

Structural, Electrical and Catalytic Properties of Ion-Implanted Oxides

B. A. van Hassel and A. J. Burggraaf

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

Received 4 November 1988/Accepted 14 March 1989

Abstract. The potential application of ion implantation to modify the surfaces of ceramic materials is discussed. Changes in the chemical composition and microstructure result in important variations of the electrical and catalytic properties of oxides.

PACS: 66.30, 81.40, 81.60, 61.70

Since the introduction of ion implantation as a surface modification technique, the electrical [1, 2], optical [3], magnetic [4], chemical [5], mechanical [6] and topographical [7] properties of solids have been modified. The potential use of ion implantation to modify the surfaces of ceramic materials has been discussed by Burggraaf et al. [56]. These changes in the macroscopic properties correspond to the changes in chemical composition and microstructure. In this paper this relationship is discussed for the electrical and catalytic properties of oxides, modified by ion implantation.

1. Ion Implantation

In the ion-implantation process, specific atoms are ionized, accelerated and mass selected [8]. Those high energetic ions (15 keV–2 MeV) penetrate in the solid and come to rest due to elastic and inelastic energy loss processes. A comprehensive treatment of the penetration of ions in solids has been given in [9 and 10]. Depending on the process parameters the depth profile can be given different shapes, the penetration depth can be varied between some nanometers and about one micrometer and the dopant concentration in the surface can be raised to about 50 at.%. When the ion beam is properly scanned over the surface, lateral very uniform concentrations of the dopant are obtained. Due to the electrical control of the ion energy and dose, the technique is very reproducible.

A major advantage of ion implantation is that a surface layer can be doped with any element, independent of its solubility in the substrate material. This means that one can produce metastable compounds, strongly supersaturated solid solutions and complex microstructures consisting of very finely dispersed precipitates with nanoscale dimensions in a matrix material. Several examples are discussed below.

2. Microstructural Changes

2.1. As-Implanted State

When an ion is implanted, it collides with the nuclei and electrons of the solid. In ionic oxides, only nuclear collisions result in defects [11]. Vacancies and interstitials are generated in both the anion and the cation sublattice. Interstitial loops nucleate and grow during irradiation. The lattice damage initially increases with the dose and finally saturates [11]. At that point as many defects are generated as annihilated by dynamic recovery processes in the solid. Dynamic recovery processes can be suppressed by cooling the target to low temperatures.

The accumulation of defects in ion-implanted solids can result in a transition from a crystalline to an amorphous phase. This has been observed for, e.g., Al_2O_3 [12, 13], CaTiO_3 [12], SrTiO_3 [12], LiNbO_3 [3], yttria stabilized zirconia (YSZ) [14] and garnets [15]. Oxides with a complex crystal structure, due to,

for instance, the ordering of defects, may transform to a simpler crystal structure (randomization) [16]. The high local stress in the surface after ion implantation may result in a phase transformation. This has been observed for yttria stabilized zirconia implanted with 2 MeV $^{15}\text{N}_2^+$ ions [17].

For most implanted ions, little is known about their charge state after ion implantation. The ions whose charge state has been studied are Fe, Au [42] and Sn [43]. This is mainly due to the fact that those ions are very suitable as a nuclide in Conversion Electron Mössbauer spectroscopy (CEMS) experiments [18]. The charge state of, e.g., Fe has been studied in Al_2O_3 [19], MgO [20], ZrO_2 [21], Mg_2SiO_4 [22], yttria stabilized zirconia [23], and garnets [24]. In the as implanted state Fe is present in three different oxidation states: Fe^{2+} , Fe^{3+} and metallic precipitates Fe^0 . The evolution of the fraction of Fe atoms in each charge state as a function of dose has been described for MgO with a statistical model [25]. The main conclusion from this model is that Fe^{3+} can only exist in MgO as an isolated impurity. The fraction of Fe^{2+} and Fe^0 is determined by the probability that, respectively, two Fe atoms and three or more Fe atoms aggregate.

Sputtering of the target arises also from ion implantation. This may result in the preferential loss of one of the components in a compound target. If an oxide shows a preferential loss, it is rather oxygen than metal. Mechanisms to explain this phenomenon have been reviewed by Kelly [26]. For ionic oxides the preferential loss of oxygen can be explained in terms of differences in the surface binding energy. In, e.g., ZrO_2 , the surface binding energy amounts to 7.1 eV for oxygen and to 32.2 eV for Zr. This results in the preferential loss of oxygen from ZrO_2 during sputtering. Consequently, the stoichiometry of a thin layer is changed by the implantation process.

