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In-Depth Compositional Analysis of Ceramic $(Bi_2O_3)_{0.75}(Er_2O_3)_{0.25}$ by AES and XPS*

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Abstract. The chemical composition of dense ceramics of erbia-stabilized δ-Bi_2O_3 was analyzed by Auger electron spectroscopy (AES) depth profiling using Ar^+ ion sputtering. The relative sensitivity factors (rsf) and sputter rates of bismuth and erbium in this material have been determined by electron probe microanalysis (EPMA) and chemical analysis. These results, supplemented by data from angle resolved X-ray photoelectron spectroscopy (ARXPS), shows a bismuth enrichment at the surface. Evidence has been found for reduction of the bismuth-oxide at the outermost part of the surface layer.

Key words: AES, ceramic, sputtering, XPS.

As discussed by Burggraaf and Winnubst [1] the chemical composition of grain boundaries and surfaces of ceramic materials controls sintering behaviour, grain growth and related properties such as fracture strength, toughness, wear resistance and also electrochemical and catalytic properties. Ceramic erbia stabilized δ-Bi_2O_3 may find commercial use in oxygen pumps, sensors and solid oxide fuel cells because of its high oxide ion conductivity. The aim of our research is to elucidate a possible segregation at the surface of this type of material.

Auger electron spectroscopy (AES) can be applied for quantitative analysis of surfaces, provided that the relative sensitivity factors (rsf) are known. The rsf values of the elements are known from literature [2] but often not applicable for composite materials, as for example shown by Keim and Aïte [3] for silicon nitride. Experi-

* Dedicated to Professor Günther Tölg on the occasion of his 60th birthday

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mental rsf values can be obtained from materials where the stoichiometry is known. A similar approach applies to the sputter yield of the different components.

In-depth information was obtained by Ar^+ ion sputtering followed by AES analysis together with angle resolved X-ray photoelectron spectroscopy (ARXPS). Electron probe micro analysis (EPMA) and chemical analysis were performed to permit calibration of sputter yields and rsf values of data obtained from a fractured sample.

Experimental

The preparation of $(Bi_2O_3)_{0.75}(Er_2O_3)_{0.25}$ samples, henceforth indicated as BE25, by a coprecipitating routine has been described by Kruidhof et al. [4]. The samples were annealed at 850°C during 1 h with heating and cooling rates of 3°C/h.

The analyses of the BE25 samples have been performed with AES (PHI 600 SAM (scanning Auger microscope) with facilities for scanning electron microscopy (SEM) and Ar^+ ion depth-profiling), XPS (Kratos XSAM 800 with angle resolved facilities) and EPMA (ARL-SEMQ).

In the Auger experiments the primary electron beam (beam energy 10 keV, beam current 100 nA, beam diameter 0.5 μm, angle of incidence with the surface normal 60°) was rastered over a surface area of 100 μm^2. Under these conditions sample charging could be avoided. The resolution of the cylindrical mirror analyzer had been set at 0.6%. The differentially pumped ion gun was adjusted to produce an argon ion beam with an ion energy of 3.5 keV and a FWHM of 200 μm. The ion beam was rastered over a surface area of 2×2 mm^2, while the angle of incidence with the sample surface was 75°.

The XPS measurements have been performed at a base pressure of $1.33 \cdot 10^{-7}$ Pa with 1253.6 eV-Mg(K_α)-photon irradiation (300 W). The pass energy of the analyzer was adjusted at either 20 or 40 eV.

The EPMA measurements were performed at a primary beam energy of 10 keV with a sample current of 5 nA. The Bi and Er intensity measurements ($\lambda_{BiM\alpha_1} = 511.8$ nm, $\lambda_{ErL\alpha_1} = 178.4$ nm) involved a PET and an LiF crystal, respectively, both in combination with a xenon detector. The concentrations were calculated by means of the ZAF correction procedure (MAGIC-IV computer program). The reference standards were 99.99% pure Bi and 99.9% pure Er produced by C. M. Taylor Corporation. The BE25 sample had been covered with a thin gold film to avoid charging.

Results and Discussion

A typical Auger survey spectrum of BE25 is given in Fig. 1. No further decrease of carbon contamination could be detected after electron irradiation of the sample for 30 min under the same conditions as during the Auger measurements.

