

SURFACE MODIFICATION OF $ZrO_2 - Y_2O_3$ ss BY ION IMPLANTATION

D. SCHOLTEN and A.J. BURGGRAAF

Twente University of Technology, Department of Chemical Engineering, Laboratory of Inorganic Chemistry and Materials Science, P.O. Box 217, 7500 AE Enschede, The Netherlands.

With $^{56}Fe^+$ implantations in oxygen ion conducting solid solutions of $0.86ZrO_2-0.14YO_{1.5}$ [ZY14] electronic conductivity is introduced in a surface layer of less than 70 nm. The theoretically expected Gaussian distributions of Fe ions as calculated by computer simulation are compared with results of analyses by AES and RBS. Mean projected ranges (Rp) agree but remarkable differences in peakheight and halfwidth are found. Surface concentrations up to $6 \cdot 10^{21}$ ZY Fe/cm³ have been achieved using mediate doses of $2-4 \cdot 10^{16}$ Fe/cm² and energies ranging from 15-110 KeV. Concurrent sputtering during high dose implantations ($8-40 \cdot 10^{16}$ Fe/cm², 15 and 110 KeV) causes a peakshift towards the solid-gas surface. With these high doses high concentrations up to $24 \cdot 10^{21}$ Fe/cm³ were obtained. The implanted profile shapes remain stable under heat treatments up to 900°C. Higher temperatures cause a decrease in topconcentration and broadening of the distribution. After annealing during 25 hrs. at 1500°C all implanted iron was dissolved in the ZY matrix and no precipitates were formed as indicated by XRD.

1. INTRODUCTION

Ion implantation is a widely used technique in semiconductor technology¹. In recent years it has been utilized to alter the mechanical and chemical properties of metals² as well as optical³, electrical⁴, catalytical⁵ and mechanical properties of insulators and special ceramics⁶. The purpose of the present series of investigations is to study the possibilities of preparing thin layers within the surface region of oxygen ion conduction oxides leading to a composition different from the bulk. More specifically our aims are the introduction of electronic conduction and of catalytic activity for redox reactions involving gaseous oxygen, to enhance the adsorption-desorption characteristics and to improve some mechanical properties. This requires a surface concentration of the dopant ions of (in most cases) several atom percent or more and consequently the use of a high implantation dose of dopant ions.

Yttrium stabilized zirconia (afterwards

called ZY) has been chosen as oxygen ion conducting substrate material because its properties are well known and it is used in fuel cells, chemical sensors, oxygen pumps and electrocatalytic devices^{7,8}. Furthermore it has been shown that oxygen ion conducting Ca stabilized zirconia layers can be prepared and modified by implantation⁹.

Ion implantation for this purpose involves two problem fields: i) problems related with the chemical state and structure of the layer and ii) the distribution of the implanted ions (profile) which does not always have a suitable shape. These two fields will be discussed shortly and specific problems to be addressed will be mentioned. An advantage of implantation is the independency of dopant introduction on temperature and thermodynamics. This implies however that a number of different situations can arise. Implanted (metal) ions can react with each other forming (metal) precipitates or they can react with the matrix and form normal

or supersaturated solid solutions or form new compounds. Finally metastable compounds can be formed. Very few is known in a systematic way of the course of these processes as a function of relevant parameters like chemical composition, implantation dose, temperature during implantation and heat treatments¹⁰. Interesting effects can be expected however (metastable states, formation of very small metal clusters). With normal implantation techniques a Gaussian profile to a depth of 10-100 nm is achieved with a top concentration below the surface. Often manipulation of the profile shape and of the concentration at the surface is necessary, the latter being bound to a maximum which is dependent on implanted ion and type of substrate.

