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Study of oxygen self-diffusion in oxides by ion beam techniques: comparison between nuclear reaction analysis and SIMS

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Oxygen self-diffusion in $Fe_{1-x}O$ single crystals has been studied by means of the isotope exchange method in $H_2/H_2{}^{18}O$ atmospheres. The ^{18}O concentration profiles were determined by using two different techniques based on ion beams: secondary ion mass spectrometry (SIMS) and nuclear reaction analysis (NRA); the latter by means of the narrow nuclear resonance reaction $^{18}O(p, \alpha)^{15}N$ at 629 keV, $\Gamma = 2.1$ keV. The diffusion coefficients obtained from the analysis of the measured profiles are in good agreement with those found in the literature. To compare the depth resolution and sensitivity of both techniques, the ^{18}O profiles of implanted Cr_2O_3 single crystals ($E_{^{18}O} = 50$ keV, fluence $= 1.6 \times 10^{16}$ ions/cm^2) were also measured.

1. Introduction

Isotopic tracing with ^{18}O is a major tool for studying the microscopic mechanisms of chemical reaction or transport processes involving oxygen. Oxygen self-diffusion in ceramics oxides is one of the topics in which the use of isotopic tracing is mandatory.

Among the different techniques for surface characterization, two are able to perform depth profile analysis with isotopic sensitivity: nuclear reaction analysis (NRA) [1] and secondary ion mass spectrometry (SIMS) [2]. Both techniques are based on the interaction of energetic ions with matter, but in a very different range of energy. The interaction of low-energy heavy ions with the atoms at the surface results in the sputtering of the sample, which produces charged particles that can be analyzed by mass spectrometry or time of flight techniques. A well-known problem of sputter-based analytical techniques is the preferential sputtering. It is especially important in materials containing both low- and high-mass elements as is the case of some ceramics. To quantify such measurements the use of standards as close as possible to those of the material studied are necessary. On the other hand, when high-energy light projectiles, such as protons and deuterons, are used as the probe beam, the lack of accuracy of the nuclear cross-sections and the deviation from Bragg's rule for the electronic stopping power of compound materials are the main limitations for quantitative analysis using nuclear reactions.

The aim of this paper is to compare the study of oxygen self-diffusion in $Fe_{1-x}O$ single crystals by means of SIMS and NRA techniques. In the former, the natural abundance of ^{18}O is used as an internal standard for the ^{18}O concentration depth profiles. The accurate value for the nuclear resonance cross-section $^{18}O(p, \alpha)^{15}N$ at 629 keV measured by Christensen et al. [3] was adopted to obtain absolute ^{18}O concentration depth profiles using the NRA technique. To com-

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pare the depth resolution and sensitivity of both techniques, the ^{18}O profiles of implanted Cr_2O_3 single crystals were also determined.

2. Experimental procedure

2.1. Sample preparation

High purity single crystals of $Fe_{1-x}O$ and Cr_2O_3 were prepared by conventional techniques. Typically, they had a diameter of 5 mm and were 2 mm thick. The samples were mirror-polished and then annealed in inert atmosphere during 1 h at 1100°C to remove any residual damage caused by the polishing procedure.

The ^{18}O diffusion in $Fe_{1-x}O$ crystals was studied by means of the isotope exchange method. The samples were annealed at 700°C in H_2/H_2O (^{18}O 30% rich) atmospheres with the partial pressure of oxygen, determined by the ratio P_{H_2O}/P_{H_2}, ranging from 1.22×10^{-21} to 5.15×10^{-22} atm. Details of this experimental apparatus are published elsewhere [4]. Single crystals of Cr_2O_3 were implanted with ^{18}O ions (energy = 50 keV, fluence = 1.6×10^{16} ions/cm^2) at room temperature. After the implantation and before the oxygen profiling, these samples were annealed at 1400°C during 1 h in an argon atmosphere to remove the radiation damage.

2.2. SIMS profiling

The depth profiles of ^{18}O and ^{16}O in $Fe_{1-x}O$ and Cr_2O_3 crystals were investigated by means of negative secondary-ion mass spectrometry induced by 10-keV Cesium ion bombardment in a Cameca IMS 4F apparatus at the Laboratoire de Physique des Matériaux, CNRS, Bellevue. The ^{16}O signals were detected by a Faraday cup which has an efficiency 1200 times smaller than the electron multiplier used to measure the ^{18}O signals. The ^{56}Fe (or ^{52}Cr) signals were also monitored.

The thickness of the analyzed layer, and so the depth scale calibration, was obtained by measuring the crater depth with a stylus profilometer (DekTak II). A typical result for an ^{18}O implanted Cr_2O_3 crystal is shown in fig. 1. It clearly shows a constant concentration profile for ^{16}O and ^{52}Cr, while the ^{18}O profile has the typical Gaussian shape of implanted species.

