. For $+x$, the U self-diffusion mechanism is vacancy diffusion, while for $-x$, that is the interstitial diffusion. Based on this, the result shows small change of $x$ could make large change in the diffusion coefficient. Further experiment was done later by Hawkins and Matzke, etc, experimental results supported the large effect of impurities and non-stoichiometry as expected. This would be discussed in the following paragraphs.

Hawkins and Alcock [13] measured the diffusion coefficients for $\text{UO}_{2+x}$ as a function of $x$. He found that a very small departure from the stoichiometric composition produced a large change in the cation diffusion coefficient, e.g. $0 \leq x \leq 0.02$, the change of volume diffusion coefficient increased about two orders of magnitude at 1400°C. He explained the differences in the results obtained by different workers before on uranium self-diffusion in nominally stoichiometric $\text{UO}_2$ by applying the results of rapid increase in $D$ with departure from stoichiometry.
Later, Matzke has done a substantial study on cation self-diffusion, anion self-diffusion, radiation enhanced diffusion, in different materials, UO\textsubscript{2}, UC, (U, Pu)O\textsubscript{2}, etc. Here we focus on the uranium self-diffusion only. Self-diffusion of uranium in sintered and single crystal UO\textsubscript{2}, dependence of diffusivity on x of UO\textsubscript{2+x}, and diffusivity in UO\textsubscript{2} + Nb\textsubscript{2}O\textsubscript{5} were all presented [15]. Diffusion coefficients for sintered uranium were found to be slightly higher than those for single crystals and low diffusivity were found compared to previously published results. The author attributed this to the reason that either the effect of impurities with valence <4 or else reduction of the UO\textsubscript{2} to substoichiometry. Again, for non-stoichiometric study, UO\textsubscript{2+x}, an increase in x yields an appreciable increase in diffusivity were found. The results from UO\textsubscript{2} + Nb\textsubscript{2}O\textsubscript{5}, which were to simulate hyperstoichiometric UO\textsubscript{2}, showed higher diffusion coefficients than those in UO\textsubscript{2}. The activation enthalpy was found to be ~1.8 eV, which is much lower than the suggested value of ~4.8 eV for UO\textsubscript{2}. Just as the author presented in 1965 [16] that an addition of Nb\textsubscript{2}O\textsubscript{5} should enhance cation diffusion by creating anion interstitials, conversely, additions of La\textsubscript{2}O\textsubscript{3} and Y\textsubscript{2}O\textsubscript{3} should increase the concentration of anion vacancies, thus reduce the cation diffusion because the decrease of cation vacancies. The effect of addition of La\textsubscript{2}O\textsubscript{3} or Y\textsubscript{2}O\textsubscript{3} is related to our present work (we use Nd as a tracer layer, which is also at 3+ valence state). This will be discussed in details in chapter 7.

Marin [17] did similar research on UO\textsubscript{2+x}. The results of diffusion coefficient can be described by log \( D = -10.8 + 1.9 \log x \). Compared with the result of Matzke by log \( D = -10.85 + 1.5 \log x \). The factor before log x is near to 2.0 in both relations. These two sets of experiments may represent a reasonable confirmation of the model.
In 1983, Matzke published a paper in which the near-surface effect (NSE) was emphasized [21]. Due to the noncongruent evaporation, the anisotropy of the surface energy, and the mechanical damage in as-polished sample, etc, all these surface effects gave rise to erroneous results. Then he argued that, in most of the previously published literature studies, the reported $D$ can be wrong up to 3 or 4 orders of magnitude. Because of the complexities of the surface, it is not representative of the bulk composition. Also, due to the strongly dependence of $D$ on the deviation from stoichiometry, the NSE is an important effect in uranium self-diffusion measurements.

The first study of uranium self-diffusion in $\text{UO}_2$ by SIMS was reported to be done by Sabioni et al [18]. Uranium self-diffusion coefficient in $\text{UO}_2$ single crystals was measured by secondary ion mass spectrometry (SIMS). The result showed a very low diffusion coefficient of the order of $10^{-19}\text{cm}^2/\text{s}$ at $1498{}^\circ\text{C}$. The effect of surface was also found in the experiment, which might be caused by the evaporation-condensation from the powder to crystal surface.

Very limited research had been done on radiation enhanced diffusion in $\text{UO}_2$. HöH and Matzke [19] published the first direct measurements of the fission-induced self-diffusion in $\text{UO}_2$ in 1973. This was the preliminary work for their future study of radiation enhanced diffusion in $\text{UO}_2$, which was published in 1983 by Matake [20]. Radiation enhanced diffusion coefficient $D'$ was measured during fission in a nuclear reactor from $130{}^\circ\text{C}$ to $1400{}^\circ\text{C}$. Results showed that metal atom diffusion in $\text{UO}_2$ was enhanced during reactor irradiation, but $D'$ was found to be completely temperature independent below about $1000{}^\circ\text{C}$. The author stated that the fission process itself was the main cause of radiation enhanced metal diffusion in $\text{UO}_2$ other than the
neutrons contribution. In the temperature region between 1000 °C and 1200 °C it showed some temperature dependence effect, but details were not clear in this region.

Hocking et al. studied the radiation induced segregation and diffusion in 1993 [30]. Depth profile of rubidium and cesium ion-implanted in UO$_2$ and UO$_2$-based SIMFUEL had been measured by SIMS and XPS. Cs and Rb were found to be redistributed as a pronounced spike near the sample surface. The radiation-induced diffusion effects during ion-implantation might be the reason for the redistribution. A net enhancement of thermal spikes was thought to be the reason for RED. This was further supported by the molecular dynamics simulation (MDS) study of thermal spikes. Their results of radiation enhanced diffusion and segregation offered new insight in oxide nuclear fuels.

Radiation enhanced diffusion is very important in material science because it affects mechanical properties in complex systems. A brief review of radiation enhanced diffusion, metal atom self-diffusion in UO$_2$ and the study on RED in UO$_2$ has been made up to this point. The present work of RED in UO$_2$ will be shown in the next chapters.
CHAPTER 4: EXPERIMENTS

Single crystal $\text{UO}_2$ thin films were grown on YSZ (Yttria Stabilized Zirconia) substrates (1 cm x 1 cm x 0.5 cm) using a reactive-gas sputtering system at 650 °C. Research grade Ar was used as the sputtering gas and research grade $\text{O}_2$ was used as the reactive gas. A depleted uranium metal target and a neodymium target were used as the sputtering targets. Typical sandwich-structure film was grown in this system, that is, a single crystal $\text{UO}_2$ film with a discrete layer of Nd at the film mid-plane. A list of film growth conditions for the single crystal films studied here is given in Table 4.1. Current control was used during film growth and the atomic ratio of Nd to U is about 1/5 in the Nd layer (from the RBS analysis), which is consistent with the current ratio. The voltage and power were not recorded because of the difficulty of doing this in a very short time for Sample 32 and 36. The stoichiometry of uranium oxide was controlled by adjusting the oxygen partial pressure during growth.