The sputtering of the target effects the concentration of implanted ions which can be obtained [8, 27, 62]. Initially the implanted ions come to rest in a Gaussian depth profile and the concentration of implanted ions in the outermost surface layer is negligible. So, if sputtering occurs, only target atoms are sputtered away. After successive ion bombardments the concentration of implanted ions has been increased and the surface has moved inwards. At this moment the implanted ions are also sputtered. Finally, a steady-state region is obtained in which as many ions are implanted as ions are sputtered away. The maximum concentration of the implanted ion in this region is inversely proportional to its sputter yield in the compound target.

The erosion of a surface due to sputtering is laterally not always uniform and may result in

topographical changes. This subject has been reviewed in [7].

It can be concluded that ion implantation results in a nonequilibrium system. Many defects are present and the concentration of the implanted atom may be far above its solubility level. The evolution of this system towards its equilibrium state is discussed below.

2.2. Effect of Annealing

Thermal annealing results in the annihilation of point defects and the growth of extended defects. In the case of Fe implanted MgO the V^- centers disappear for an annealing temperature near 500°C and all other defects disappear at 700°C [28]. Extended defects, such as dislocation loops, could be observed in H^+ implanted TiO_2 after annealing at 800°C [11].

Crystalline surfaces, which have been transformed to the amorphous state by ion implantation, may recrystallize in an epitaxial way. This has been observed for, e.g., YSZ [14], CaTiO_3 , SrTiO_3 and Al_2O_3 [12]. In particular, the study of White et al. [12] about the recrystallization of CaTiO_3 , SrTiO_3 , and Al_2O_3 has given much insight in the recrystallization process.

The implantation of Pb in both CaTiO_3 and SrTiO_3 single crystals at liquid nitrogen temperature (LNT) turned a thin surface film amorphous. Annealing at temperatures well below the melting point of these oxides resulted in a recrystallization of the amorphous film by solid state epitaxy. During recrystallization, Pb was substitutionally incorporated into the lattice. In the low-concentration regime, the regrowth kinetics was not influenced by the Pb concentration. In the case of CaTiO_3 , the regrowth rate was strongly influenced by the crystallographic plane. At the temperature of recrystallization, the implanted Pb was again substitutionally incorporated into the lattice. Subsequent heat treatments at higher temperatures resulted in the precipitation of the implanted Pb. This indicates that the solid solution of Pb in CaTiO_3 , such as obtained after recrystallization at low temperatures, was metastable.

$\alpha\text{-Al}_2\text{O}_3$ showed a considerably more complex recrystallization process. A thin amorphous Al_2O_3 film was obtained by a stoichiometric implant at liquid nitrogen temperature. A stoichiometric implant means that Al and O are implanted with an energy adjusted to obtain a similar projected range and with an ion dose in the appropriate stoichiometric ratio. In this way an amorphous film can be obtained without the addition of any impurity. During annealing at relative low temperatures, the amorphous film first crystallized into $\gamma\text{-Al}_2\text{O}_3$ and finally transformed into the $\alpha\text{-Al}_2\text{O}_3$ phase.

When the amorphous film of Al_2O_3 was obtained by the implantation of Fe at LNT, the transformation rate from the γ - to the α -phase was increased. During this transformation Fe was substitutionally incorporated in the lattice. This solid solution is considered to be metastable [12]. Earlier investigations showed an extensive precipitation of Fe containing precipitates after annealing at high temperatures in both reducing and oxidizing atmosphere [19].

Sood et al. [29] studied the epitaxial recrystallization of α - Al_2O_3 after turning the Al_2O_3 amorphous by implanting In and Zn at LNT. In this study the intermediate γ - Al_2O_3 phase was not observed. The regrowth kinetics was strongly influenced by the presence of In or Zn.

The studies mentioned above illustrate that the crystallization kinetics of an amorphous film are strongly dependent on the crystallographic plane and the presence of certain impurities in the amorphous film.

High-dose ion implantation results in a high local concentration of the implanted element. Depending on the solid solubility and the anneal treatment, a solid solution is formed or precipitation takes place of an extrinsic phase.

Solid solutions which are obtained after annealing at low temperatures are often metastable. This has been discussed for CaTiO_3 and Al_2O_3 . High-dose ion implantation of Fe in yttria stabilized zirconia results also in a metastable solid solution [23]. Annealing of Fe implanted yttria stabilized zirconia in air at 400°C results in the rapid oxidation of Fe towards the three valent oxidation state. CEMS measurements indicated two Fe^{3+} components were present. The first component could be ascribed to small paramagnetic Fe_2O_3 precipitates (< 5 nm) and the second component could be ascribed to Fe^{3+} substitutionally incorporated for Zr in the yttria stabilized zirconia lattice. A combination of the CEMS results with the Fe depth profile revealed that 6.5 mol% Fe_2O_3 was soluble in yttria stabilized zirconia. This is more than three to four times higher than the equilibrium solubility of Fe_2O_3 in YSZ.