A quantitative elemental composition of the surface layer has been deduced from the measurements using the same approach as described in refs. [2, 5]. The atomic concentration of an element is derived by comparing the peak to peak Auger amplitude of this element with those of all present elements, where the rsf values and scale factors for the different Auger amplitudes are taken into account. Therefore, the rsf values of the Auger peaks of the elements in BE25 have to be known. However, elemental rsf values of Bi and Er are only reported in literature for 5 keV primary beam energy [2], while the rsf values for the elements in the compound BE25 are unknown. These values have been obtained by comparison of peak to peak heights in the $dN(E)/dE$ Auger spectrum of a surface with known composition. The composition of BE25 in a surface layer of about 1 μm has been determined by means of EPMA and chemical analysis. The ratio Bi/Er was found to be 3.00 ± 0.02. The correction procedure (ZAF), which determines the weight fractions of bismuth

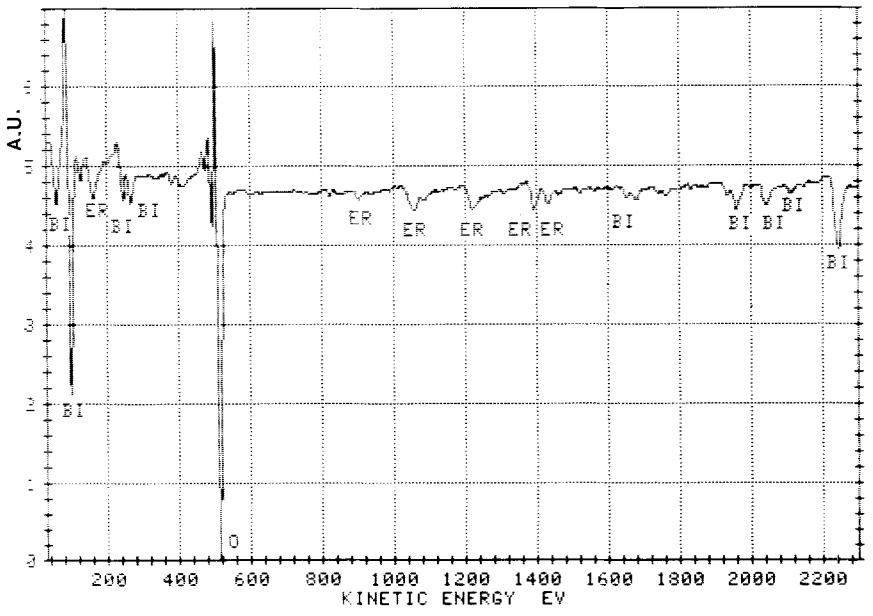

Fig. 1. AES survey spectrum of a BE25 sample after 30 min electron beam irradiation

Table 1. Experimental rsf values for the Bi, Er and O Auger transitions at kinetic energy E_{kin}. The column rsf_{lit} gives the literature values in the elemental state

	E_{kin}	rsf_{lit}	rsf
Bi	101 eV	0.370[a]	0.203
Er	162 eV	0.218[a]	0.050
O	515 eV	0.350	0.350

[a] At a primary electron beam energy of 5 keV, other data at 10 keV

and erbium from the detected X-ray intensity, assumed that Bi and Er were present in the sample as Bi_2O_3 and Er_2O_3. This seems to be justified because the averaged sum in weight per cent, calculated by this ZAF correction procedure, is close to 100%. The atomic concentration of the bulk material is Bi : Er : O = 3 : 1 : 6, which is in agreement with chemical analysis.

The calculated rsf values of Bi, Er and O, given in Table 1, were obtained from Auger data measured from a sample which was introduced into the vacuum system immediately after fracturing. The composition of this fractured surface, neglecting segregation at room temperature, has also been obtained from EPMA measurements. Low energy Auger transitions of Bi (101 eV) and Er (162 eV) have been used because of the improved signal-to-noise ratio and a higher surface sensitivity [6] in comparison with high energy transitions. In Fig. 2 the results are given from AES depth-profiling. The atomic concentrations have been determined with the calcu-