Typically $\text{U}_3\text{O}_8$ was grown under the oxygen partial pressure of the order of $10^{-4}$ Torr on r-plane sapphire substrate. We haven’t tried to grow $\text{U}_3\text{O}_8$ on YSZ substrate yet. $\text{UO}_2$ was grown under the oxygen partial pressure of the order of $10^{-8}$ to $10^{-7}$ on both r-plane sapphire and YSZ substrates. No further control of x had been found for $\text{UO}_{2+x}$ although our $\text{UO}_2$ films were expected to be slightly departure from the stoichiometric $\text{UO}_2$. It was found that our $\text{UO}_2$ films grown on YSZ substrate were slightly super stoichiometry on the film surface. More details of film growth can be found in the related paper [22].
The rocking curve scans show a narrow component with FWHM~0.05°, and a broad component with FWHM~0.8°. Lattice strain (ε) in the [0 0 1] direction is about $3 \times 10^{-3}$. It should be noted that the oxygen pressure in the table reflects trends, not absolute values because the oxygen pressure response of the mass spectrometer was calibrated separately using the capacitance manometer, but this calibration most valid at higher partial pressures ($\sim 10^{-4}$ to $10^{-3}$ Torr) [22].

X-Ray Diffraction (XRD) analysis has been done for samples both as grown and after irradiation. Wide-angle specular and off-specular $2\theta-\omega$ scans of (0 0 1) plane of UO$_2$ lattice, in-plane $\varphi$ scans in (1 1 1) plane, $\Omega$ rocking curve scans near the first strongest peak~32.75°, and glancing-angle specular reflectivity (XRR) scans which provide the film thickness have all been performed using a Philips X’Pert diffractometer with a Cu-K$_\alpha$ source ($\lambda=1.5406\text{Å}$).

Rutherford Backscattering Spectrometry (RBS) has been done with High Voltage Engineering Van de Graaff accelerator. 2 MeV He$^+$ beam with an incident angle of 22.5° and scattering angle of 150°. Data was fitted with SIMNRA 6.04 with energy calibration based on the binary collision between helium ion and elements on the sample free surface: uranium and oxygen, which undergo collision without electrostatic energy loss assuming the binary kinetics.
<table>
<thead>
<tr>
<th>Sample</th>
<th>32</th>
<th>36</th>
<th>38</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>UO₂ + NdₓOᵧ</td>
<td>UO₂ + NdₓOᵧ</td>
<td>UO₂ + NdₓOᵧ</td>
</tr>
<tr>
<td>T (°C)</td>
<td>650</td>
<td>650</td>
<td>650</td>
</tr>
<tr>
<td>P(O₂) (Torr)</td>
<td>1.0x10⁻⁷</td>
<td>1.0x10⁻⁷</td>
<td>1.2x10⁻⁷</td>
</tr>
<tr>
<td>Current (A)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>0.090</td>
<td>0.090</td>
<td>0.090</td>
</tr>
<tr>
<td>Nd</td>
<td>0.018</td>
<td>0.018</td>
<td>0.018</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>309</td>
<td>312</td>
<td>312</td>
</tr>
<tr>
<td>Nd</td>
<td>-</td>
<td>-</td>
<td>307</td>
</tr>
<tr>
<td>Power (W)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>29</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td>Nd</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>ΔΩ (degree)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Narrow</td>
<td>0.05</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>Broad</td>
<td>0.88</td>
<td>0.62</td>
<td>0.80</td>
</tr>
<tr>
<td>ε[001][x10⁻⁴]</td>
<td>25</td>
<td>37</td>
<td>22</td>
</tr>
<tr>
<td>Thickness [Å]</td>
<td>666</td>
<td>780</td>
<td>906</td>
</tr>
</tbody>
</table>
Each sample was cut into 6 to 10 pieces for thermal and irradiation (ion bombardment) treatments. Energetic heavy-ion bombardment with 1.8 MeV Kr$^+$ was performed by using HVE Van de Graaff accelerator. Samples were mounted to a heating stage with silver paint for the 400 °C - 600 °C irradiation. Temperature of the stage was measure by a thermal couple directly attached to the sample stage. The film surface temperature was about the same as the stage temperature within this temperature range. For the 700 °C - 800 °C irradiation treatments, the samples were mounted on another stage with a screw and washer because of the possible failure of silver paint at this high temperature. The film surface temperature was measured directly by attaching the thermal couple on the film surface because of the large temperature gradient between the stage and the film surface within this temperature range. All the irradiation was performed under a vacuum about $3 \times 10^{-7}$ Torr. Three sets of experiments were performed: a set of different doses (fluences) $\Phi$ varied from 0 to $3 \times 10^{16}$ ions/cm$^2$ at room temperature, a set of constant dose $\Phi = 1.0 \times 10^{16}$ ions/cm$^2$ at different temperatures from 400 °C to 800 °C, and a set of constant dose $\Phi = 1.0 \times 10^{16}$ ions/cm$^2$ and constant temperature at 600 °C with different dose rates (fluxes). Another set of thermal only measurement without ion bombardment was done from 400 °C to 800 °C using a different furnace.

In the room temperature, dose dependence experiments, beam currents of 100-200 nA with a 4.5mm×4.5mm beam aperture were used for irradiation. The beam current was measured periodically by insertion of a Faraday cup for assure steady state current. Irradiation time varied for different doses from 0 to 162 minutes. Sample 36 was used for this measurement.

In the constant dose, temperature dependence measurements, the same beam size was used as above. A dose of $1.0 \times 10^{16}$ ions/cm$^2$ required irradiation time of 54 minutes with current of 100
nA. A part of the sample, which underwent the same thermal history but without irradiation was also measured, although no diffusion was found in this temperature range. Sample 32 was used for this set of measurements.

Another set of thermal only experiments was done individually in the lab furnace for longer annealing times and no diffusion was found either. Details will be shown in chapter 5. Samples from the thermal part of 32 and 36 were used for the thermal diffusion measurements.

For the constant dose of $1.0 \times 10^{16}$ ions/cm$^2$, constant temperature at 600 °C, with dose rate dependence measurements with a beam aperture of 3mm×3mm. The beam current was varied from 30 nA to 300 nA for different dose rate irradiation. Irradiation times varied from 8 minutes to 80 minutes which correspond to the different beam currents used.

