Oxidation State of Fe and Ti Ions Implanted in Yttria-Stabilized Zirconia Studied by XPS

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Abstract. The oxidation state of Fe and Ti ions implanted in yttria stabilized zirconia (YSZ) was studied by XPS (X-ray photoelectron spectroscopy) in combination with depth profiling using Ar^+ sputtering. In the “as-implanted” state of the sample Fe was found to be present as Fe^{3+} , Fe^{2+} and as metallic Fe^0 . This is in agreement with earlier conversion electron Mössbauer Spectroscopy measurements. For Ti-implanted YSZ in the “as-implanted” state the majority of the Ti is present as Ti^{4+} , Ti^{3+} , and Ti^{2+} ions, while a part of the Zr cations is present in the divalent oxidation state (Zr^{2+}). After oxidation in air, the Fe and Ti ions are present only in the valence three and four oxidation states, respectively.

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X-ray photoelectron spectroscopy (XPS) is frequently used to study the chemical nature of surfaces [1]. It gives information on the chemical composition as well as the oxidation state of the elements present in the surface. Ion beams can be used for surface cleaning or depth profiling. Hence in principle it is possible to study the oxidation state of elements in thin films as a function of the depth.

During sputtering preferential removal of elements may occur. These effects originate from differences in the surface binding energies and from mass differences [2]. In oxides the lattice oxygen generally is sputtered preferentially with respect to the metal ions [2, 3]. The remaining electrons of oxygen cause reduction of cations present in a thin surface layer, with a thickness comparable to the penetration depth of the bombarding ions [4]. It seems, however, not yet to be possible to correct sputtering depth profiles for these preferential sputtering effects.

This study, which is part of a larger research effort [5], is intended to give information on the oxidation state of Fe and Ti ions in the “as-implanted” state of YSZ. These results are of importance for the study of the structure [6] and electrochemical properties [7] of these implanted layers. Most information available on the charge state has been obtained with conversion electron Mössbauer spectroscopy (CEMS) [8–11]. With CEMS the oxidation state of the implanted ions, in a shallow surface layer of about 100 nm thickness, is analyzed in a non-destructive way. Few elements, however, have suitable isotopes for this

technique. The charge state of ^{57}Fe ions [11–18] can be studied very well, but the charge state of Ti cannot.

In order to obtain results without any detailed description of the sputtering process at hand, a careful analysis of the evolution of the oxidation states of the cations as a function of the sputtering time is carried out with XPS. The data obtained from the samples in the “as-implanted” state are compared with the data, obtained under similar conditions, from samples with all cations in the highest oxidation state (“oxidized state”). From this analysis conclusions are drawn on the oxidation state of Fe and Ti ions in the “as-implanted” state of the YSZ sample.

A disadvantage of this method is the destructive nature of the depth profiling technique and the inability to correct for changes in the oxidation state of the cations during ion bombardment, making it still impossible to quantify the results. An advantage of the method is that the oxidation state of implanted ions can be studied for elements which lack suitable isotopes for Mössbauer spectroscopy.

1. Experimental

Yttria stabilized zirconia powder [Zircar, type: ZYP (ZrO_2)_{0.87}($\text{YO}_{1.5}$)_{0.13}] was isostatically pressed (400 MPa) and subsequently heated first for three hours at 1300°C and finally for three hours at 1400°C. Rods were

obtained with a density of 5.89 g cm^{-3} (=99% of theoretical density). From these YSZ rods discs were cut (diameter: 10 mm, thickness: 1 mm). The discs were mechanically polished, first with SiC (29, 9, 7, and $5 \mu\text{m}$) and finally with diamond paste (7 and $3 \mu\text{m}$).

The ion implantations were performed at room temperature in a vacuum of $5 \times 10^{-5} \text{ Pa}$. The YSZ discs were implanted with 15 keV Fe or Ti, up to a dose of $8 \times 10^{16} \text{ at cm}^{-2}$, using the isotope separator of the Laboratory for General Physics (LAN) of the State University of Groningen. The beam was perpendicular to the sample surface, with a current density of $2 \mu\text{A cm}^{-2}$. Further details concerning the ion implantation process can be found in [5, 6].