For this reason in the present work special attention has been paid to the study of some of the factors which determine the profile shape and specifically the surface concentration in the first 5 nm below the surface. Iron has been chosen as a dopant material for several reasons. In preliminary work¹¹ we determined the solubility and the effect of Fe in ZYss. In normally prepared ZY materials the solubility limit of Fe_2O_3 is about 1.7 mol%.^{*} At high temperatures (1500°C) however much more Fe can be present in the bulk of quenched ZY specimen (10 mol %). Preliminary SEM and XRD observations however indicate the onset of precipitation phenomena on the grainboundaries after slow cooling instead of quenching of the material. Electronic conductivity arises in the bulk only at a Fe concentration higher than about 6 mol% Fe_2O_3 . From studies of Fe implanted in MgO ^{12,4} something is known of the chemical state of Fe in oxides at high doses. Finally with Fe or iron oxides catalytic activity in some redox reactions can be expected, mechanical effects

have been shown in related oxides and iron beams of high current density are easily obtained.

2. EXPERIMENTAL

In this paper $^{56}Fe^+$ implantations in a solid solution with composition 0.86 mol% ZrO_2 -0.14 mol % $YO_{1.5}$ (ZY14) are investigated. These experiments were carried out using a 120 KeV ion implantation machine. The $^{56}Fe^+$ ions were produced in a hot cathode ion source filled with $FeCl_2$. Beam currents were kept lower than $1 \mu A/cm^2$ in order to avoid electrical charge up of the oxidic target surface. Implantation conditions were selected with the help of the implantation computer simulation program DIMUS¹ which gives top concentration depths below the surface (R_p) and the standard deviations of the distributions (ΔR_p) for any combination of dopant and matrix material. Direct determination of the composition of the surface layer has been achieved by Rutherford Backscattering Spectroscopy (RBS) with a Van der Graaff generator producing a 2 MeV 4He beam. The detection angle is 170°. The RBS spectra were converted into concentration profiles using theoretical values for scattering and stopping cross sections¹³.

Profile measurements in the implanted samples are also achieved by Auger Electron Spectroscopy (AES). These results have been made (semi-)quantitative by comparison with the results on standard materials of known compositions. Sensitivity factors have to be determined for elements in the oxidic materials separately. This method is published elsewhere¹⁴. The sensitivity factor for Fe is determined from synthetically prepared bulk samples ZY with 10 mol % Fe_2O_3 and with 6 mol % Fe_2O_3 , which last material has also been used for electrical measurements. No preferential sputtering is found using an Ar^+ beam during AES depth

* note : 1 mol % Fe_2O_3 in ZYss is equal to about 2 cation percent.

profiling.

Preliminary electrical surface conductivity measurements on the implanted samples have been executed using a two-point electrode-cell. The distance between Pt-electrodes (on one surface) is 7mm.

3. RESULTS AND DISCUSSION

The results of computer simulations using DIMUS for $^{56}Fe^+$ implantations in ZY14 with acceleration energies of 110, 55 and 15 keV and doses of 3.3×10^{16} , 2.76×10^{16} and 2×10^{16} Fe at/cm² respectively give the Gaussian curves as shown in figure 1. The position of the maxima (R_p) is proportional to the acceleration voltage and ranges for Fe in ZY14 from 7 to 40 nm using 15 to 110 kV. Results of AES sputterprofiling on distributions, introduced under these conditions, are given in figure 2. The same figure contains results of RBS analyses on these specimen. However RBS analyses of the first 5 nm are not reliable due to the experimental uncertainty level. For this region

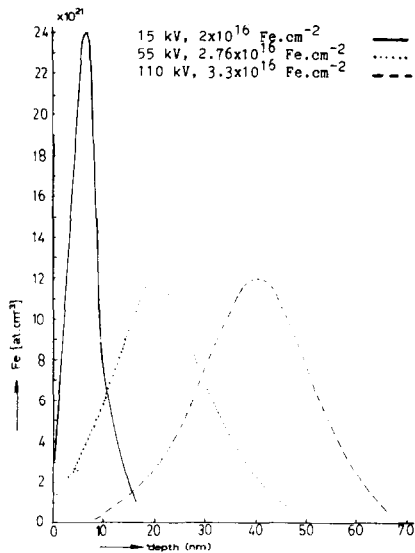


Figure 1: DIMUS computer simulations of Fe implantations in ZYss.