Precipitation of the implanted ion may take place independent of the matrix element, or it may form compounds with the matrix elements. The parameters which govern the precipitation process have been reviewed by Perez and Thevenard [25, 11]. As no general rules have yet been formulated which can explain all precipitation phenomena, two representative examples will be discussed.

Abouchacra et al. [30] studied the thermal evolution of metallic silver particles in Ag implanted MgO single crystals. Up to temperatures of 800°C , the radii of the silver particles remained the same (1–5 nm) and

only their volume fraction increased. The researchers attributed this to a diffusion controlled nucleation of neutral silver atoms at nucleation sites which had been formed during the implantation process in the irradiated area. At higher temperatures a coarsening of the silver particles occurred due to the Ostwald ripening phenomenon. After annealing during 1/2 h at 1200°C , however, no evaporation of silver was found yet and their particle size was still very small (25.5 nm). This extreme thermal stability of the silver dispersion will be due to the lack of surface or gas diffusion of Ag which so rapidly increases the cluster size of Ag metal particles on porous ceramic supports.

Perez [31] studied the annealing behavior of high dose Fe implanted MgO. Annealing in air at 800°C resulted in the precipitation of super paramagnetic MgFe_2O_4 particles (20 nm in diameter). So, a compound was formed with the matrix elements. Annealing in vacuum resulted, however, in a solid solution of Fe^{2+} in the MgO matrix.

This illustrates that oxidation and reduction reactions take place during annealing in an oxidizing or reducing atmosphere. Due to those reactions the electrical conductivity of oxides is strongly influenced. This will be discussed in Sect. 3.

Apart from the charge state of the implanted ion, the annealing atmosphere may also influence its depth distribution. In an oxidizing atmosphere, a pronounced redistribution of Fe towards the surface was found by McHargue et al. [19] in Fe implanted Al_2O_3 . This was not observed in a reducing atmosphere.

The thermal stability of the implanted depth profile is of great practical importance if the implanted surface has to be used at high temperatures. This is, for instance, the case with most ion-implanted solid electrolytes. If the depth profile is not stable at the working temperature, then the beneficial effect of the implanted ions may be lost due to the diffusion of ions into the bulk or evaporation of them at the surface. This has been studied by Scholten et al. [32] for Fe implanted yttria stabilized zirconia. Up to temperatures of 800°C no significant redistribution of Fe was observed. Annealing at 1450°C resulted, however, in the complete dissolution of Fe into the bulk of the material.

The redistribution of an implanted ion during thermal annealing depends of course on the chemical diffusion coefficient in the particular matrix. From a careful study of the change in the depth profile after annealing, an estimate for the chemical diffusion coefficient of Ti in yttria stabilized zirconia could be obtained [33]. This diffusion coefficient amounted to $1.2 \cdot 10^{-16} \text{ m}^2 \text{ s}^{-1}$ at 980°C in air. This value for the diffusion coefficient resulted in a decrease of the maximum surface concentration from 0.73 to 0.44

mol% TiO₂ after annealing at 980°C during 30 minutes. The diffusion of Ti will be influenced by the radiation damage in the implanted layer.

3. Electrical Conductivity

Ion implantation has been used since 1960 to control the conductivity of mainly semiconductors [2]. The electrical conductivity changes in oxides are less well studied. The changes in electronic and ionic conductivity will be discussed below.

3.1. Electronic Conductivity

When MgO is implanted with a high dose of Fe ions ($> 3 \times 10^{16}$ at·cm²), a conductivity increase of three orders in magnitude is observed at room temperature [34]. Annealing in air between 300–600°C resulted in a recovery of the insulating properties of the MgO crystal. The type of conductivity has been identified as a hole like polaron (Fe³⁺) transport between Fe²⁺ sites [35]. The recovery of the insulating properties resulted from the complete oxidation of all iron atoms towards the three valent oxidation state.

The implantation of Sb in an n-type semiconducting SnO₂ resulted after thermal activation in an increase of the conductivity by two orders in magnitude. The opposite effect was obtained after implantation of In [36]. This is an example of the conductivity behaviour after doping an n-type semiconductor with a donor and an acceptor, respectively.