Due to the Fe or Ti implantation, the YSZ discs showed a brown metallic or silver colour, respectively. The chemical state of the sample after the ion implantation process and before any annealing treatment is given will be called, the "as-implanted" state of the sample. After oxidation of these discs in air at 400°C the Fe-implanted sample obtained an orange colour and the Ti-implanted sample regained its original white colour. This chemical state of the sample will be called the "oxidized state".

Rutherford backscattering (RBS) experiments have been performed with the 5 MeV Van der Graaff accelerator of the LAN of the State university of Groningen. A more detailed description of the RBS analysis can be found in [5, 6].

X-ray photoelectron spectroscopy (XPS) measurements were performed with the Kratos XSAM-800 apparatus of the Centre for Materials Science (CMO) of Twente University. The spectra have been recorded with $\text{Mg-K}_{\alpha 1,2}$ (1253.6 eV) radiation. The photoelectrons were analyzed in a concentric hemisphere analyzer (CHA) which was located perpendicular to the sample surface. The energy resolution of the CHA was 0.99 eV (FWHM) at the pass energy of 20 eV . Background corrections were applied following the method developed by Shirley [19].

Corrections for surface charging ($2\text{--}5 \text{ V}$) were applied using the C 1s signal (285.1 eV), of surface impurities, as a reference. This resulted in a binding energy of 530.2 eV for the O 1s electron. When the C 1s signal disappeared due to sputtering than the O 1s signal was taken as a reference. The deconvolution of the spectra was performed with a computer program also provided by Kratos. This program allows a maximum of 8 peaks to be fitted to the experimental data. Peak widths were not allowed to be larger than 3.5 eV .

In order to obtain a sputtering depth profile and to study the evolution of the oxidation state of the previous implanted Fe or Ti ions in time, a 3 keV Ar^+ ion beam was used with a sputter rate of 0.6 nm min^{-1} for Ta_2O_5 . The corresponding sputter rate for YSZ was calculated by adjusting the value of the sputter rate until a best agreement was obtained between the RBS and XPS depth profile. This resulted in a sputter rate of 0.6 nm min^{-1} and 0.43 nm min^{-1} for respectively the Fe- or Ti-implanted layer in the "oxidized state". This difference in sputter rate may be due to an experimental problem in positioning the sample reproducibly in the Ar^+ ion beam.

For the quantitative analysis of the XPS data accurate atomic sensitivity factors had to be obtained [1]. Those values were obtained by comparing the RBS with the XPS depth profile. This method has been described previously [5, 6].

2. Results and Discussion

2.1 Surface Modification

Implantation depth profiles for the oxidized samples as determined by RBS are shown in Fig. 1 together with XPS results. The shape of the depth profiles differ from the Gaussian like peak shape expected for low dose ion implantation, due to the simultaneous occurrence of sputtering during high dose ion implantation. This results in a diffusion like dopant profile with a maximum concentration which is inversely proportional to its sputter yield in the compound target [20]. A more detailed study with ion scattering spectroscopy (ISS) showed that the outermost surface layer with an estimated thickness of less than 2 nm consisted mainly of Fe_2O_3 or TiO_2 . A more detailed discussion of the thermal stability and microstructure of the implanted layer can be found in [5, 6].

2.2 XPS Results of Fe-Implanted YSZ

Figure 2a. shows the photoelectron spectra for $\text{Fe}(2p_{3/2,1/2})$ obtained after different times of Ar^+ sputtering in the case of the Fe-implanted YSZ sample in the "oxidized" state. The spectrum of $\text{Fe}(2p_{3/2})$ for a non-sputtered sample shows a peak at 711.2 eV binding energy and 2.5 eV FWHM, after background subtraction. As shown in Table 1, this peak position corresponds to Fe^{3+} [21–23]. According to previously published CEMS measurements [11] all the Fe cations in the Fe depth profile of the oxidized sample are initially present in the trivalent state.

After 5 min of ion bombardment the peaks shift towards lower binding energies and a narrow peak appears at a binding energy of 706.7 eV and 2 eV FWHM. A deconvolution of the $2p_{3/2}$ peaks was made using the parameters of Table 1. The new lines were ascribed to suboxides according to literature data [21–22]. A deconvolution of the spectrum with respect to the original components is shown in Fig. 3a.