Secondary Ion Mass Spectrometry (SIMS) was used to measure the depth profile for the irradiated and un-irradiated samples by using a Physical Electronics PHI Trift III instrument. This instrument runs in the Time-Of-Flight mode and has excellent mass resolution. It can detect impurities at atom densities less than one part per million atomic (ppma) for almost all elements, and 10 ppba for some elements [23]. A 2 keV O$_2^+$ beam with an incident angle of 42° to the sample normal was used as a sputtering beam, which made a $400 \times 400 \mu m$ crater. A 22 keV Au$^+$ beam with an actual incident angle of about 38° which has been accounted for the sample potential effect due to the ions created during surface scan was used as the analytical beam. The $50 \times 50 \mu m$ Au$^+$ beam was centered in the $400 \times 400 \mu m$ crater. Then depth profiles were produced by cycling the O$_2^+$ sputtering erosion beam and the Au$^+$ analytical beam. The depth scale was set by using the known thickness from XRR measurements for the as-grown samples. Because of the sputtering effect on the sample free surface by Kr$^+$ during irradiation, for the
irradiated samples, depth scale was set by using the thickness between Nd peak center and the film-substrate interface as the known thickness which can be obtained from the corresponding as-grown sample measurements. One example of SIMS depth profile is shown in Figure 4.1. The asymmetry of the Nd peak is because of two reasons: one is that the Nd could be mixed with U on the substrate side of the Nd peak by sputtering during the depth profile measurement, the other is that the diffusion could happen on the film free surface side of the Nd peak. Both effects of sputtering mixing and diffusion during growth are small because the counts are in the background level and they do not affect the Gaussian properties of the Nd peak, as plotted in the linear scale in Figure 5.4 to Figure 5.6.

Because there are 6 isotopes of Nd with atomic mass ranging from 142 to 150, as shown in Figure 4.2, all the isotopes are summed for both Nd and NdO (the strongest signal) to get good statistics for the analysis of the Nd peaks. The tails on the lower mass direction for every peak is due to the initial velocity of the sputtered species before they have been accelerated. From the relation \( m = \frac{2E}{v^2} \), the increase of \( v \) makes the mass go to the lower mass direction.
Figure 4.1

One example of depth profile measurements obtained by SIMS. The arrow indicates the interface of film and substrates, which is around 666 Å.
Nd isotope peaks from SIMS. There are 7 isotopes of neodymium, which are all detected by SIMS as separate peaks. Abscissa is the atomic mass, and ordinate is the counts.
CHAPTER 5: RESULTS

Specular $2\theta - \omega$ scans from XRD measurements show single crystal feature of the UO$_2$ film, as shown in Figure 5.1. Film peaks are the two low intensity, left-hand-side peaks, which are marked as (0 0 2) and (0 0 4) plane. The strong, right-hand-side peaks are from the substrate. As-grown film (Room-Temperature, without irradiation) indicates a preferential [0 0 l] growth direction. Another higher order (0 0 6) peak around 115.53° could also been seen from the XRD measurements. For the convenience of comparison, they are not shown here. The small peak around 71° may due to the existence of Nd in the film (Samples without Nd in the film haven’t showed this peak). The possible compounds of Nd are listed in Table 5.1. The area under the small peak is about 1% of the (004) peak, which is negligible. The high-temperature, irradiated film maintains the single crystal feature of the as-grown film.

Table 5.1
Compounds of Nd which show peaks near 71° [24].
(Fixed Slit Intensity – Cu K1 1.54056Å)

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>$2\theta$ (degree)</th>
<th>Intensity</th>
<th>h</th>
<th>k</th>
<th>l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>70.3816</td>
<td>7</td>
<td>1</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>NdO$_2$</td>
<td>71.4249</td>
<td>4</td>
<td>-3</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Nd$<em>6$UO$</em>{12}$</td>
<td>70.4778</td>
<td>2</td>
<td>5</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

In-plane (1 1 1) $\phi$ scans shown in Figure 5.2 further demonstrates the one domain, single crystal feature of the film. The four-fold symmetry of the $\phi$ scan is the expected result of single crystal UO$_2$. A highly textured polycrystalline film may show similar specular $2\theta - \omega$ as the
true single crystal film. However, the former would not exhibit sharp peaks but instead would either be featureless or be broad weak peaks in an in-plane $\varphi$ scan. Figure 5.2 also shows that the high-temperature, heavy ion bombardment does not affect the single crystal structure. The shift of the two sets of peaks occurs because samples are not loaded exactly in the same orientation.

It is very important that the $\mathrm{UO}_2$ film studied here is single crystal rather than a polycrystalline or a highly textured polycrystalline film because it allows us to attribute the measured Nd diffusivities to a cation diffusion process that is not influenced by large angle grain boundaries. Although a previous study did not show significant effect of grain boundaries between polycrystalline and single crystal $\mathrm{UO}_2$ in terms of uranium self-diffusion [17], the justification of the single crystal film for the RED study would exclude the possibly effects of grain boundaries.

A series of rocking curve scan was shown in Figure 5.3. The rocking curve of the as-grown film is characterized by a narrow component (FWHM~0.05°) and a broad component (FWHM~0.88°), which is consistent with a portion of the film in registry with the YSZ substrate and a portion of the film not in registry, respectively. For the at-temperature irradiated films, the narrow components gradually disappear and the broad components gradually increase as the temperature increases. This implies that the high-temperature heavy ion bombardment increases the mosaic broadening as the temperature increases. A systematic increase of the area under the broad component of each rocking curve is shown in Table 5.2. The FWHM decreases after irradiation but there is no systematic change with the temperature for the irradiated films.
Table 5.2

Characteristics of the rocking curves after high temperature irradiation.