Not only the implanted ion itself may result in electronic conductivity, but also the preferential sputtering of oxygen from oxides may give that result. This has been observed for, e.g., V₂O₅, MoO₃, and TiO₂ [37, 38]. In the case of TiO₂ implanted with 30 keV Kr⁺ ions ($> 10^{17}$ at·cm⁻²), an increase of the conductivity by three orders in magnitude was observed at room temperature. Electron diffraction data revealed the presence of Ti₂O₃ in the surface layer after implantation. Annealing in air between 300–600°C resulted in the oxidation from Ti₂O₃ towards TiO₂ and the recovery of the insulating properties.

Ion implantation followed by a thermal treatment may result in a fine dispersion of metal in an insulating matrix. Such a layer is called a cermet. Cermets show a threshold in the conduction if the volume concentration of the metal is increased [39]. This has been observed for Si₂O₃ which was recoil implanted with Al or Ti [40]. At a critical metal concentration of 35–40 vol.% the resistance of the dielectric Si₂O₃ film dropped by 3–4 orders in magnitude.

The conductivity threshold can be explained with the percolation theory [39]. This theory predicts a threshold volume fraction (q_c) between 0.15–0.29, if the

conducting and non-conducting regions have similar shapes. However, most ion implanted systems show a high degree of asymmetry between the shape of those regions. Consequently percolation is only possible at a higher volume fraction of the conducting phase ($0.3 < q_c < 0.5$) [39]. Most cermets which have been obtained by direct ion implantation do not have a sufficiently large volume fraction of the conducting phase in order to show percolation [41, 30].

3.2. Ionic Conductivity

Apart from electronic conducting surface layers, also ionic conducting thin films have been prepared by ion implantation. Schnell et al. [50] introduced oxygen ion conductivity in ZrO₂ thin films by implanting Ca ions. From bulk conductivity measurements of calcium stabilized zirconia it is known that a maximum in the ionic conductivity exist at a concentration of 13–15 mol% CaO [51]. At higher Ca concentrations the ionic conductivity decreases due to the ordering of Ca and oxygen vacancies. This decrease in ionic conductivity after exceeding the optimum Ca concentration was not observed for the Ca implanted ZrO₂ films. The researchers suggested that the relative low anneal temperature of the implanted film prevents that ordering does occur.

Cohen et al. [14] intended to increase the oxygen ion conductivity of yttria stabilized zirconia by Yb implantation. This resulted in a highly damaged surface layer. Annealing in air at 1000°C resulted in an epitaxial regrowth of the Yb implanted layer. The Yb was substitutionally incorporated for Zr. No conductivity data have been reported.

Proton conducting thin layers of β-alumina have been prepared by Schnell et al. [52, 53]. Mg was implanted in an amorphous alumina thin film and subsequently a solid state reaction was performed in a Na₂O rich atmosphere. In bulk studies of β-alumina, Mg serves to stabilize the β"-alumina phase. Other ions which suit that purpose are, e.g., Li and Mn [54]. The stabilization of the β"-alumina phase results in a good chemical stability and higher ionic conductivity. The conductivity of the β-alumina thin film was, however, one order of magnitude lower than that of a β"-alumina single crystal. This was attributed to a bad crystallinity of the thin film.

The implantation of Mn in a β-alumina single crystal introduced substantial disorder in a surface layer with a thickness of twice the projected range of the ion [55]. The recrystallization of this layer was not epitaxial but in small slightly misoriented crystallites. Mg was substitutionally incorporated for Al.

The conductivity of an ion-conducting solid strongly depends on its crystal structure. So, it is

expected that the ionic conductivity is influenced by radiation damage. In the case of epitaxial recrystallization, the original transport properties may be recovered. If the recrystallization takes place in small misoriented crystallites, then extra grain boundaries are introduced. Grain boundaries in fast ion-conducting solids show a higher resistance to the ionic transport than the grains themselves. As a consequence, the crystallization in misoriented crystallites may reduce the ionic conductivity of the ion-implanted layer. Those effects of amorphization and recrystallization on the ionic conductivity are at the moment speculative and have not yet been experimentally verified.

3.3. Mixed Conductivity

A mixed-conducting solid exhibits both electronic and ionic conductivity. In this section only the effect of ion implantation on the electronic conductivity in an oxygen ion conducting solid electrolyte will be discussed.

