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## Diffusion study of oxygen implanted in nickel oxide

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**Résumé.** — L'étude de la diffusion de l'oxygène 18 implanté dans des monocristaux d'oxyde de nickel a été réalisée dans un domaine de température compris entre 1 300 et 1 500 °C en utilisant des doses de  $10^{17}$  ions/cm<sup>2</sup>. Les profils de concentration en oxygène 18 obtenus après implantation et après recuit de diffusion sont mesurés à l'aide d'un analyseur à émission ionique secondaire. Les valeurs des coefficients de diffusion  $D$  sont déterminées en ajustant sur chaque profil expérimental une courbe théorique correspondant à l'évolution par diffusion d'un profil gaussien. Ces valeurs sont en bon accord avec celles des coefficients d'autodiffusion de l'oxygène dans l'oxyde de nickel, mesurées récemment, par échange isotopique, dans le même domaine de température.

**Abstract.** — The study of the diffusion of 18 oxygen implanted in NiO single crystals has been carried out between 1 300 and 1 500 °C with implanted ion doses of  $10^{17}$  ions/cm<sup>2</sup>. The <sup>18</sup>O concentration profiles are measured after the implantations and the diffusion anneals with a secondary ion beam microanalyzer. The diffusion coefficients values are obtained by fitting to the experimental profiles, theoretical curves giving the diffusion profiles corresponding to initial gaussian distributions. These values are in good agreement with those of the oxygen self-diffusion coefficients measured recently by isotope exchange in the same temperature range.

**1. Introduction.** — Ion implantation has already proved to be an interesting method of tracer introduction in some diffusion experiments. By implanting carbon ions in niobium carbide, it has been possible to study carbon diffusion in stoichiometric samples [1]. This method is also very useful when the diffusing species are not soluble in the investigated matrix as for example copper and silver in beryllium [2]. This technique has also the advantage of avoiding the surface contamination problems during the tracer introduction.

As implantation produces defects and a local variation of the chemical composition in the implanted layer, it is of great interest to study the diffusion of the implanted species so as to understand the mechanisms involved during the equilibration process. Such a study has been carried out for Zn implanted in GaAs<sub>1-x</sub>P<sub>x</sub> [3].

This paper deals with the diffusion of oxygen implanted in nickel oxide; the experiments are carried out by annealing between 1 300 and 1 500 °C nickel oxide single crystals implanted with <sup>18</sup>O<sup>+</sup> ions. As there are experimental results available about the self-diffusion of oxygen in nickel oxide [4] it is interesting to check if the oxygen self-diffusion mechanism is involved during the diffusion process of the implanted oxygen ions. In the implanted layer, the oxygen concentration is higher than in the other part of the nickel oxide sample and it would be very interesting to know about the evolution of this local supersaturation and if the radiation defects play an important role during the diffusion of the implanted species.

**2. Experimental.** — Nickel oxide single crystal samples are implanted with <sup>18</sup>O<sup>+</sup> ions and annealed at different temperatures 1 100, 1 300, 1 400 and 1 500 °C in air.

There are six stages in the experimental procedure :

— The samples are preannealed at the temperature chosen for the diffusion study.

— The implantations are performed with <sup>18</sup>O<sup>+</sup> ions : the energy of these ions is 40 keV and the implanted doses are  $10^{17}$  ions/cm<sup>2</sup>.

— The concentration profiles of <sup>18</sup>O are measured after the implantations with a secondary ion beam microanalyzer.

— The diffusion anneals then occur, depending on the temperature they may last from 8 to 70 hours.

— The concentration profiles of <sup>18</sup>O are measured after the anneals with the same method as the implantation profiles.

— The values of the diffusion coefficients are then calculated.