The stepwise reduction of the Fe cations in the Fe-implanted YSZ sample as a function of the sputtering time is clearly shown in Fig. 4a. The apparent existence of Fe species in the reduced state in deeper layers of this oxidized sample is due to the preferential sputtering of oxygen and a corresponding change in oxidation state of the Fe cations during ion bombardment. These measurements performed on the oxidized sample indicate how severely the oxidation state of the Fe cations is affected by ion bombardment.

The measurements discussed above have been repeated for the Fe-implanted sample in the "as-implanted"

Fig. 1. Depth profile of the implanted ions in YSZ after oxidation, presented as cation fraction, as determined by XPS combined with sputtering (squares) and RBS (solid lines), (a) for 15 keV Fe and (b) for 15 keV Ti, both at a dose of $8 \times 10^{16} \text{ at cm}^{-2}$.

Fig. 2. Photoelectron spectra for Fe($2p_{3/2,1/2}$) recorded after different sputtering times, (a) for the oxidized sample, (b) for the "as-implanted" sample. Indicated sputtering times are in minutes.

Table 1. Binding energies of Fe in YSZ

Oxidation state	Line	E_b [eV]	FWHM [eV]	E_b [eV]	FWHM [eV]	E_b [eV]
				[21]		after [22]
Fe^{3+}	$2p_{3/2}$	710.7 ± 0.2	3.4 ± 0.2	710.8	3.3	711.0
Fe^{2+}	$2p_{3/2}$	709.2 ± 0.2	3.0 ± 0.6	709.4	3.3	709.5
Fe^0	$2p_{3/2}$	706.7 ± 0.2	1.7 ± 0.2	707.2	2.0	706.9

state. The corresponding spectra are shown in Fig. 2b and the results of the deconvolution are shown in Figs. 3b and 4b. The outermost surface layer was oxidized due to the transfer from the "end station" of the ion implanter to the XPS apparatus in air. But judging from the peak width,

the sample transfer did not result in a complete oxidation to Fe^{3+} , since an appreciable amount of Fe^{2+} is still present in the spectrum of the non-sputtered sample.

Comparing the XPS spectra in Fig. 2 taken after identical sputtering times (e.g., 11 min) convincingly

Fig. 3. Deconvolution of the Fe 2p_{3/2} peak, recorded after 5 min of sputtering, (a) for the oxidized sample and (b) for the "as-implanted" sample

Fig. 4. Fractions of the different oxidation state of Fe as function of sputtering time, (a) for the oxidized sample and (b) for the "as-implanted" sample

Table 2. The oxidation state of implanted ⁵⁷Fe ions in YSZ obtained by CEMS [11], as the fraction of the total number of Fe atoms in the implanted layer

Energy [keV]	Dose [at cm ⁻²]	Oxidation state		
		Fe ⁰	Fe ²⁺	Fe ³⁺
15	8 × 10 ¹⁶	0.27	0.14	0.34

shows the presence of a larger amount of reduced Fe species (Fe²⁺ and Fe⁰) in the "as-implanted" state than in the oxidized state of the Fe-implanted YSZ sample. Comparing the depth profiles of the various Fe species of Fig. 4 also leads to the same conclusion. In the "as-implanted" state, a steep increase in the metallic Fe⁰ fraction is observed, whereas in the "oxidized" state only a very gradual increase takes place as a function of sputtering depth. These results suggest Fe³⁺ to be mainly present in the outermost surface layer for the sample in the "as-implanted" state.

This confirms the results obtained by CEMS that Fe is present as Fe³⁺, Fe²⁺, and Fe⁰ in the "as-implanted" state of the sample [11]. The relative abundance of each Fe oxidation state, as obtained by CEMS, integrated over the first 100 nm of the Fe-implanted sample, is shown in Table 2.

2.3 XPS Results of Ti Implanted YSZ

Figure 5a shows the photoelectron spectra for Ti(2p_{3/2}, 1/2) obtained after different times of sputtering in the case of the Ti-implanted YSZ sample in the "oxidized" state. The spectrum of Ti(2p_{3/2}, 1/2) for a non-sputtered sample shows peaks at 458.5 eV binding energy and 1.7 eV FWHM (Ti2p_{3/2}) and at 464.1 eV binding energy and 2.5 eV FWHM (Ti2p_{1/2}). As shown in Table 3, these peak positions correspond well to the literature data of Ti⁴⁺ [4, 21].