The properties of an ionic conducting substrate may be combined with the microstructural features which enhance the electronic conductivity of an insulating oxide. This approach was followed by Burggraaf et al. [63]. Both transition metals (Fe, Ti, Cr) and noble metals (Pt, Ag) are implanted in yttria stabilized zirconia. Yttria stabilized zirconia is an oxygen-ion-conducting solid electrolyte. It is applied in oxygen sensors, oxygen pumps and fuel cells. Electronic conduction in the surface of the solid electrolyte may improve its performance in the applications mentioned above. Transition metals were selected as they are reasonably soluble in yttria stabilized zirconia. Transition metal oxides show also different oxidation states of the metal ion. The presence of different oxidation states may result in electronic conduction. As discussed before, CEMS measurements showed that in Fe-implanted yttria stabilized zirconia, Fe is present in three different oxidation states [23]. This resulted in an increase of the conductivity [57, 63]. Unfortunately, annealing in air resulted in the rapid oxidation of Fe to the three valent oxidation state and the loss of most of the electronic conductivity.

Noble metals are implanted in order to create a cermet in the oxygen ion conducting matrix. As explained in Sect. 3.1, electronic conduction may take place in a cermet if the volume fraction of the metal is higher than the percolation threshold. Moreover, Ag and Pt are catalytic active in the oxidation and reduction processes which take place at the surface of the solid electrolyte. Interesting transport properties are expected at the interface of the noble metal precipitate and the oxygen ion conducting matrix [58].

The effect of a mixed conducting surface layer on the oxygen exchange between the gas and solid phase are currently under investigation.

4. Surface Reactions

4.1. (Electro) Catalytic Reactions

In the past ten years, ion-beam techniques have been fruitful in both fundamental and more applied investigations of the catalytic activity of surfaces. Interesting results have been obtained for both gas-solid and liquid-solid catalytic reactions.

Since the early work of Rabette et al. [44, 45], no additional results have been published concerning ion beam modified catalysts for gas-solid reactions. This is mainly due to experimental problems in studying catalytic reactions at very low surface areas. In the study of Rabette et al., Pt was implanted in Al_2O_3 and MgO single crystals. Due to the ion implantation process, the initial surface concentration of Pt was very low. The surface concentration of Pt could be increased by a proper annealing treatment. This thermal treatment resulted in the case of a Pt-implanted (110) surface of Al_2O_3 in Pt metal clusters with the (111) crystal plane preferentially oriented towards the surface. The increased surface concentration was reflected in an increased catalytic activity. The activity of Pt metal at the surface of the different single crystalline supports could not be normalized to the active Pt surface area. It was too small to be determined experimentally.

Interesting systems for catalytic measurements in the gas phase include further gold and silver implanted TiO_2 and MgO single crystals [46, 30, 42]. Extensive data about the nature of the precipitates and their thermal evolution are available. For studying the catalytic activity of those noble metal dispersions, the ion-implantation parameters and thermal treatment have to be adjusted in order to obtain a higher surface area of the catalytic active element.

Electrocatalytic studies in the liquid phase have been performed by Schultze et al. [47, 48], Kelly et al. [59] and Wolf et al. [49, 60, 61].

Schultze et al. [47, 48] studied the changes in electronic properties of TiO_2 and HfO_2 layers on Ti and Hf metal electrodes after implantation with Fe, Xe, and Pd ions. Both due to the radiation damage and the chemical nature of the implanted ion, localized electronic states were generated in the bandgap of the semiconducting or insulating oxide. These localized electronic states increased the capacity and electronic conductivity of the metal oxide layer. The localized electronic states introduced by the implantation of Pd ions were more active in electron transfer reactions

($\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{Ce}^{4+}/\text{Ce}^{3+}$, H^+/H_2 , and $\text{H}_2\text{O}/\text{O}_2$) than the localized electronic states introduced by the radiation damage processes.

Metallic conducting $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ layers could be prepared by ion implantation of Ru in Ti metal electrodes and subsequent anodic oxidation [59]. Ion implantation was chosen to prepare those layers in order to circumvent the lateral inhomogeneous nature of conventionally prepared $\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ electrodes. The ion implanted oxide layers were very useful for studying the fundamental properties of the Cl_2 evolution reaction at those electrodes.

In view of the high costs of noble metals, Wolf et al. [49, 60, 61] studied how electrocatalysts for fuel-cell reactions could be prepared by ion beam techniques. Pt was incorporated in non-metallic supports (RuO_2 , C, WC) by direct ion implantation, recoil implantation and sputtering. The resulting electrocatalysts were tested in important fuel cell reactions like the evolution of hydrogen and oxygen and the oxidation of methanol and formic acid.