<table>
<thead>
<tr>
<th>Temperature (deg.)</th>
<th>Dose (ions/cm²)</th>
<th>FWHM</th>
<th>Area of Broad Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>R. T.</td>
<td>0</td>
<td>0.8804</td>
<td>0.8583</td>
</tr>
<tr>
<td>400</td>
<td>1 E16</td>
<td>0.5718</td>
<td>0.8944</td>
</tr>
<tr>
<td>580</td>
<td>1 E16</td>
<td>0.6258</td>
<td>0.9174</td>
</tr>
<tr>
<td>800</td>
<td>1 E16</td>
<td>0.5818</td>
<td>0.9188</td>
</tr>
</tbody>
</table>
Figure 5.1

Normalized specular $2\theta - \omega$ X-Ray Diffraction scans along the [0 0 1] film normal direction showing the angular range containing the (0 0 2) and (0 0 4) reflections. The (0 0 6) third order peaks are not shown here for the convenience of comparison. (Refer to [22] for more details about film growth.) Each scan is normalized to the area under the spectrum. The intensity scale is graduated in powers of ten.
Normalized X-Ray Diffraction $\varphi$ scans of the (1 1 1) in-plane reflection from representative samples. The four-fold symmetry of each spectrum demonstrates that both the as-grown film and the high-temperature, irradiated film consist of a single-lattice domain. A linear intensity scale is plotted.
Figure 5.3

Normalized X-Ray Diffraction rocking curve scans of the representative samples. A narrow component and a broad component characterize each film. The increase of the area of the broad components of the irradiated films as the temperature increase indicates more film volume out of registry. The narrow component is finally eliminated by heavy ion bombardment at 800 °C. A linear intensity scale is plotted.
Depth profiles of Nd from the room temperature set of irradiations measured by SIMS are shown in Figure 5.4. Each depth profile has been fit with a Gaussian distribution. The Nd peaks have been normalized by setting the area under each peak to one for all depth profiles. Because each sample originated from the same sample (Cut from a big sample and the uniformity has been checked by SIMS and RBS) and the loss of Nd from the samples is not expected to occur under heavy ion bombardment, the normalization assumes that the total amount of Nd in each sample remains the same.

The depth scale is set by the following method: first, set the point at which UO (the strongest signal from the UO$_2$ film) and Y (the strongest signal from the YSZ substrate) mass signals cross as the film and substrate interface, as indicated by the arrow in Figure 4.1. Second, set the sample free surface as the zero depth for the as-grown samples. The distance from zero depth to interface is the total sample thickness, which can be obtained from the XRR results. Then the scale of converting sputtering time to depth can be determined from the ratio of the total sputtering time and the total thickness. Third, for the irradiated samples, the distance from the center of Nd peak to the interface remains unchanged, even though surface sputtering occurs during irradiation (10-50Å of the film could be sputtered depending on the dose and temperature). From the known distance from Nd peak center to interface, which is the same as the as-grown samples, and the sputtering time, then we can convert time to depth. All the depth scales are set under the assumption that a constant sputtering rate is maintained during SIMS measurement, which is reasonable because the oxygen current is quite stable. Besides, the film is uniform throughout the entire thickness except on the film surface where hyper-stoichiometric UO$_{2+x}$ is expected and in the film mid-plane the solid solution of Nd in the UO$_2$ matrix may affect the
sputtering rate, we assume the effect is small because the x-value is quite small and the amount of Nd is also very small, which is hard to affect the sputtering rate.

Nd depth profiles for the at-temperature irradiations are shown in Figure 5.5. Gaussian fits are made and each peak is normalized by setting the area to 1. The standard deviations are listed in Table 5.4. It should be noted that the diffusion coefficient of the room temperature, with dose of 1.0E16 ions/cm² was calculated from sample 36 because all samples of 32 have been used. The standard deviation of the two as-grow samples are close (23.87Å versus 26.65Å ) and the room temperature ballistic mixing is close for each sample~5.0×10⁻¹⁸ cm²/sec . Based on this argument, the calculated value should be quite close to the real value.

A set of thermal diffusion measurement of Nd has been done both in the irradiation stage and in the lab furnace for longer time annealing (for sample mounted in the irradiation stage, one part of the sample was irradiated at elevated temperature and the other part was not irradiated but would undergo the same thermal history as the irradiated part). In the temperature range from 400 °C  to 800 °C , no obvious diffusion has been detected, even for a very long annealing times. Here we just show the results of the sample which had been annealed at 800 °C  for 50 hours. Two SIMS measurements were done to double check the results, as listed in Table 5.3, and shown in Figure 5.6. A very small, yet observable broadening was measured.

To verify that the experiments are in the recombination limited kinetics in the temperature regime, a set of constant temperature, constant dose, dose rate dependent measurements were performed using a different sample which has similar properties as samples mentioned above. Because of the difficulty of getting stable beam currents for different doses, and the mixing induced by SIMS, several measurements have been done and the results are listed in Table 5.5.
One important aspect deserves to be mentioned: for each set of experiment, different samples were used, e.g. sample 32 was used to study the temperature dependent RED, sample 36 was used to measure mixing parameter, sample 38 was used for dose rate dependent studies. This is due to the small substrate size and relatively big samples are needed to perform all the experiments. These samples have the similar structure, that is UO₂ thin film with Nd in the film mid-plane. The differences among these samples are the total thickness and the amount of Nd in the film. The different amount of Nd exist in the film may results in small deviation from the stoichiometric UO₂, which in turn changes the diffusion coefficient significantly. Details will be discussed in chapter 7.
Normalized Nd depth profiles for single crystal UO$_2$ irradiated at room temperature and with dose as indicated in the figure in units of ions/cm$^2$. The solid lines are best-fits to a Gaussian distribution. Standard deviations from these fits are listed in Table 5.3. A linear intensity scale is plotted.
Figure 5.5

Normalized Nd depth profiles for single crystal UO$_2$ irradiated at a dose of $1.0 \times 10^{16}$ ions/cm$^2$ at temperature indicated. The solid lines are the best-fits of Gaussian distribution. Standard deviations obtained from these fits are listed in Table 5.4.
Figure 5.6

Normalized Nd depth profiles for the sample that has been annealed at 800 °C for 50 hours. Two measurements have been made to double check the results. The solid lines are the best-fits of Gaussian distribution. Standard deviations obtained from these fits are listed in Table 5.3.
Table 5.3
Irradiation conditions, measured Nd profile standard deviations, and measured diffusivities of sample 36.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T ( °C )</th>
<th>Dose (×10^{16} ions/cm²)</th>
<th>σ (Å)</th>
<th>D (×10^{-18} cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>R. T.</td>
<td>0</td>
<td>26.65±0.27</td>
<td>-</td>
</tr>
<tr>
<td>36C2</td>
<td>R. T.</td>
<td>0</td>
<td>26.49±0.26</td>
<td>-</td>
</tr>
<tr>
<td>36A</td>
<td>R. T.</td>
<td>0.5</td>
<td>28.79±0.28</td>
<td>3.8±0.66</td>
</tr>
<tr>
<td>36A</td>
<td>R. T.</td>
<td>1.0</td>
<td>31.61±0.27</td>
<td>4.5±0.34</td>
</tr>
<tr>
<td>36A</td>
<td>R. T.</td>
<td>2.0</td>
<td>40.03±0.37</td>
<td>11±0.40</td>
</tr>
<tr>
<td>36A</td>
<td>R. T.</td>
<td>3.0</td>
<td>45.89±0.32</td>
<td>11±0.25</td>
</tr>
<tr>
<td>36C1</td>
<td>800(50hrs)</td>
<td>0</td>
<td>27.17±0.26</td>
<td>0.0090±0.0055</td>
</tr>
<tr>
<td>36C1</td>
<td>800(50hrs)</td>
<td>0</td>
<td>28.63±0.30</td>
<td>0.032±0.0061</td>
</tr>
</tbody>
</table>
Table 5.4