The ^{18}O concentration was determined by taking the ratio between $I(^{18}O^-)$ and $I(^{18}O^-) + I(^{16}O^-)$, that is:

$$n_{^{18}O} = \frac{I(^{18}O^-)}{I(^{18}O^-) + I(^{16}O^-)}, \qquad (1)$$

where $I(^{18}O^-)$ and $I(^{16}O^-)$ are, respectively, the ^{18}O and ^{16}O intensity signal as a function of the sputtering time. The ^{18}O natural abundance (0.205%) can be used as an internal standard, considering that the difference between the sputtering cross-section of the oxygen isotopes is negligible.

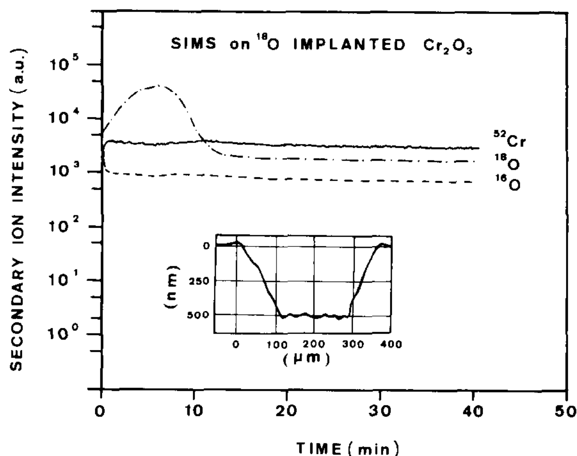

Fig. 1. SIMS profiles on an ^{18}O implanted Cr_2O_3 single crystal. The inset shows the crater profile determined by using a stylus profilometer.

2.3. NRA profiling

The nuclear reaction analyses were performed with the 4 MV Van de Graaff facility at the Departamento de Física, PUC-Rio. Two well-known nuclear reasonance reactions, $^{23}Na(p, \alpha)^{20}Ne$ and $^{27}Al(p, \gamma)^{28}Si$, were used to establish an absolute energy calibration of the accelerator at 592 and 992 keV, respectively. The energy uncertainty in the results presented here, and thus the surface position, is estimated to be less than 1 keV. The beam energy dispersion is estimated to be of order of 0.7 keV for protons with 630 keV of energy.

The reaction products were recorded by using a 450 mm^2 surface barrier detector at 150° from the beam direction (solid angle of 0.102 sr). A 6 μm thick aluminized mylar absorber was placed in front of the detector in order to stop the backscattered protons. Typically, current beams of order of 30 nA were used. The in-depth ^{18}O concentration profile was determined by increasing the proton energy in steps of 2 keV, which corresponds to a depth resolution of about 14 nm at the surface layer of $Fe_{1-x}O$ crystals for normal incidence. All the profiles were measured with the beam direction making an angle of 7° with the surface normal to reduce channelling effects.

Accurate measured value for the nuclear resonance cross-section $^{18}O(p, \alpha)^{15}N$ at 629 keV, $\Gamma = 2.1$ keV [3] was adopted to obtain absolute ^{18}O concentration depth profiles.

3. Results and discussion

Fig. 2 shows the depth profile of ^{18}O implanted ($E_{^{18}O} = 50$ keV; fluence $= 1.6 \times 10^{16}$ ions/cm^2) on a Cr_2O_3 single crystal annealed during 1 h at 1400°C in an argon atmosphere to remove radiation damage. Besides the SIMS and NR profiles, the oxygen profile simulated by the TRIM-90 code [5], is also shown. In the case of the SIMS analysis, the measured ratio of ^{18}O, $n_{^{18}O}$ – see eq. (1) – is converted to oxygen absolute concentration by using the chromium oxide density (5.21 g/cm^3). For this NR profiling, steps of 1 keV for the incident energy were used. The agreement between the profiles obtained with both techniques is excellent. However, despite the fact that the energy straggling was taken into account to convert the α-particle yield to oxygen depth concentration [1], a systematic deviation with respect to the SIMS profile was observed in the deeper part of the oxygen profile. This fact can be attributed to deviation of energy straggling from the adopted Bohr's values.

The main sources of errors are, in the case of NR profiling, the nuclear reaction cross-section, of order of 5% [3], and the stopping-power, also of order of 5%. Statistical errors are negligible and the absolute measurements of proton doses have an accuracy of 3%. For the SIMS profiling, the main source of errors is the uncertainty in the crater depth measurement, estimated to be of the order of 5%.