Depending on the non-metal support, changes in activity, selectivity and stability could be ascribed to the cluster size of Pt or a possible metal-support interaction. Pt implanted in WC showed for instance a higher catalytic activity and a better stability for the H_2 evolution reaction than a smooth Pt surface. This could be explained in terms of a metal-support interaction. Ion beam mixing of a 30 nm thick sputtered layer of Pt on RuO_2 resulted in a catalytic active surface which oxidized selectively methanol in comparison to formic acid. A possible explanation for this observation was that due to the ion beam mixing, the Pt cluster size was gradually reduced. At a certain cluster size, formic acid could still be adsorbed but methanol could not.

5. Summary

Ion implantation results in lattice damage. At a critical dose a crystalline solid may be transformed to an amorphous state. The stoichiometry of the implanted layer may be changed due to preferential sputtering and the presence of implanted ions in different oxidation states.

Annealing results in the annihilation of defects. An amorphous layer may recrystallize. The recrystallization may result in small misoriented crystallites or in epitaxially oriented layers. The crystallization kinetics is strongly dependent on the crystallographic plane and the presence of certain impurities in the amorphous layer. The crystallization of the oxide can take place at relative low temperatures in comparison to its melting point. The solid solutions which are formed after recrystallization are often metastable. This means

that annealing at temperatures higher than the recrystallization temperature results in the precipitation of the implanted ion. Dispersions of metals or oxides with nanoscale dimensions can be obtained in this way. The annealing atmosphere determines the stoichiometry of the annealed layer and of the precipitated phase.

The electrical conductivity of oxides is very sensitive to the changes in the microstructure, mentioned above. An increased electronic conductivity corresponds to the increased number of defects and the non-stoichiometric nature of the implanted layer. Annealing in an oxidizing atmosphere, however, may result in the recovery of the stoichiometry and simultaneously the recovery of the insulating properties of the oxide. The precipitation of a metal in an oxide may result in a metallic conducting surface layer if the volume fraction is higher than the percolation threshold.

Compounds which show, as a bulk property, a high ionic conductivity can also be prepared by ion implantation. In this case ions are implanted which form a solid solution with a special crystal structure.

The effect of the microstructural changes on the electronic conductivity can also be observed in ion conducting oxides. This results in a mixed (i.e., electronic and ionic) conducting surface layer on top of an ionic conducting substrate.

Another advantage of ion implantation is that a high degree of dispersion for a catalytic active element can be obtained. Unfortunately, the ions are implanted below the surface. The implantation of ions at high doses increases the surface concentration. Annealing treatments can also increase the surface concentration but this results in a loss of the degree of dispersion due to the formation of precipitates of the catalytic active element. Still very fine dispersions of, e.g., noble metals on top of an oxide can be obtained.

Such as illustrated above, the changes in electrical conductivity mirror the changes in the microstructure through all the implanted layer. The changes in the catalytic activity of oxides only mirror the microstructural changes at the surface of the implanted oxide.

Acknowledgement. The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for Scientific Research (N.W.O.).

References

1. G. Dearnaley, J.H. Freeman, R.S. Nelson, J. Stephen: In *Ion Implantation, Defects in Crystalline Solids* 8, ed. by S. Amelinckx, R. Gevers, J. Nihoul (North-Holland, Amsterdam 1973)
2. *Ion Implantation in Semiconductors*, ed. by F. Chernov, J.A. Borders, D.K. Brice (Plenum, New York 1976)