Irradiation conditions, measured Nd profile standard deviations, and measured diffusivities of sample 32.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T ( °C )</th>
<th>Dose (×10^{16} ions/cm^2)</th>
<th>σ (Å)</th>
<th>D (×10^{-18} cm^2/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>R. T.</td>
<td>0</td>
<td>23.87±0.23</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>R. T.</td>
<td>1.0</td>
<td>29.38±0.27</td>
<td>4.5±0.30</td>
</tr>
<tr>
<td>32A1</td>
<td>400</td>
<td>1.0</td>
<td>30.75±0.24</td>
<td>1.3±0.33</td>
</tr>
<tr>
<td>32C1</td>
<td>500</td>
<td>1.0</td>
<td>33.48±0.19</td>
<td>4.0±0.31</td>
</tr>
<tr>
<td>32A</td>
<td>580</td>
<td>1.0</td>
<td>35.19±0.19</td>
<td>5.8±0.30</td>
</tr>
<tr>
<td>32B</td>
<td>700</td>
<td>1.0</td>
<td>38.88±0.24</td>
<td>10.0±0.38</td>
</tr>
<tr>
<td>32C2</td>
<td>800</td>
<td>1.0</td>
<td>45.99±0.26</td>
<td>19.0±0.44</td>
</tr>
</tbody>
</table>
Table 5.5

Irradiation conditions, measured Nd profile standard deviations, and measured diffusivities of sample 36.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (°C)</th>
<th>Time (min)</th>
<th>Dose ($\times 10^{16}$ ions/cm$^2$)</th>
<th>$\sigma$ (Å)</th>
<th>$D$ ($\times 10^{-18}$ cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>R. T.</td>
<td>0</td>
<td>0</td>
<td>36.17±0.26</td>
<td>-</td>
</tr>
<tr>
<td>38H</td>
<td>R. T.</td>
<td>54</td>
<td>1.0</td>
<td>42.3±0.27</td>
<td>7.4±0.46</td>
</tr>
<tr>
<td>38H</td>
<td>R. T.</td>
<td>54</td>
<td>1.0</td>
<td>41.77±0.39</td>
<td>6.7±0.58</td>
</tr>
<tr>
<td>38C</td>
<td>600</td>
<td>12</td>
<td>1.0</td>
<td>52.18±0.27</td>
<td>66±2.8</td>
</tr>
<tr>
<td>38C</td>
<td>600</td>
<td>12</td>
<td>1.0</td>
<td>51.89±0.21</td>
<td>64±2.5</td>
</tr>
<tr>
<td>38D</td>
<td>600</td>
<td>24</td>
<td>1.0</td>
<td>52.92±0.44</td>
<td>36±1.9</td>
</tr>
<tr>
<td>38D</td>
<td>600</td>
<td>24</td>
<td>1.0</td>
<td>52.65±0.41</td>
<td>35±1.8</td>
</tr>
<tr>
<td>38E</td>
<td>600</td>
<td>48</td>
<td>1.0</td>
<td>61.15±0.55</td>
<td>34±1.3</td>
</tr>
<tr>
<td>38E</td>
<td>600</td>
<td>48</td>
<td>1.0</td>
<td>55.88±0.21</td>
<td>24±0.64</td>
</tr>
<tr>
<td>38E</td>
<td>600</td>
<td>48</td>
<td>1.0</td>
<td>55.15±0.44</td>
<td>22±0.98</td>
</tr>
<tr>
<td>38I</td>
<td>600</td>
<td>80</td>
<td>1.0</td>
<td>47.18±0.26</td>
<td>4.8±0.39</td>
</tr>
<tr>
<td>38I</td>
<td>600</td>
<td>80</td>
<td>1.0</td>
<td>48.86±0.27</td>
<td>6.5±0.41</td>
</tr>
</tbody>
</table>
CHAPTER 6: ANALYSIS

It is convenient to characterize the mixing of a buried layer in terms of the mixing parameter $\xi$, as defined in chapter 2, Eq. 2.1, which is measured by the variable dose irradiations at room temperature in $\text{UO}_2$ with the data from Table 5.3.

$$\xi = \frac{D_t}{\Phi F_o}$$  \hspace{1cm} (6.1)

where $D_t$ is obtained from Eq. 6.2 and $F_o$ is the nuclear differential energy deposition. For a thin $\text{UO}_2$ film irradiated with 1.8 MeV $\text{Kr}^+$, $F_o \approx 130\text{eV/Å/ion}$, which was calculated from TRIM, as shown in Figure 6.1.

The diffusion coefficient is obtained by using the relation:

$$2D_t = (\sigma_{irr})^2 - (\sigma_{ref})^2$$  \hspace{1cm} (6.2)

Where $\sigma$ is the standard deviation obtained from the Gaussian peak fitting. For the mixing parameter measurements and ballistic mixing, $\sigma_{irr}$ is for the room temperature, irradiated samples, $\sigma_{ref}$ is for the as-grown samples. For the at-temperature irradiation measurements, $\sigma_{irr}$ is for the at-temperature, irradiated samples, $\sigma_{ref}$ is for the corresponding room temperature, irradiated samples at the same dose. This equation assumes a one-dimension diffusion or mixing geometry, as the case with the semi-infinite buried Nd layer studied here.

The mixing parameter $\xi$ is a proportionality of the total mean square displacement ($D_t$) induced by displacement cascade damage to the total nuclear differential energy deposition.
(ΦF₀). If only direct recoil and cascade mixing (ballistic type mixing) are present, transport calculations predict a mixing parameter of approximately 1.0–2.0 Å²/ eV which is roughly independent of the material [6].

The analysis is shown in Figure 6.2 and yields $\xi = 1.65 \pm 0.13 \frac{\text{Å}²}{\text{eV}}$, which indicates that ballistic mixing is the dominant mechanism of ion mixing. The low value of mixing parameter in UO₂ is likely due to two effects. First, the melting temperature of UO₂ is high (2865 °C) and this will reduce the atomic transport during the thermal spike mixing. Second, the thermal diffusivity of the Nd in UO₂ is very low, which will reduce the marker transport during irradiation.
Figure 6.1

Differential energy deposition for \( \text{UO}_2 \) irradiated with 1.8 MeV \( \text{Kr}^+ \) from TRIM calculation.