Table 1 presents the measured values for the retained dose (ϕ), projected range (R_p) and straggling (ΔR_p). The results obtained from the TRIM simulation are also quoted. The agreement between experimental and simulated profiles is good, as the annealing used to remove radiation damage produced only a slight redistribution of the implanted species [6].

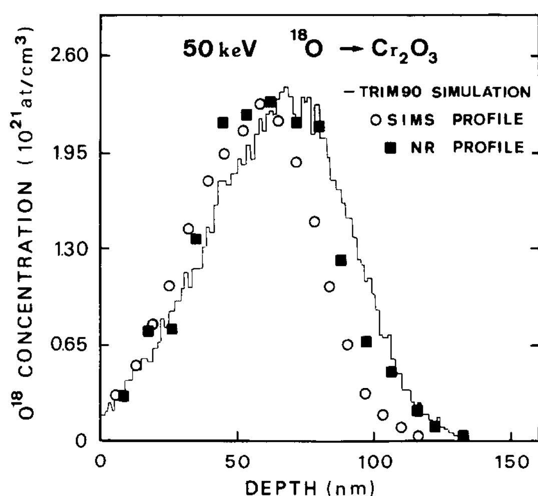

Fig. 2. ^{18}O profile measured by SIMS and NRA on a Cr_2O_3 implanted crystal ($E_{^{18}O}$ = 50 keV, fluence = 2×10^{16} ions/cm^2) annealed at 1400°C during one hour. The TRIM simulation for the implantation profile is also shown.

Table 1
Retained dose (ϕ), projected range (R_p) and straggling (ΔR_p) of 50 keV ^{18}O-implanted in Cr_2O_3 crystals after annealing during 1 h at 1400°C in an argon atmosphere. TRIM-90 results are also quoted

	ϕ [10^{16} ions/cm^2]	R_p [nm]	ΔR_p [nm]
SIMS	1.56 ± 0.08	59 ± 2	23 ± 2
NRA	1.62 ± 0.11	60 ± 8	25 ± 8
TRIM-90	1.6	67.2	26.4

Fig. 3 compares the ^{18}O diffusion profiles measured in $Fe_{1-x}O$ single crystals by using SIMS and NRA. The diffusion experiment was made by means of the isotope exchange method at 700°C during 1 h at a partial pressure of oxygen equal to 5.15×10^{-22} atm ($P_{H_2O}/P_{H_2} = 0.602$). The experimental data are normalized by the surface concentration. Again, the agreement between the SIMS and NR profiles is excellent. However, shallower oxygen diffusion is difficult to be followed by using NR due to the low depth resolution of this technique. In fact, for depths smaller than 30 nm, NR profiling makes no sense. On the other hand, for oxygen penetration much deeper than 150 nm, the use of the 629 keV resonance is complicated due to the difficulties in taking into account the off-resonance contributions to the α-particle yield. For SIMS profiling the major difficulty comes from sample inhomogeneities, e.g., grain short-circuits for oxygen diffusion, due to the very small beam size, which is of the order of tenths of microns in diameter.

The self-diffusion oxygen coefficients were determined by the solution of Fick's second law for a

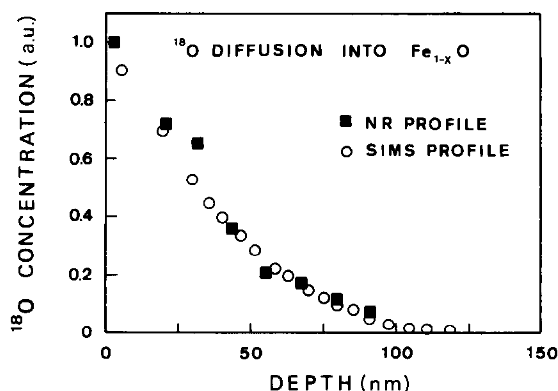

Fig. 3. ^{18}O profile measured by SIMS and NRA on a $Fe_{1-x}O$ single crystal annealed 1 h at 700°C in an atmosphere of $H_2/H_2{}^{18}O$ ($P_{O_2} = 5.15 \times 10^{-22}$ atm).