3. G. Gotz: In *Ion Beam Modification of Insulators, Beam Modification of Materials 2*, ed. by P. Mazzoldi, G.W. Arnold (Elsevier, Amsterdam 1987) pp. 412–448
4. P. Gerard: In *Ion Beam Modification of Insulators, Beam Modification of Materials 2*, ed. by P. Mazzoldi, G.W. Arnold (Elsevier, Amsterdam 1987) pp. 449–500
5. G.K. Wolf, K. Roessler: In *Ion Beam Modification of Insulators, Beam Modification of Materials 2*, ed. by P. Mazzoldi, G.W. Arnold (Elsevier, Amsterdam 1987) pp. 558–584
6. C.J. McHargue: In *Ion Beam Modification of Insulators, Beam Modification of Materials 2*, ed. by P. Mazzoldi, G.W. Arnold (Elsevier, Amsterdam 1987) pp. 223–244
7. *Ion Bombardment Modification of Surfaces, Fundamentals and Applications, Beam Modification of Materials 1*, ed. by O. Aucielli, R. Kelly (Elsevier, Amsterdam 1984)
8. H. Ryssel, I. Ruge: *Ion Implantation* (Wiley, Chichester 1986)
H. Ryssel, H. Glawisching (eds.): *Ion Implantation Techniques*, Springer Ser. Electrophys. **10** (Springer, Berlin, Heidelberg 1982)
9. J.F. Ziegler, J.P. Biersack, U. Littmark: In *The Stopping and Range of Ions in Solids, The Stopping and Ranges of ions in Matter 1*, ed. by J.F. Ziegler (Pergamon, New York 1985)
10. J.P. Biersack: In *Ion Beam Modification of Insulators, Beam Modification of Materials 2*, ed. by P. Mazzoldi, G.W. Arnold (Elsevier, Amsterdam 1987) pp. 1–56
11. A. Perez, P. Thevenard: In *Ion Beam Modification of Insulators, Beam Modification of Materials 2*, ed. by P. Mazzoldi, G.W. Arnold (Elsevier, Amsterdam 1987) pp. 156–194
12. C.W. White, L.A. Boatner, P.S. Sklad, C.J. McHargue, J. Rankin, G.C. Farlow, M.J. Aziz: Nucl. Instrum. Methods Phys. Res. **B 32**, 11–22 (1988)
13. A.P. Mouritz, D.K. Sood, D.H. St John, M.V. Swain, J.S. Williams: Nucl. Instrum. Methods Phys. Res. **B 19/20**, 805–808 (1987)
14. C. Cohen, J. Siejka, M. Berti, A.V. Drigo, M. Croset, M.M. Tosic: Radiat. Eff. **64**, 221–231 (1982)
15. P. Gerard: Nucl. Instrum. Methods Phys. Res. **B 19/20**, 843–850 (1987)
16. R. Kelly: In *Ion Bombardment Modification of Surfaces, Fundamentals and Applications, Beam Modification of Materials 1*, ed. by O. Aucielli, R. Kelly (Elsevier, Amsterdam 1984)
17. H. Hasegawa, T. Hioki, O. Kamigaito: J. Mater. Sci. Lett. **4**, 1092–1094 (1985)
18. B.D. Sawicka, J.A. Sawicki: In *Mössbauer Spectroscopy II*, ed. by U. Gonser. Topics Current Phys. **25** (Springer, Berlin, Heidelberg 1981) pp. 139–166
19. C.J. McHargue, G.C. Farlow, P.S. Sklad, C.W. White, A. Perez, N. Kornilios, G. Marest: Nucl. Instrum. Methods Phys. Res. **B 19/20**, 813–821 (1987)
20. A. Perez, G. Marest, B.D. Sawicka, J.A. Sawicki, T. Tyliczszak: Phys. Rev. **B 28**, 1227–1238 (1983)
21. J.A. Sawicki, G. Marest, B. Cox, S.R. Julian: Nucl. Instrum. Methods Phys. Res. **B 32**, 79–84 (1988)
22. S. Massouh, A. Perez, J. Serughetti: Nucl. Instrum. Methods Phys. Res. **B 32**, 71–74 (1988)
23. A.J. Burggraaf, D. Scholten, B.A. van Hassel: Nucl. Instrum. Methods Phys. Res. **B 32**, 32–36 (1988)
24. N. Kornilios, G. Marest, A. Perez, M. Brunel, B. Gilles, P.H. Gerard, F. Ravel: Nucl. Instrum. Methods Phys. Res. **B 19/20**, 860–864 (1987)
25. A. Perez: Nucl. Instrum. Methods Phys. Res. **B 1**, 621–627 (1984)
26. R. Kelly: In *Ion Beam Modification of Insulators, Beam Modification of Materials 2*, ed. by P. Mazzoldi, G.W. Arnold (Elsevier, Amsterdam 1987) pp. 57–113
27. W. Moller, W. Eckstein: Nucl. Instrum. Methods Phys. Res. **B 2**, 814 (1984)
28. G. Abouchacra, G. Chassagne, J. Serughetti: Radiat. Eff. **64**, 189–196 (1982)
29. D.K. Sood: Proc. NATO Advanced Study Institute: “Structure-Property Relationships in Ion-Beam Surface-Modified Ceramics – Theory and Applications”, Il Ciocco, Castel Vecchio Pascoli, Italy (August 28–September 9, 1988) (to be published)
30. G. Abouchacra, J. Serughetti: Nucl. Instrum. Methods Phys. Res. **B 14**, 282–289 (1986)
31. A. Perez, M. Treilleux, L. Fritsch, G. Marest: Nucl. Instrum. Meth. **182/183**, 747–751 (1981)
32. D. Scholten, A.J. Burggraaf: Surf. Interface Anal. **9**, 467–471 (1986)
33. B.A. van Hassel, A.J. Burggraaf: To be published
34. A. Perez, J. Bert, G. Marest, B. Sawicka, J. Sawicki: Nucl. Instrum. Methods Phys. Res. **209/210**, 281–287 (1983)
35. R. Meaudre, A. Perez: Nucl. Instrum. Methods Phys. Res. **B 32**, 75–78 (1988)
36. S. Chang: J. Vac. Sci. Technol. **A 1**, 524–528 (1983)
37. T.E. Parker, R. Kelly: J. Phys. Chem. Solids **36**, 377–385 (1975)
38. H.M. Naguib, R. Kelly: J. Phys. Chem. Solids **33**, 1751–1759 (1972)
39. S. Kirkpatrick: Rev. Mod. Phys. **45**, 574–588 (1973)
40. J.G. Perkins, J. Non-Cryst. Solids **3**, 349–364 (1972)
41. M. Treilleux, P. Thevenard, M.O. Ruault, H. Bernas, J. Chaumont: Nucl. Instrum. Methods Phys. Res. **B 12**, 375–381 (1985)
42. J.A. Sawicki, G. Abouchacra, J. Serughetti, A. Perez: Nucl. Instrum. Methods Phys. Res. **B 16**, 355–360 (1986)
43. J. Li, Bai-Xin, Liu, Heng-De Li, W. Wang, N.F. Gao: Nucl. Instrum. Methods Phys. Res. **B 28**, 251–254 (1987)
44. P. Rabette, A.M. Deane, A.J. Tench, M. Che: Chem. Phys. Lett. **60**, 348–352 (1979)
45. H.J. Matzke, A. Turos, P. Rabette: Radiat. Eff. **65**, 241–249 (1982)
46. M. Guermazi, P. Thevenard, J.P. Dupin, C.H.S. Dupuy: Nucl. Instrum. Methods **182/183**, 397–406 (1981)
47. J.W. Schultze, B. Danzfuss, O. Meyer, U. Stimming: Mater. Sci. Eng. **69**, 273–282 (1985)
48. J.W. Schultze, L. Elfenthal, K. Leitner, O. Meyer: Mater. Sci. Eng. **90**, 253–262 (1987)
49. G.K. Wolf, K. Zucholl, H. Folger, W.E. O’Grady: Nucl. Instrum. Methods Phys. Res. **209/210**, 835–840 (1983)
50. J.P. Schnell, M. Croset, D. Dieumegard, G. Velasco, J. Siejka: Nucl. Instrum. Methods **209/210**, 1187–1191 (1983)
51. W.L. Worrell: In *Solid Electrolytes*, ed. by S. Geller, Topics Appl. Phys. **21** (Springer, Berlin, Heidelberg 1977) pp. 143–168
52. J.P. Schnell, G. Velasco, D. Dubreil, D. Dieumegard, M. Croset, Ph. Colombar: Solid State Ionics **9 & 10**, 1465–1468 (1983)
53. Ph. Schnell, G. Velasco, Ph. Colombar: Solid State Ionics **5**, 291–294 (1981)
54. R. Collongues, J. Thery, J.P. Boilot: In *Solid Electrolytes, General Principles, Characterization, Materials, Applications*,