The thickness of \( \text{UO}_2 \) film is set to be 780Å, which is the same as that of sample 36.
Product $Dt$ (the total mean squared displacement in one-dimensional diffusion) versus dose for heavy ion bombardment at room temperature. The solid line is a linear fitting which is forced through the origin (zero displacement at zero dose).
An Arrhenius plot (log \( D \) versus 1000/T) of the measured radiation enhanced diffusivity \( D_{RED} \) is shown in Figure 6.3. It can be seen that the temperature dependence of \( D_{RED} \) for the Nd diffusion has only one behavior in the temperature range from 400 °C to 800 °C. By fitting the data to an Arrhenius equation of the form

\[
D_{RED} = D_o \exp\left(\frac{-E_a}{kT}\right)
\]  

(6.3)

Where \( k \) is the Boltzmann’s constant, \( E_a \) is the activation enthalpy, \( D_o \) is the pre-exponential factor or diffusion constant. From the Arrhenius plot, we can calculate

\[
E_a = 0.41 \pm 0.04 \text{eV}, \quad D_o = 1.62 \times 10^{-15} (\pm 1.05) \text{cm}^2/\text{sec}.
\]

As shown by Eq. 2.15 and Eq. 2.19, the diffusion mechanisms can be distinguished by the dependence of \( D_{RED} \) on the defect production rate \( K_o \). \( K_o \) is proportional to the ion flux or dose rate \( \phi \) for a given ion irradiation. So, we can assume the measured dependence was determined by a power law of the form

\[
D_{RED} = A\phi^n
\]  

(6.4)

Or

\[
\log(D_{RED}) = \log A + n \log(\phi)
\]  

(6.5)

Where \( A \) is a constant, \( n \) is the power or the slope if plotted in logarithmic scale. As shown in chapter 2, \( n=0.5 \) characterizes the recombination limited kinetics, while \( n=1.0 \) characterizes the sink limited kinetics.
The plot of dose rate dependence at constant temperature and dose is shown in Figure 6.4. More than one measurement was performed and these were plotted as individual data points. Experiments were done at 600 °C, with dose of $1.0 \times 10^{16}$ ions/cm$^2$ and variable irradiation time ranges from 12 minutes to 80 minutes. The solid line is the linear fitting of the first three set of points from right to left, which results in $n=0.65\pm0.11$. The last two data points which are two measurements of the slowest dose rate are also plotted in the figure. The sudden change of the slope may indicate a diffusion kinetics change. More details will be discussed in the chapter 7.

One important phenomenon is that the diffusion coefficient in the dose rate study is much higher than the corresponding one in the Arrhenius plot (38E versus 32A, shown in Table 5.5 and Table 5.4). The difference of temperature (600 °C versus 580 °C) alone cannot account for the big change because even at 700 °C the diffusion coefficient is smaller than the one measured here. Small deviation from stoichiometry which may be caused by the different amount of Nd in the film could be the reason for the large difference. A detailed discussion will be shown in chapter 7.
Arrhenius plot of the measured radiation enhanced diffusion coefficient at elevated temperature during heavy ion bombardment. The diffusivity associated with ballistic mixing at room temperature, with dose of $1.0 \times 10^{16}$ ions/cm$^2$, is shown as a thick horizontal line. The resulting equations for the radiation enhanced diffusion is: $D_{\text{RED}} = 1.62 \times 10^{-15} \exp\left(\frac{-0.41}{kT}\right)$. 
Figure 6.4

Plot of dose rate dependence measurement at 600 °C with constant dose of $1.0 \times 10^{16}$ ions/cm$^2$. More than one measurement was performed at a given time and these were plotted as individual data points. The irradiation time varied from 12 minutes, 24 minutes, 48 minutes to 80 minutes corresponding in the figure from right side to the left side. Solid line is the linear fitting of the 12, 24, and 48 minutes data points.
CHAPTER 7: DISCUSSION

Uranium self-diffusion in $\text{UO}_{2+x}$ from the literatures is compared with the present results in Figure 7.1. Data from Auskern and Belle [10], Lindner and Schmitz [11] were considered to be nominal $\text{UO}_2$. Hawkins and Alcock [13], Marin and Contamin [17] measured the diffusivity dependence on oxygen stoichiometry which is shown in the parentheses in the legend. Matzke’s results are plot as open points at $1500^\circ$C. An approximate extrapolation to lower temperature indicated as two dashed lines shows that the present results of diffusivity of Nd thermal diffusion in $\text{UO}_2$ lies in the extrapolation region, although the uncertainty is about two orders of magnitude large. We couldn’t make the conclusion that the present two points are the uranium self-diffusion coefficient because the existence of the Nd impurities, but we can expect that the diffusivity would be very small at $800^\circ$C and below (no uranium self-diffusion has been reported below $1200^\circ$C to the best of our knowledge).

Room temperature with variable dose measurements result in a mixing parameter

$$\xi = 1.65 \pm 0.13 \text{Å}^2 / \text{eV}$$

on the cation sublattice, a low value indicative of ballistic mixing is the dominant mechanism of ion mixing and thermal spikes are not significant. Other comparable examples of a measured mixing parameter at room temperature in a ceramic compound are

$$\xi = 3.6 \pm 0.5 \text{Å}^2 / \text{eV}$$ for $\text{CeO}_2$ on the cation sublattice [14], and $$\xi = 1.3 \text{Å}^2 / \text{eV}$$ for MgO on the cation sublattice (Ca and Zn) [9]. Since La and Nd are both commonly found in $+3$ valence state, and they have similar ionic radius and other atomic properties, we could expect similar diffusion behavior of these two elements in the same lattice system. Atomic number of uranium is higher
than cerium, this cannot account for the lower mixing parameter of $\text{UO}_2$ than that of $\text{CeO}_2$ because thermal spike mixing is most prominent in materials with high atomic number which could result in high mixing parameter. And due to the fact that both $\text{UO}_2$ and $\text{CeO}_2$ have almost the same thermal conductivity ($6-7 \text{ W/m/}^\circ\text{C}$) at $100^\circ\text{C}$ [25], the difference of melting point ($2865^\circ\text{C}$ for $\text{UO}_2$ versus $2400^\circ\text{C}$ for $\text{CeO}_2$) could be one reason for the relatively large difference of mixing parameter between $\text{UO}_2$ and $\text{CeO}_2$. The product of $Dt$ versus dose for $\text{UO}_2$ and $\text{CeO}_2$ is shown in Figure 7.2. The slope for $\text{UO}_2$ is about half of that for $\text{CeO}_2$ and the differential energy deposition is close ($F_0 \approx 130\text{eV/Å/ion}$ for $\text{UO}_2$, $F_0 \approx 115\text{eV/Å/ion}$ for $\text{CeO}_2$), which result in a smaller mixing parameter for $\text{UO}_2$.