The sample preparation and the annealing conditions have already been described [4]. To have a good sensitivity in profile determination, the analysis are carried out with negative secondary ions : <sup>18</sup>O<sup>-</sup> and <sup>58</sup>Ni<sup>-</sup> [5]. The implantation profiles have the expected gaussian shape, but it is necessary to analyse each sample in order to check the homogeneity of the implantation on the whole specimen and also to determine the values of the mean range and range straggling of the implanted oxygen ions.

The main difficulties encountered during the diffusion anneals are due to the possible evaporation of NiO. Two implanted specimens are annealed at the same time, they are located inside the open space of a large sintered NiO crucible with the implanted surfaces of the samples in contact; in these conditions, the evaporation of the implanted surfaces is made smaller.

The diffusion coefficients are calculated by fitting the experimental concentration profiles measured by secondary ion analysis to theoretical ones issued from a mathematical solution of the problem of the diffusion from an implanted layer [6]. This solution

is obtained by assuming the following initial conditions: a surface acting as a total through, a constant diffusion coefficient and a gaussian initial distribution. The resulting equation has been slightly modified to fit our experimental conditions; two more parameters have been introduced a transparency coefficient  $Cotr$  ( $0 \leq Cotr < 1$ ) taking into account that the surface does not act as a total through and another parameter  $E$  equal to the thickness of the evaporated layer;  $E = 0$  when no noticeable evaporation occurs. The resulting equation used to calculate the theoretical curves fitted to the experimental ones by adjusting the values of  $D$  is given by:

$$C(x) = \frac{N_D}{2\sqrt{2\pi}\sigma} \left[ \exp \frac{-(R_p - x)^2}{2\sigma^2} \left( 1 + \operatorname{erf} \frac{a^2 R_p + x}{a\sqrt{2}\sigma} \right) - \operatorname{Cotr} \times \exp \frac{-(R_p + x)^2}{2\sigma^2} \left( 1 + \operatorname{erf} \frac{a^2 R_p - x}{a\sqrt{2}\sigma} \right) \right] \quad (1)$$

with

$$\sigma = \sqrt{\Delta R_p^2 + 2Dt}, \quad a = \frac{\sqrt{2Dt}}{\Delta R_p}, \quad R_p = R_{pi} - E$$

where

$N_D$  is the ion dose,

$R_{pi}$  is the mean range of the implanted ions,

$\Delta R_p$  is the range straggling,

$t$  is the time of the diffusion anneal.

**3. Results and discussion.** — All the implantation profiles have a gaussian shape and the measured values of  $R_{pi}$  and  $\Delta R_p$  vary slightly from one implanted sample to the other. The mean range value varies between 150 and 200 Å and the range straggling between 275 and 325 Å.

The shapes of the concentration profiles are noticeably modified by the diffusion anneal and the depths corresponding to the maximum concentrations are shifted from  $R_{pi} \simeq 175$  Å towards higher values generally larger than 1 000 Å (Figs. 1 and 2).

The theoretical curves computed with equation (1) are fitted to the experimental concentration profiles obtained for annealing temperatures (Figs. 1 and 2) by adjusting the values of  $D$  and  $Cotr$ . The calcula-

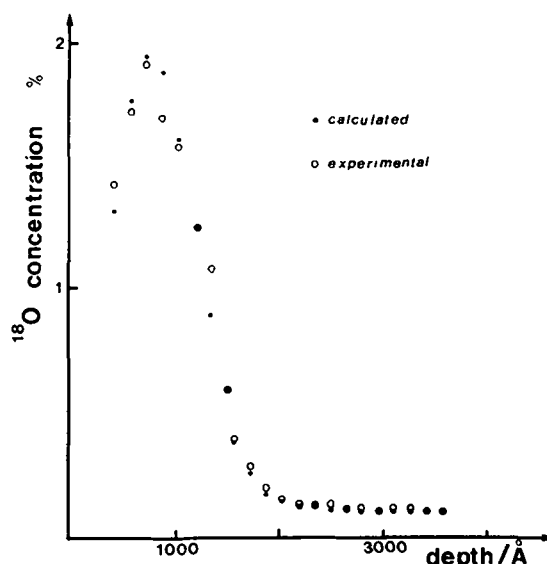


Fig. 1. — Experimental and calculated curves giving the  $^{18}\text{O}$  concentration versus depth after annealing 60 hours at 1 300 °C a NiO sample implanted with  $10^{17} \text{ }^{18}\text{O}^+/\text{cm}^2$ .