- ed. by P. Hagenmuller, W. van Gool (Academic, New York 1978) pp. 253–276
55. W.L. Roth, R.E. Benenson, C. Ji, L. Wielunski, B. Dunn: *Solid State Ionics* **9 & 10**, 1459–1464 (1983)
56. A.J. Burggraaf, P.J. Gellings, D. Scholten: In *High Tech. Ceramics*, ed. by P. Vincenzini (Elsevier, Amsterdam 1987) pp. 779–794
57. D. Scholten: Surface modification of yttria stabilized zirconia by ion implantation, Dissertation, University of Twente, The Netherlands (1987)
58. M. Goge, K. Heggstad, M. Gouet: *Solid State Ionics* **18 & 19**, 1228–1231 (1986)
59. E.J. Kelly, D.E. Heatherly, C.E. Vallet, C.W. White: *J. Electrochem. Soc.* **134**, 1667–1675 (1987)
60. G.K. Wolf, R. Spiegel, K. Zucholl: *Nucl. Instrum. Methods Phys. Res. B* **19/20**, 1030–1033 (1987)
61. G.K. Wolf, K. Zucholl, H. Folger: *Nucl. Instrum. Methods Phys. Res. B* **1**, 240–245 (1984)
62. D. Scholten, A.J. Burggraaf: *Radiat. Eff.* **97**, 191–197 (1986)
63. D. Scholten, A.J. Burggraaf: *Solid State Ionics* **16**, 147 (1985)