The diffusivity under heavy ion bombardment can be separated into different temperature regimes. At low temperature, mobile point defects recombine with their anti-defect whereas the loss of point defects to sinks is low and the contribution of the thermal vacancy population to the observed diffusivity is small. The result would show a linear increase of diffusivity as temperature increase in the Arrhenius plot which is characterized by recombination limited kinetics. However, sink limited kinetics would show a horizontal line in the same plot.

In the temperature region from $400^\circ\text{C}$ to $800^\circ\text{C}$ in the present work, the dependence of $D_{\text{RED}}$ on the temperature shows a linear increase as temperature increase in the Arrhenius plot and this could be characterized by recombination limited kinetics, as shown in Figure 6.3. The measured activation enthalpy is $E_a = 0.41 \pm 0.04\text{eV}$. From Eq. 2.16, the migration enthalpy is $E_m = 2E_a = 0.82 \pm 0.08\text{eV}$. The corresponding value for $\text{CeO}_2$ is $E_a = 0.19 \pm 0.03\text{eV}$ and $E_m = 0.38 \pm 0.06\text{eV}$ respectively [14]. The formation energy and migration energy of Nd in
cation sublattice of UO$_2$ is about twice as large as that in CeO$_2$, although La was used in
the latter case as a tracer, we expect similar diffusion behavior of Nd and La in the same lattice
structure as discussed above.

Because of the similarity of the two RED experiments (La diffusion in CeO$_2$ and Nd
diffusion in UO$_2$ both under 1.8 MeV Kr$^+$ ion bombardment), a plot of both of the two results
are shown in Figure 7.3 for comparison. Apparently the radiation enhanced diffusivity in CeO$_2$
is larger than that in UO$_2$: about 30 to 50 times larger. As mentioned above, a very small but
observable thermal diffusion was found at 800$^\circ$C of Nd in UO$_2$. The open square points in
Figure 7.3 (two SIMS measurements) indicate the thermal diffusion coefficient after 50 hours
anneal at 800$^\circ$C. $D_{RED}$ is about 3 orders of magnitude larger than the thermal diffusion at 800
$^\circ$C. However, obvious thermal diffusion of La in CeO$_2$ could be measured above 600$^\circ$C, two
points are shown in Figure 7.3 as open triangle at 700$^\circ$C and 800$^\circ$C. Room temperature
ballistic mixing is also indicated by the two horizontal lines. It can be seen that although the two
materials share the same lattice structure and a similar lattice constant, melting point, etc., they
show different diffusion behaviors under heavy ion bombardment. The main reason may lie in
the difference of valence state between uranium and cerium in their oxidized compound. Cerium
is found in Ce$^{2+}$, Ce$^{3+}$, Ce$^{4+}$ valence states, however, uranium could be found in U$^{3+}$, U$^{4+}$, U$^{5+}$,
U$^{6+}$ valence states. Based on this, the result of the introduction of a valence state of 3+ impurity
in UO$_2$ and CeO$_2$ could be different. CeO$_2$ must create an oxygen vacancy but UO$_2$ could go to
higher valence states (U$^{5+}$, U$^{6+}$) instead of creating oxygen vacancy. The diffusion mechanism
could be different if this was what happened in the film. More details of valence states will be discussed later.

The radiation enhanced diffusion of U-233 in UO₂ during fission in a nuclear reactor measured by Matzke [20] has shown different diffusion phenomena. The radiation enhanced diffusion coefficient was found completely temperature independent below 1000 °C. The so-called “thermal rods” [26-28] which is interpreted as a molten zones along the track of the fission fragment might be the reason for the athermal effects. In the present work we found a temperature dependence effect and measured the activation energy. The main differences of these two sets of experiment are the diffusion tracers and radiation species. We use 1.8MeV Kr⁺ to simulate the fission fragments which have larger atomic weight (~110) and much higher energy (~100MeV). The thermal rods effect might not be important for 1.8MeV Kr⁺ but on the opposite side for fission fragments. More research needs to be done to explain the difference of the two results.

Although the properties of uranium self-diffusion is different from radiation enhanced diffusion of impurities in UO₂, some important phenomena must be addressed. The measured diffusivity of uranium-self diffusion coefficient commonly ranges from 10⁻¹⁶ to 10⁻¹² cm²/sec in the temperature range of 1300°C to 1900°C. A very large difference in the diffusion coefficient is due to the small deviation from stiochiometry as mentioned in chapter 3. The RED results in the present work shows $D_{RED}$ ranges from 10⁻¹⁸ to 10⁻¹⁶ cm²/sec, which is even smaller than the uranium self-diffusion coefficient although the temperature is much lower. The low diffusion coefficient of uranium self-diffusion could be an important reason for the low value of $D_{RED}$, however, another effect of introduction of impurities should be noticed, too. As stated by Matzke
[16], the addition of La₂O₃ and Y₂O₃ in UO₂ should reduce the cation diffusion coefficient by creating anion vacancies, thereby decreasing the concentration of cation vacancies. Conversely, an addition of Nb₂O₅ should enhance cation diffusion by creating anion interstitials. This might be true for CeO₂ because cerium cannot go to higher valence state, as shown in Eq. 7.1. In the case of UO₂, if uranium did not have higher valence state than U⁴⁺, Eq. 7.2 might be true and an oxygen vacancy is created in the presence of Nd³⁺. Since uranium has valence states of U⁵⁺ and U⁶⁺, there is no need to create an oxygen vacancy (the formation energy of the O-Frenkel pair is ~3.0-4.0eV [29]) if U⁴⁺ went to higher valence state U⁵⁺ or U⁶⁺ with the addition of Nd³⁺ impurity. In addition, uranium with higher valence state in UO₂ was found on the surface of the film [22]. Thus, the existence of higher valence state uranium may be quite reasonable with the addition of Nd³⁺ because it was energetically favorable.

\[
\begin{align*}
\text{La}_2\text{O}_3 & \xrightarrow{\text{CeO}_3} 2\text{La}'_{\text{Ce}} + 3\text{O}^\text{X}_0 + V^\text{**}_o \\
\text{Nd}_2\text{O}_3 & \xrightarrow{\text{UO}_2} 2\text{Nd}'_{\text{U}} + 3\text{O}^\text{X}_0 + V^\text{**}_o
\end{align*}
\]

(7.1) (7.2)

The quasi-chemical point defect equations above (Eq. 7.1 and Eq. 7.2) are written by employing the Kröger-Vink notation. "V" indicates a vacancy, the subscript "Ce" indicates the lattice site, and the ' represents a 1-minus charge, the double-dot superscript "" represents a 2-plus charge relative to the perfect lattice. O²⁻ going on O²⁻ sites is electrically neutral and the neutrality is frequently designated with a superscript "X", which is really not necessary.