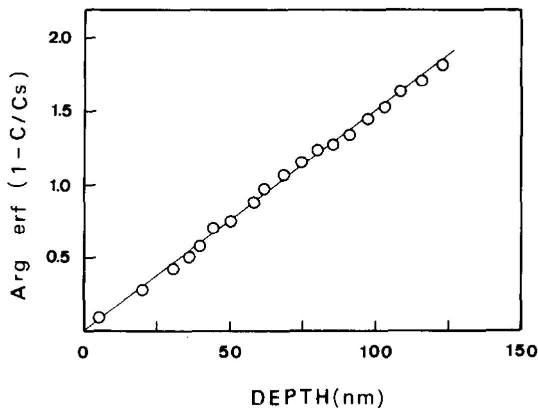

Fig. 4. Arg erf$(1-C/C_s)$ as a function of depth for the ^{18}O profile shown in fig. 3. C_s is the ^{18}O surface concentration.

semi-infinite medium with constant surface concentration [7]:

$$1 - C/C_s = \operatorname{erf}\left[x/2(Dt)^{0.5}\right], \quad (2)$$

where C_s is the ^{18}O surface concentration, C is the concentration of ^{18}O at a depth x, t is the annealing time and D is the diffusion coefficient. The natural abundance of ^{18}O is subtracted in C and C_s.

Considering that the argument of the error function is proportional to x as shown in fig. 4, we have:

$$\arg \operatorname{erf}(1 - C/C_s) = ax, \quad (3)$$

where

$$a = 1/\left[2(Dt)^{0.5}\right]. \quad (4)$$

Then, the determination of the slope of the line in fig. 4 permits the calculation of the diffusion coefficient.

The solution of Fick's second law described by eq. (2) is valid when the incorporation time of the tracer element at the sample surface is small compared to the diffusion time. In the case of slower incorporation kinetics or sample surface evaporation, more complex solutions should be considered [8,9]. In table 2 we present our experimental diffusion coefficients obtained by SIMS and NRA.

Table 2
^{18}O diffusion parameters in $Fe_{1-x}O$ crystals. The errors in the diffusion coefficients are of order of 10% for SIMS analysis and 15% for RN profiling

T [°C]	P_{O_2} [atm]	t [s]	D [cm²/s]	
			SIMS	RN
700	1.22×10^{-21}	3.72×10^{3}		3.2×10^{-15}
700	2.82×10^{-21}	$3.6\ \times10^{3}$		2.1×10^{-15}
700	5.15×10^{-22}	$3.6\ \times10^{3}$	2.9×10^{-15}	3.5×10^{-15}

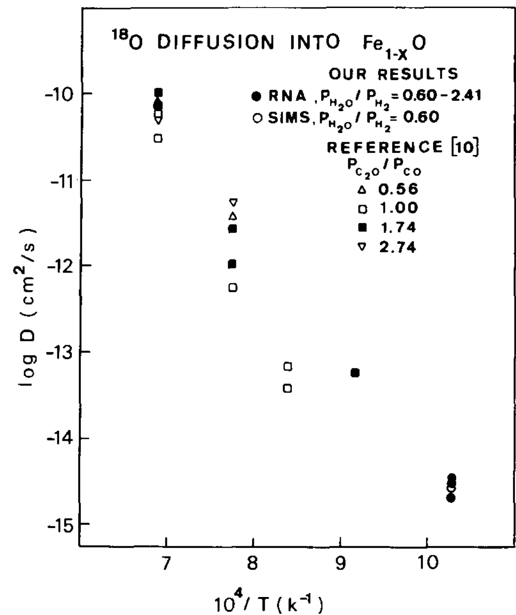

Fig. 5. ^{18}O diffusion coefficient in $Fe_{1-x}O$ as a function of temperature.

For oxygen self-diffusion in $Fe_{1-x}O$, the results published by Yamaguchi and Someno [10] are the only ones that can be found in the literature. They studied the ^{18}O diffusion in $Fe_{1-x}O$ polycrystalline samples obtained by the oxidation of iron foils. The grain size was of order of 3 mm. The isotopic exchange method was also employed, with the oxygen partial pressure controlled by the gaseous mixture of CO and CO_2, the last containing ^{18}O. The temperature range was 820°C to 1182°C and the SIMS technique was used to measure the profile of the oxygen isotopic tracer. Their results are presented in fig. 5. When extrapolated to lower temperatures, they are in good agreement with our values obtained using RN and SIMS.

The influence of the oxygen partial pressure on the structure of point defects in the oxygen sublattice and, consequently, on the oxygen diffusivity, will be discussed in another publication [4].

4. Summary and conclusion

The oxygen self-diffusion in $Fe_{1-x}O$ crystals was studied by means of the isotopic exchange method at 700°C with the ^{18}O profiles being determined by SIMS and NR.

Our results showed that, for shallow oxygen diffusion, the diffusion coefficients determined by both techniques are consistent with other results found in the literature. Despite the better resolution and sensitivity of the SIMS technique, the nuclear reaction

analysis can be used with good results, when the resonance at 629 keV in the $^{18}O(p, \alpha)^{15}N$ reaction is chosen for the determination of the oxygen tracer diffusion profile.

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