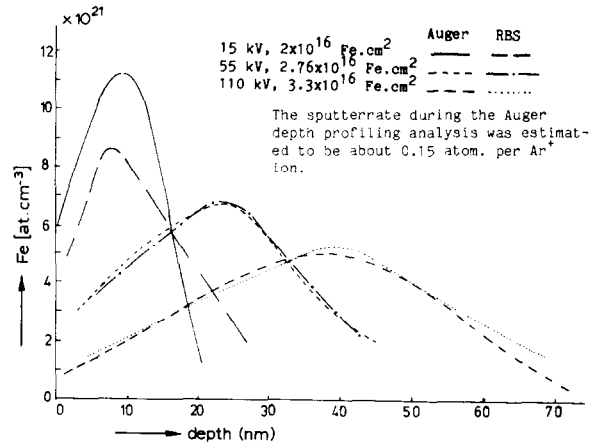


Figure 2: RBS and AES analyses of implanted Fe profiles in ZY:

sputterprofile analysis by AES is an indispensable technique for measurements of the surface concentration.

The results of both techniques are in rather good agreement but large differences are found with the calculated profiles. Although the analyzed R_p values agree with the computer calculated ones, the top values of the distributions as analyzed are much lower than expected from the computer simulations. The implanted profiles are broader and skewed. The measured total iron content in the sample is about 17% lower than the imposed implantation dose. Skewness and broadening of the profile may be caused by increasing stopping power during implantation as a function of Fe concentration in the matrix. A second and more important reason is the occurrence of sputtering during implantation.

This causes a backwards retreating surface and results in profile shapes and surface concentrations which are different from the expected ones. This effect of sputtering is proportional with sputtering time and so it will be the more important the higher the dose (keeping the beam current constant). Indeed effect of

sputtering on the implantation profile has been found as is shown by comparing 4×10^{17} Fe/cm², 110 keV and 8×10^{16} Fe/cm², 15 keV implantations (Fig. 3) with the lower dose implantation profiles shown in Fig. 2. The top concentrations of distributions in Fig. 3 are shifted towards the solid-gas surface and maxima of 24 and 15×10^{21} Fe/cm³ respectively were found by RBS. So with high dose implantation the top concentration of dopant ions is situated at or close to the surface and a high surface concentration is achieved while the slope of the distribution profile is steep. The total process of simultaneous implantation and sputtering can be described by a model and provided the sputtering rates are known, surface concentrations and profile shapes can be calculated. This will be published in a forthcoming paper. A multistep implantation procedure, using different energies and doses (e.g. 110 keV, 3.3×10^{16} , followed by 55 keV, 2.76×10^{16} ; 24 keV, 0.72×10^{16} and 15 keV, 0.58×10^{16} Fe⁺ cm⁻²), leads to a broad and flat profile as shown in fig. 4.

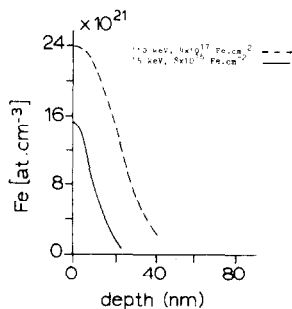


Figure 3: RBS analyses of implanted Fe profiles in ZY.