Based on the discussion above, the higher valence state of uranium in the UO₂ sublattice may reduce the diffusion coefficient because of the stronger chemical bond even under heavy ion
bombardment. This could also be one of the reasons that the $D_{RED}$ value is much smaller in $\text{UO}_2$ than that in $\text{CeO}_2$.

The dose rate dependence experiment results in $n=0.65\pm0.11$, which is close to the value $n=0.5$ for the recombination limited kinetics. Due to the difficulty of distinguishing the small changes of diffusion coefficient and experimental error, which might be as large as 0.1, we can say that the result of dose rate dependence further proves that the RED is in the recombination limited regime.

The small value for the longest irradiation time (lowest dose rate) might show a shift from recombination limited regime to sink limited regime because point defects could move to sinks before they combine with each other if the dose rate was low at elevated temperature. On the contrary, the sink density would have to be extremely high for substantial loss of such slowly moving defects which would dominate at the higher dose rates, too. More experiments would need to be done to prove the transition.

The larger value of $D_{RED}$ in this set of experiments (Figure 6.4) than that in the temperature dependent RED study (Figure 6.3) at temperature around 600°C may be caused by the different amount of Nd in the sample (two different samples). Different amount of Nd in the film may result in different oxygen stoichiometry, which would result in large change in the diffusivity. Or the valence state of uranium in $\text{UO}_2$ might be different. Experiments done with the same sample for both temperature dependence and dose rate dependence will be carried out in the future to get further details about the diffusion properties of $\text{UO}_2$. 
Figure 7.1

Comparison of uranium self-diffusion and Nd impurities diffusion in UO$_2$. The black solid line is the linear fitting of the RED results. The two dashed lines indicate the extrapolation of uranium self-diffusion from literature. The two individual solid square points between the dashed lines are the two measurements of Nd thermal diffusion coefficient at 800°C after 50 hours annealing of the present work. The numbers in the parentheses in the legend are the oxygen stoichiometry. The ones without oxygen stoichiometry were considered to be nominal UO$_2$. 

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Figure 7.2

Comparison of product Dt versus Dose for UO$_2$ and CeO$_2$. The dashed line is a linear fitting of the data of CeO$_2$ from Pappas and Heuser [14]. The solid line is the linear fitting of the present work. Both of the fittings are forced through the origin (zero displacement at zero dose).
Figure 7.3

Comparison of diffusion properties of UO$_2$ and CeO$_2$. The dashed line is a linear fitting of the data of CeO$_2$ from Pappas and Heuser [14]. Solid line is the linear fitting of the present work.
Measurements of a buried tracer layer of Nd in a \( \text{UO}_2 \) thin film spreading following energetic heavy ion bombardment with 1.8 MeV Kr\(^+\) have been conducted. Recombination limited kinetics has been observed for radiation enhanced diffusion on the cation sublattice from 400 °C to 800 °C. The results indicate that diffusion equation could be expressed in the following:

\[
D_{\text{RED}} = 1.62 \times 10^{-15} \exp\left(\frac{-0.41}{kT}\right) \text{ cm}^2/\text{sec},
\]

The activation energy \( E_a = 0.41 \pm 0.04 \text{eV} \) and corresponding migration energy \( E_m = 0.82 \pm 0.08 \text{eV} \).

The mixing parameter, \( \xi = 1.65 \pm 0.13 \text{Å}^3/\text{eV} \), is within the range of the predicted value 1.0 – 2.0 Å\(^3\)/eV which indicates ballistic mixing is dominate while thermal spikes are not significant during ion mixing.

A very small yet observable thermal diffusion coefficient of Nd in \( \text{UO}_2 \) thin film at 800 °C has been measured, which is in the range of the extrapolation region of the uranium self-diffusion results in literature. A comparison of radiation enhanced diffusion in the cation sublattice between \( \text{UO}_2 \) and \( \text{CeO}_2 \) has shown different diffusion properties in the two systems. The mixing parameter, \( \xi = 3.6 \pm 0.5 \text{Å}^3/\text{eV} \), activation energy, \( E_a = 0.19 \pm 0.03 \text{eV} \), and migration energy, \( E_m = 0.38 \pm 0.06 \text{eV} \), for La diffusion in \( \text{CeO}_2 \) are about half of the
corresponding values for Nd diffusion in UO₂. Generally the radiation enhanced diffusivity in UO₂ is about 30 to 50 times smaller than that in CeO₂. And CeO₂ has shown an apparent thermal self-diffusion from 600°C, but no diffusion could be measured for UO₂ in this temperature range (from 400°C to 800°C). Due to the similarity of La and Nd as impurities for diffusion, we may say that the values of parameters for diffusion in UO₂ system is different from that in CeO₂ although they share the same lattice structure, similar lattice constant, melting point and other properties. One important reason for the difference between the two is that uranium has higher valence states than U⁴⁺ but cerium does not. The other is that the diffusion coefficient is very sensitive to the oxygen stoichiometry in UO₂. Based on this, the large difference between UO₂ and CeO₂ could be expected.
CHAPTER 9: FUTURE WORK

Because of the complexities of the surface and the strong dependence of diffusion coefficient on stoichiometry, it is crucial to make progress on understanding these two issues. More experiments will be done with different amount of Nd in UO$_2$ film to study the effect of departure from stoichiometry. Nd concentration would be determined by X-ray Photoelectron Spectroscopy (XPS) or by Auger Electron Spectroscopy (AES). Due to the relatively low concentration of Nd in the film as expected from film growth and RBS, and the low sensitivity of AES, it might be hard to distinguish the different concentrations of Nd among different samples by AES. This was also the case for oxygen stoichiometry. Based on these, XPS would be used first to determine the stoichiometry for both Nd and oxygen, or at least the relative concentrations of Nd for different samples. Also, better results could be expected by using the same sample for both the temperature dependent and dose rate dependent experiments. Because of the small size of YSZ substrates, 3 to 4 substrates could be used once during film growth. And higher temperature experiments could be conducted to better understand different diffusion mechanisms in UO$_2$. A transition from recombination limited kinetics to sink limited kinetics could be expected at temperature higher than 800 °C and then merge with the thermal vacancy self diffusion (VSD) at even higher temperatures. RED study on the anion sublattice could also be done to make a complete research of the diffusion behavior in UO$_2$ thin film in the future.
References


[22] M. M. Strehle, B. J. Heuser, M. S. Elbakhshwan, X. Han, D. J. Gennardo, H. K. Pappas, H. Ju, to be published.