tions are started with  $E$  equal to zero and if the fit is bad, it generally means that a sample evaporation has occurred during the diffusion anneal, consequently

Table I. — Values of the diffusion coefficients of oxygen implanted in NiO measured for the three different temperatures. The values of the transparency coefficient ( $Cotr$ ) corresponding to each calculation are also indicated.

$T/^\circ\text{C}$	1 300	1 400	1 500
$D/\text{cm}^2 \text{ s}^{-1}$ ( $Cotr$ )	$3 \times 10^{-17}$ (0.75)	$2 \times 10^{-16}$ (0.3)	$3 \times 10^{-15}$ (0.35)
	$4 \times 10^{-17}$ (0.4)	$2 \times 10^{-16}$ (0.3)	$3 \times 10^{-15}$ (0.4)
	$4 \times 10^{-17}$ (0.85)	$3 \times 10^{-16}$ (0)	$3.5 \times 10^{-15}$ (0.45)
	$4.5 \times 10^{-17}$ (0.4)		$5 \times 10^{-15}$ (0.35)
	$4.5 \times 10^{-17}$ (0.75)		

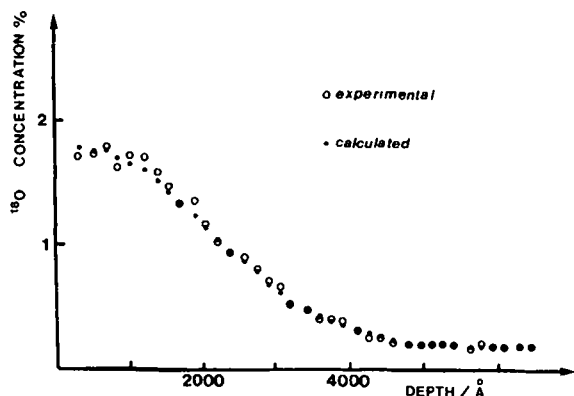


Fig. 2. —  $^{18}\text{O}$  concentration profiles as for figure 1. The annealing conditions are 8.1 hours at 1 500 °C

it is necessary to take into account the thickness  $E$  of the evaporated layer, the values of  $E$  are usually smaller than 75 Å.

The values of  $D$  obtained for a same temperature do not depend on Cotr (see Table I) but they may differ significantly from each other. The scattering of the experimental results is mainly due to the error on depth measurements (10 %) which gives uncertainties on the determinations of  $R_{p1}$ ,  $\Delta R_p$  and on the diffusion profiles. The values of  $\text{Log } D$  are plotted versus  $1/T$  in the figure 3, they vary linearly with the inverse of the temperature between 1 300 and 1 500 °C. The Arrhenius plot corresponding to the oxygen self-diffusion studied in NiO by the isotope exchange method [4] is also presented on this figure. There is a good agreement between the values of  $D$  measured with the two methods, those corresponding to the implantation of  $^{18}\text{O}$  are a little lower. The activation energy for the diffusion of implanted oxygen in NiO is equal to  $5.4 \pm 1$  eV, this value is quite close to the one ( $5.6 \pm 0.5$  eV) measured for the activation energy of the oxygen self-diffusion in thermodynamic equilibrium [4]. It is also interesting to notice that the results obtained with the ion implantation technique confirm the recent values measured with the isotope exchange method which were differing significantly from earlier results giving an activation energy of 2.5 eV and oxygen diffusion coefficients  $10^4$  times higher [7].