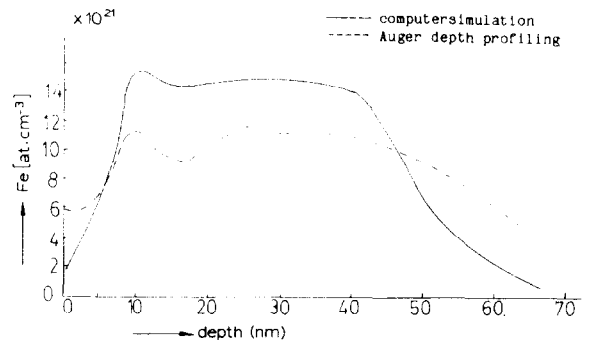


Figure 4: Fe profile in a ZY specimen after subsequent (multistep) implantation with 110 keV, 3.3×10^{16} Fe cm⁻²; 55 keV, 2.76×10^{16} ; 24 keV, 0.72×10^{16} ; 15 keV, 0.58×10^{16} Fe.cm⁻².

Untill here only unannealed profiles were described. However annealing is necessary for the removal of radiation damage which is introduced during implantation and to influence the chemical state of the dopant. By annealing a reorganization of a distorted lattice is expected, while precipitates, (super saturated) solid solutions or (metastable) compounds may be formed¹⁰. Special heat treatments will alter the dopant distribution by diffusional processes. Some experiments have been carried out to investigate the influence of temperature treatments in air on profile shape in order to enlarge the surface concentration. Experiments show that up to 900°C implanted profiles (as shown in Fig. 2) remain stable for at least 25 hours. Higher temperatures (1000°C, 1 hr.) show redistribution effects as given in Fig. 5 for implantations with 15 or 55 keV. Distributions are flattened and yield a broad maximum of 3 to 4×10^{21} at Fe/cm³ ZY. This value is still higher than the solubility of standard ZY material chemically doped with Fe₂O₃ at this temperature which amounts ± 1.5 mol % Fe₂O₃ = 1×10^{21} at Fe/cm³. A decrease in Fe surface concentration for the 15 keV implantation was

found, contrary to a slight increase for the 55 keV one. Further experiments will be carried out to investigate whether diffusion towards the surface and consequently surface enrichment can be achieved.

At high temperature (1500°C, 25 hrs.) pronounced cation diffusion occurs and Fe profiles could not be detected anymore by RBS. With AES a very broad "profile" with a Fe concentration lower than 1.5×10^{21} Fe/cm³ has been measured. This is much lower than the solubility of Fe₂O₃ in ZY14 standard material which is at least 10 mol % Fe₂O₃ at this high temperature. XRD results on the implanted material revealed no precipitation. The Fe ions were fully dissolved in the ZYss. Substitution of Fe causes a decrease of the cubic lattice parameter proportional with the Fe concentration as is shown for the chemically prepared specimens¹¹. The implanted material also exhibit a decrease of the lattice parameter after this high temperature anneal. At all anneal temperatures colour changes from silvery/red to orange/white are found. This indicates a change in the chemical state which probably involves an oxidation process from a state with dominant Fe²⁺ and Fe atoms present to one with dominant Fe³⁺ ions. The minimal Fe dopant concentration needed to achieve electronic conductivity was estimated

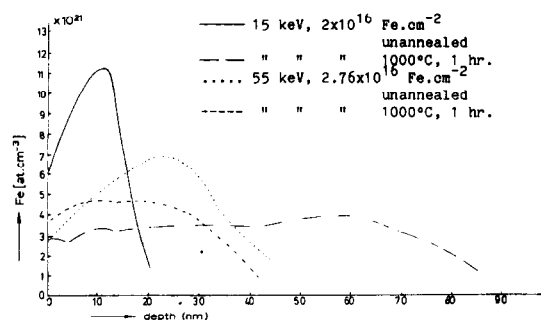


Figure 5: AES analyses of profile changes after heat treatment at 1000°C in air for 1 hr.