After 5 min of ion bombardment the peaks broaden. A deconvolution of the peaks was made using the parameters of Table 3. The new lines were ascribed to suboxides according to literature data [4, 21]. A deconvolution of the spectrum with respect to the original components is shown in Fig. 6a. The deconvolution of the spectra was performed as described above. In order to obtain consistent results the distance between the 2p_{3/2} and 2p_{1/2} peak of each oxidation state was fixed, as was the intensity ratio. The peak width was not allowed larger than 2.5 eV. The stepwise reduction of the Ti cations in the Ti-implanted YSZ sample as a function of the sputtering time is clearly shown in Fig. 7a.

It is assumed for this oxidized sample that all the Ti cations in the Ti depth profile initially are present in the four valent oxidation state. The apparent existence of Ti species in the reduced state in deeper layers of this oxidized sample is due to the preferential sputtering of oxygen and a corresponding change in oxidation state of the Ti cations during ion bombardment.

Fig. 5. Photoelectron spectra for $\text{Ti}(2p_{3/2,1/2})$ recorded after different sputtering times, (a) for the oxidized sample, (b) for the "as-implanted" sample. Indicated sputtering times are in minutes

The measurements discussed above have been repeated for the Ti-implanted sample in the "as-implanted" state. The corresponding spectra are shown in Fig. 5b and the results of the deconvolution are shown in Figs. 6b and 7b. As in the case of the Fe-implanted sample, the outermost surface layer of this sample was also oxidized due to the sample transfer.

Comparing the XPS spectra in Fig. 5 after the same sputtering time convincingly shows the presence of a larger amount of reduced Ti species (Ti^{3+} and Ti^{2+}) in the "as-implanted" state than in the oxidized state of the Ti-implanted YSZ sample. This is shown more quantitatively in Fig. 7. In the "as-implanted" state, the Ti^{4+} fraction drops much faster as a function of the sputtering time and it ends at a lower level in comparison with the oxidized state. The Ti^{3+} fraction initially shows a much steeper rise as a function of time in the "as-implanted" state than in the "oxidized" state but finally decreases to a lower level. In the "oxidized" state, the Ti^{2+} fraction shows a slow

increase with sputtering time and ends up at a level below both the Ti^{4+} and Ti^{3+} fraction, whereas in the "as-implanted" state the Ti^{2+} fraction increases much faster and ends at a level higher than both the Ti^{4+} and Ti^{3+} fraction. The Ti^0 species are hardly present in the "oxidized" sample, but some increase in the Ti^0 fraction can be observed for the "as-implanted" sample.

In our opinion, this leads to the conclusion that part of the reduced Ti species in the "as-implanted" state of the sample, should already have been present before the ion bombardment was started. Thus the Ti cations are present as Ti^{4+} , Ti^{3+} , Ti^{2+} in the "as-implanted" state of the sample. The amount of implanted ions present in a metallic state (i.e. Ti^0), if present, is far less than in the case of Fe-implanted YSZ in the "as-implanted" state.

A more quantitative conclusion on the relative abundances of the Fe or Ti species in different oxidation states as a function of the depth is not possible, because until now corrections of the sputtering depth profiles for the

Table 3. Binding energies of Ti in YSZ

Oxidation state	Line	E_b [eV]	FWHM [eV]	E_b [eV]		E_b [eV]	
				[21]		[4]	
Ti^{4+}	$2p_{3/2}$	458.5 ± 0.1	1.7 ± 0.2	458.7	1.5	458.9	1.6
	$2p_{1/2}$	464.2 ± 0.1	2.5 ± 0.1	464.6	2.5	464.6	2.5
Ti^{3+}	$2p_{3/2}$	457.0 ± 0.1	2.5 ± 0.1	457.2	2.0	457.2	1.9
	$2p_{1/2}$	462.9 ± 0.1	2.5 ± 0.2	463.0	2.5	462.9	2.4
Ti^{2+}	$2p_{3/2}$	455.3 ± 0.1	1.9 ± 0.1	455.3	2.0	455.2	1.9
	$2p_{1/2}$	461.0 ± 0.1	2.7 ± 0.1	461.0	2.3	461.0	2.4
Ti^0	$2p_{3/2}$	453.2 ± 0.2	1.5 ± 0.1			453.6	1.6
	$2p_{1/2}$	459.6 ± 0.2	1.8 ± 0.1			460.0	2.0

Fig. 6. Deconvolution of the Ti $2p_{3/2}$ peak, recorded after 5 min of sputtering, (a) for the oxidized sample and (b) for the "as-implanted" sample

preferential sputtering of oxygen and the corresponding change in oxidation state of the cations present cannot be performed.