This good agreement between the experimental results strongly suggests that the mechanism governing the diffusion of the implanted oxygen is the equilibrium self-diffusion. It also proves that the radiation defects introduced during the implantation have no significant influence on the diffusion process. This has already been noticed for smaller ion doses when the diffusion length is much larger than the range of the ions [8, 9].

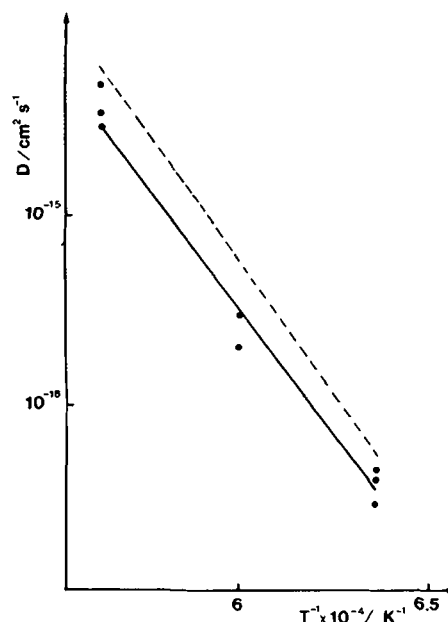


Fig. 3. — Arrhenius plot for the values of the implanted oxygen diffusion coefficients measured between 1 300 and 1 500 °C (solid line). The dash line corresponds to the Arrhenius plot obtained by the isotope exchange method [4] for the equilibrium self-diffusion of oxygen in NiO.

The value of  $D$  measured for 1 100 °C ( $1.3 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ ) is high and does not give a linear relationship between  $\text{Log } D$  and  $1/T$  with the values measured at higher temperature. This modification of the diffusion behaviour at lower temperature is probably due to the influence of the dislocations and had also been noticed in the experiments using the isotope exchange method [4].

**4. Conclusion.** — The diffusion behaviour of  $^{18}\text{O}$  implanted in nickel oxide single crystals has been studied between 1 300 and 1 500 °C. In this temperature range, the implanted oxygen diffusion is governed by the mechanism of the equilibrium self-diffusion. The radiation defects do not apparently play a significant role in the diffusion process, this is probably because the experimental times of anneal are very long compared to the time of equilibration of the defects. The role of radiation defects could be studied by the investigation of the early stages of the implanted layer evolution. This cannot be done with the profile analysis method used in this work because the depth measurements are not accurate enough.

The diffusion process of the implanted oxygen being governed by the self-diffusion mechanism, it is interesting to think of the oxygen implantation for the study of the influence of the oxygen partial pressure on the oxygen diffusion coefficients.

## DISCUSSION

*Question.* — R. J. FRIAUF.

This is a question about the boundary conditions at the surface during the diffusion problem. You apparently introduce the transparency coefficient in order to allow for the possibility that some fraction of the oxygen tracers can escape from the surface after they diffuse back to it. On a physical basis this seems to be a very likely possibility.

*Reply.* — M. MEYER.

Shimko has calculated his equation in assuming that the concentration of the diffusing species is equal to zero at the surface. The introduction of a transparency coefficient leads to a surface concentration different from zero and consequently, only one fraction of the oxygen tracer can escape from the surface.

*Question.* — T. E. MITCHELL.

I am surprised there is no evidence for radiation effects. Annealing at  $\sim 1\,200\text{ }^{\circ}\text{C}$  should cause clustering into interstitial dislocation loops, leaving excess vacancies to produce at least a transient effect on diffusion.

*Reply.* — M. MEYER.

The radiation defects do not play a significant role between  $1\,300$  and  $1\,500\text{ }^{\circ}\text{C}$ . This is probably because the transient stage is very short compared to the time of the diffusion anneal. The other explanation may be that the oxygen self-diffusion and the defect annealing are governed by the same mechanism.

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