separately in chemically prepared specimens. ZY materials containing 6 mol% Fe₂O₃ showed mixed electronic and ionic conductivity. So with ⁵⁶Fe⁺ implantations at 110 kV with doses of 8×10^{16} Fe/cm² and 4×10^{17} Fe/cm² mixed conductivity could be expected because the maxima of the introduced distributions exceed the necessary threshold concentration level with more than three to six times respectively. Surface conduction measurements in the two point cell show indeed improved conduction for material implanted in this way (Fig. 6). A drop in resistances at 225°C is found during the first measurement run for the unannealed Fe implanted material. This drop is followed by a rapid increase (fig. 6, T = 300°C, curve b and c). Note that under these conditions no changes in shape of the profile occur. Only colour changes from silvery to orange were observed. In a second measurement run no time dependent changes in resistance at 200-300°C were found anymore and curve d in figure 6 is followed. For the specimen implanted with 4×10^{17} Fe/cm², 110kV a resistance is obtained which is 2-3 times lower than found for unimplanted material. The reason for the behaviour during low temperature anneal at 200-300°C is not known for the moment. Probably oxidation phenomena play a role as is indicated by the colour change. The influence of damage implantation on the conductivity was investigated by the use of Ar⁺ implantation (15kV, 8×10^{16} Ar/cm²) Fig. 6 curve e).

The conductivity was found to be comparable with that of the untreated sample. The method used for the conductivity measurement gives no information which part of the total conductivity at elevated temperature should be attributed to electronic or oxygen ionic conductivity. As shown by the Ar⁺ implantation in fig. 7 the effect of radiation damage is negligible. So all changes in resistances found must be attributed to the presence of implanted

iron. We expect that the increase in the overall surface conductivity found in the implanted materials is caused by introduction of electronic conductivity because iron has proven to yield some decrease in oxygen ion conductivity¹⁵.

From literature it is known that radiation damage may influence the hardness of implanted material. B.R. Appleton c.s. found improved hardness of Al_2O_3 after implantation with Cr, Zr or Ti and subsequent annealing treatments. Preliminary experiment on our material indicate hardness effects in ZY as well and further investigations are in progress.

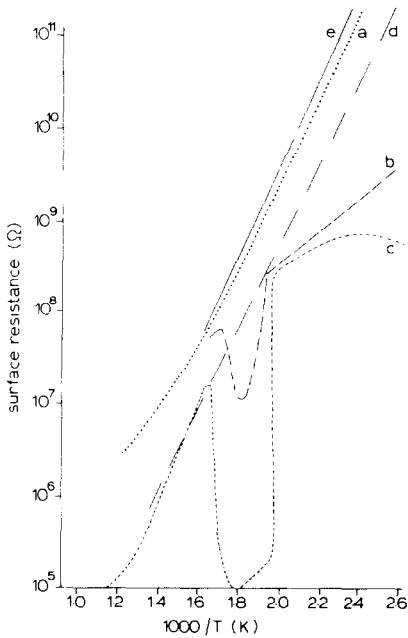


Figure 6: Change of surface resistance of ion implanted ZY14 between two Pt point electrodes at a distance of 7 mm; first heating run.
 a) non implanted ZY14
 b) 110 kV, $8 \cdot 10^{16}$ Fe at cm^{-2}
 c) 110 kV, $4 \cdot 10^{17}$ " "
 d) sample c, second heating run (so heat treated)
 e) 15 kV, $8 \cdot 10^{16}$ Ar at cm^{-2}
 Due to the measuring instrument used (Keithley 602) the position of the curves in the figure is uncertain by a factor ± 1.5 .