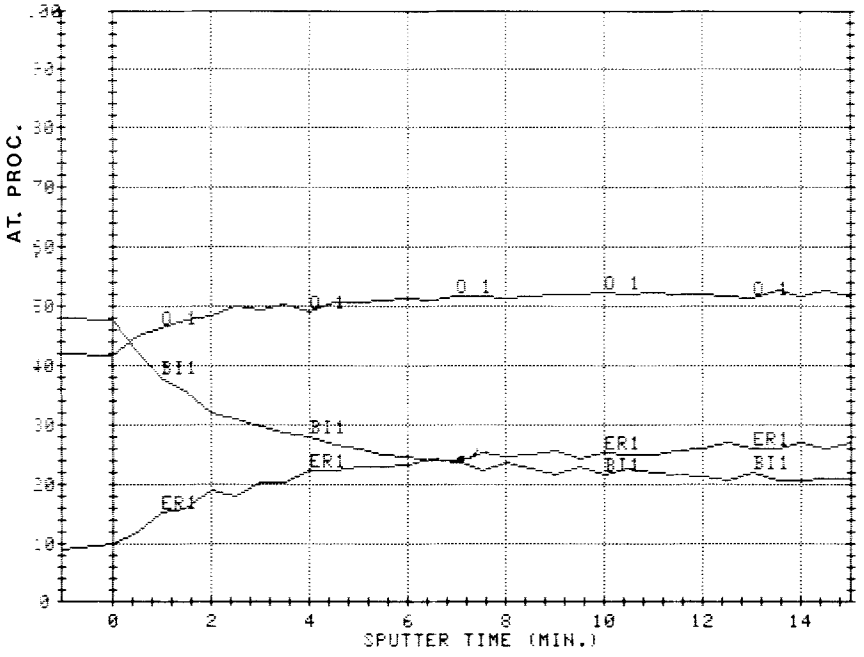

Fig. 2. AES depth profile of a BE25 sample. Results calculated from the Bi (101 eV), Er (162 eV) and O (515 eV) Auger transitions and plotted in atomic per cent

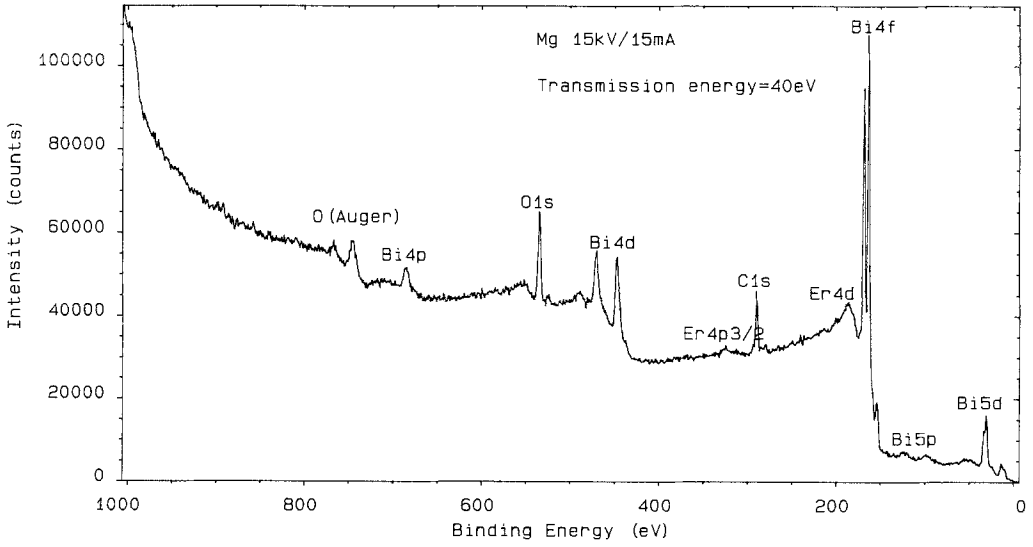

Fig. 3. XPS survey spectrum of a BE25 sample after a mild Ar^+ ion bombardment

lated rsf values given in Table 1. The total sputter time was 15 min. The sputter yield for Ta_2O_5 is approx. 30 nm under these conditions. From Fig. 2 we observe a Bi enrichment at the surface and a preferential sputtering of Bi with respect to Er.

Fig 3 shows an XPS survey spectrum of the BE25 sample after a mild argon ion sputtering. Besides the expected Bi, Er, O also C has been detected. From