2.4 Oxidation State of Zr

The implantation of Fe or Ti in yttria-stabilized zirconia affects the oxidation state of the Zr^{4+} cations. This is illustrated in Fig. 8 with photoelectron spectra for Zr ($3d_{5/2, 3/2}$) in the case of Ti-implanted yttria stabilized zirconia. Both in the "oxidized" state as in the "as-implanted" state of the sample, the spectrum of Zr ($3d_{5/2, 3/2}$) for a non-sputtered sample shows peaks at 182.2 eV binding energy and 1.4 eV FWHM ($Zr3d_{5/2}$) and at 184.5 eV binding energy and 1.4 eV FWHM ($Zr3d_{3/2}$), as shown in Fig. 8a. According to literature (Table 4) those peaks correspond to Zr^{4+} [4].

In the "oxidized" state of the Ti implanted sample, 15 min of Ar^+ sputtering results in a broadening of the Zr^{4+} peaks from 1.4 eV (FWHM) to 1.8 eV (FWHM), but no significant amount of Zr in a lower oxidation state is found (Fig. 8b). Hence Ar^+ sputtering does not result in the reduction of the Zr^{4+} cations. In the "as-implanted" state of the sample, 15 min of Ar^+ sputtering resulted also in a peak broadening from 1.4 eV FWHM to 2.0 eV

Fig. 7. Fractions of the different oxidation state of Ti as function of sputtering time, (a) for the oxidized sample and (b) for the "as-implanted" sample

FWHM, but two new peaks are clearly present at 181.0 eV binding energy and 2.0 eV FWHM and at 183.3 eV binding energy and 2.0 eV FWHM (Fig. 8c). Those new peaks can be ascribed to Zr^{2+} , resulting from the ion implantation procedure.

3. Conclusions

The oxidation state of elements present in a thin surface layer can be qualitatively studied as a function of the depth by XPS in combination with sputtering. Full quantification of the results is not yet possible due to an incomplete understanding of the preferential effects during sputtering. The preferential sputtering of oxygen for instance seriously affects the oxidation state of the implanted transition metal cations whereas the oxidation state of Zr is not influenced.

From the XPS measurements in combination with sputtering it can be concluded that the implantation of Fe in YSZ results in a non-stoichiometric surface layer in which the Fe cations are present as metallic Fe^0 , and as Fe^{2+} and Fe^{3+} ions. This was concluded previously from CEMS measurements. The implantation of Ti results also in a non-stoichiometric surface layer, in which the Ti cations are present as Ti^{4+} , Ti^{3+} , and Ti^{2+} ions. The

Fig. 8. Photoelectron spectra for Zr($3p_{5/2,3/2}$) in Ti-implanted YSZ recorded for the oxidized sample: (a) before sputtering and (b) after 15 min sputtering, and for the "as-implanted" sample: (c) after 15 min sputtering

fraction of the Ti cations present in a metallic state was found to be not significant. It can also be concluded that in the "as-implanted" state of the Ti-implanted yttria-stabilized zirconia sample, the Zr cations are mainly present in the valence four oxidation state (Zr^{4+}), but some are present in the divalent oxidation state (Zr^{2+}).

After oxidation in air at 400°C, the stoichiometry of the samples is restored and all cations are present in their highest oxidation state (Zr^{4+} , Y^{3+} , Fe^{3+} , and Ti^{4+}).

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Table 4. Binding energies of Zr in YSZ

Oxidation state	Line	E_b [eV]	FWHM [eV]	E_b [eV]	FWHM [eV]
[4]					
Zr^{4+}	$3d_{5/2}$	182.2 ± 0.1	1.8 ± 0.2	182.3	1.8
	$3d_{3/2}$	184.5 ± 0.1	1.8 ± 0.2	184.7	1.8
Zr^{2+}	$3d_{5/2}$	181.0 ± 0.1	1.8 ± 0.2	180.7	1.8
	$3d_{3/2}$	183.3 ± 0.1	1.8 ± 0.2	183.1	1.8
Zr^0	$3d_{5/2}$			178.5	1.8
	$3d_{3/2}$			180.9	1.8

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