4. CONCLUSIONS

- It is possible to predict the position of the concentration maximum (R_p) by computer simulation. However considerable deviations between the shape of the calculated Gauss profiles and the shape of the experimental curves is found.
- RBS and AES are used to analyse the concentration profiles and give comparable results. AES is used to determine the surface concentration.
- Implantation energies of 15 - 110 keV in combination with medium ion doses of $2 - 4 \cdot 10^{16}$ at/ cm^2 yield surface concentrations of $1 - 4 \cdot 10^{21}$ Fe at/ cm^3 which is 1/10 - 1/4 of the top concentration. By the use of prolonged implantation times, and consequently a high dose of $8 - 40 \cdot 10^{16}$ at/ cm^2 , the implantation profile is considerably modified by a simultaneously occurring sputtering process. This leads to a shift of the top of the concentration profile towards the surface. In this case a surface concentration of $16 - 24 \cdot 10^{21}$ Fe at/ cm^3 has been obtained. Broad and flat profiles are realized by multistep implantation.
- Annealing at temperatures below 900°C do not change the shape of the profile. Annealing at 1000°C or higher for prolonged times broadens the profile and generally leads to a decrease of the top concentration. After a long annealing time (25 hrs.) at 1500°C all implanted Fe was dissolved in the ZY matrix. No second phases (precipitates) were found by XRD and consequently solid solutions of $ZrO_2 - Y_2O_3 - Fe_2O_3$ can be prepared.
- The surface conductivity of ZY materials is strongly increased when high surface concentrations of Fe are present. Annealing results in a decrease of the enhanced conductivity of the implanted material and stable conductivity values are found which are 2 - 3 times higher than that of unimplanted

material. Consequently mixed conducting layers can be prepared on stabilized ZrO_2 by Fe implantation.

ACKNOWLEDGEMENTS

The authors like to thank Dr. E.H. du Marchie van Voorthuysen and Mr. J.J. Smit of the State University of Groningen for their help with the ion implantations; also Drs. E.W.A. Young of the State University of Utrecht for his help with RBS measurements. Philips Elcoma, Eindhoven is thanked for the Auger facilities. The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from Z.W.O.

REFERENCES

1. Ion Implantation Techniques, eds. H. Rijssel, H.G. Glawischnig (Springer Verlag, Berlin Heidelberg New York, 1982).
2. J.M. Poate, A.G. Cullis, Implantation Metallurgy-Metastable Alloy Formation, in: Treatise on Materials Science and Technology, Vol. 18, ed. J.K. Hirvonen (Academic Press, New York, London, Toronto, Sydney, San Francisco, 1980) pp. 85-131.
3. W.A. Sibley, Nucl. Instrum. & Methods in Physics Research B1 (1984) 419.
4. A. Perez, J. Bert, G. Marest, B. Sawicka, J. Sawicki, Nucl. Instrum. & Methods 209/210 (1983) 281.
5. G.K. Wolf, K. Zucholl, H. Folger, Nucl. Instrum. & Methods in Physics Research B1 (1984) 240.
6. P.J. Burnett, T.F. Page, Changing the Indentation Behaviour of MgO by Ion Implantation, in: Materials Research Society Symposia Proceedings, Vol. 27, eds. G.K. Hubler, O.W. Holland, C.R. Clayton, C.W. White (North-Holland, New York, Amsterdam, Oxford, 1984) pp. 401-406.
7. J. Olmer, J.C. Vigue, E.J. Schouler, Solid State Ionics, 7 (1982) 23.
8. M. Stoukides, C.G. Vayenas, J. Catalysis 70 (1981) 137.
9. C. Cohen, J. Siejka, M. Berti, A.V. Drigo, M. Croset, M.M. Tosic, Radiat. Eff. 64 (1982) 221.
10. B.R. Appleton, H. Naramoto, C.W. White, O.W. Holland, C.J. McHargue, G. Farlow, J. Narayan, J.M. Williams, Nuclear Instruments and Methods in Physics Research B1 (1984) 167.
11. A.J.A. Winnubst, D. Scholten A.J. Burggraaf, to be published.
12. A. Perez, Nucl. Instrum. & Methods in Physics Research B1 (1984) 621.
13. Wei-Kan Chu, J.W. Mayer, M-A. Nicolet, Backscattering Spectrometry (Academic Press, New York, San Francisco, London, 1978).
14. A.J.A. Winnubst, P.J.M. Kroot, A.J. Burggraaf, J. Phys. Chem. Solids 44 (1983) 955.
15. M.J. Verkerk, A.J.A. Winnubst, A.J.A. Burggraaf, J. Mat. Sc. 17 (1982) 3113.