Table 2. The Bi/O ratio corresponding to various take-off angles θ

θ	90°	60°	30°
Bi/O	0.59	0.62	0.75

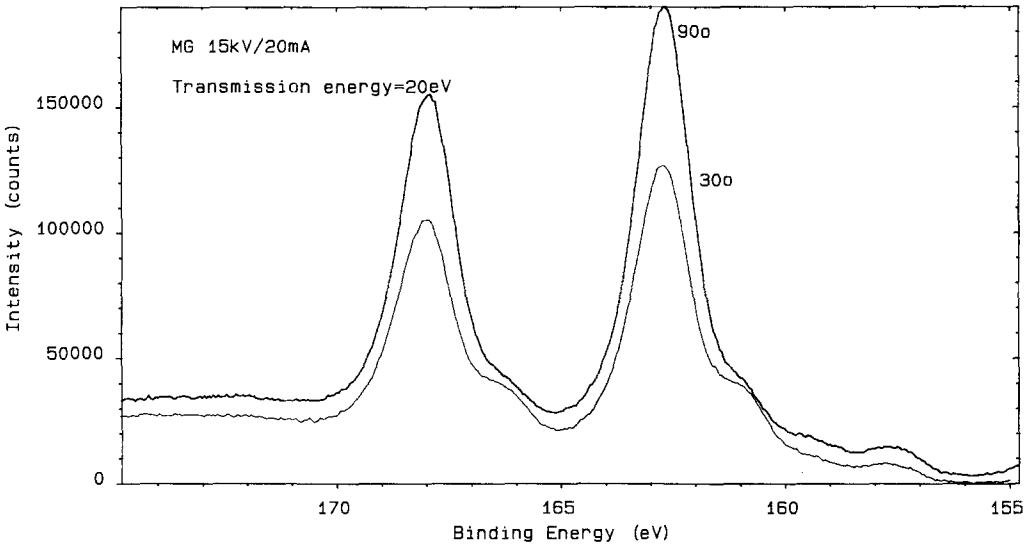

Fig. 4. ARXPS spectrum of Bi_{4f} of a BE25 sample at take-off angles of 90° and 30°

the Auger measurements we conclude that carbon is only present as surface contamination.

ARXPS measurements were performed at take-off angles of 90°, 60° and 30° at Bi_{4f} and O_{1s} energy levels. The Er measurements are not evaluated because the Er_{4p} peak was too small while the Bi_{4f} has a strong interference with the Er_{4d} peak (Fig. 3). The calculated Bi/O ratios are given in Table 2. Decreasing the take-off angle results in an increase of the surface sensitivity. Therefore the change of the Bi/O ratio as a function of the take-off angle indicates a higher Bi concentration at the surface.

In Fig. 4 ARXPS results for Bi_{4f} are represented at angles of 90° and 30°. At an angle of 30° a second peak emerges at a lower binding energy, which indicates a reduction of Bi_2O_3 at the outermost part of the top-layer. This reduction could be caused by the mild argon ion sputtering as observed by Holm and Storp [7] for Bi_2O_3. The maximum of the distribution of the argon ions after a mild sputtering is situated significantly below the surface [8]. This means that the ion-induced reduction is probably not caused by the implanted argon ions in rest.

Conclusion

Relative sensitivity factors at a primary electron beam energy of 10 keV were determined for Bi (101 eV), Er (162 eV) and O (515 eV) Auger transitions measured

on a BE25 sample. AES and ARXPS measurements indicate Bi enrichment at the surface. The sputter yield ratio between Bi and Er in BE25 is approximately 3. This is about twice the ratio which has been calculated by Zalm [9] for Bi and Er in the elemental state, indicating the influence of the matrix. The low energy feature in the ARXPS meaurements at a take-off angle of 30° indicates a reduction of Bi-oxide at the outermost part of the surface.

References

[1] A. J. Burggraaf, A. J. A. Winnubst, *Surface and Near-Surface Chemistry of Oxide Materials* (J. Nowotny, L. C. Dufour, eds.), Elsevier, Amsterdam, 1989, p. 449.

[2] L. E. Davis, H. C. MacDonald, P. W. Palmberg, G. E. Riach, R. E. Weber, *Handbook of Auger Electron Spectroscopy, 2nd Ed.*, Physical Electronics Industries, Eden Prairie, MN, 1976.

[3] E. G. Keim, K. Aïte, *Fresenius' Z. Anal. Chem.* **1989**, *333*, 319.

[4] H. Kruidhof, K. Seshan, B. C. Lippens Jr., P. J. Gellings, A. J. Burggraaf, *Mater. Res. Bull.* **1987**, *22*, 1635.

[5] D. Briggs, M. P. Seah, *Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*, Wiley, Chichester, 1983.

[6] M. P. Seah, W. A. Dench, *Surf. Interface Anal.* **1979**, *1*, 2.

[7] R. Holm, S. Storp, *Appl. Phys.* **1977**, *12*, 101.

[8] A. H. M. Holtslag, *Thesis*, Twente University of Technology, Enschede, 1986, p. 15.

[9] P. C. Zalm, *Surf. Interface Anal.* **1988**, *11*, 1.

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