Fresenius J Anal Chem (1995) 353 : 707–712

Fresenius' Journal of Analytical Chemistry

© Springer-Verlag 1995

Characterization of thin alumina films prepared by metal-organic chemical vapour deposition (MOCVD) by high resolution SEM, (AR)XPS and AES depth profiling

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Received: 16 January 1995 / Accepted: 31 January 1995

Abstract. Thin alumina films deposited by metal-organic chemical vapour deposition (MOCVD) on AISI 304 substrate have been analyzed using the combination of Scanning Electron Microscopy (SEM), Auger Electron Spectroscopy (AES) and Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS). Both the surface and the alumina/substrate interface region have been analyzed in terms of chemical composition and elemental distribution. Only OH-groups (bounded as AlO(OH):boehmite) have been found as an impurity in the surface region of the oxide film. No carbon was detected. Due to higher temperature deposition, the concentration of OH-groups decreased. After annealing, the oxide/substrate interface changes as a result of chromium penetration into the alumina matrix. Carbon impurities have been detected on both delaminated and annealed alumina film surfaces. Also small amounts of sulfate groups as well as Ca and C impurities have been found on delaminated alumina film after prolonged high-temperature annealing.

1 Introduction

Alumina films are widely used as protective coatings on metal substrates in the field of high-temperature corrosion [1, 2]. Several techniques are available to deposit Al_2O_3 films [3–5], but recently much attention has been paid to metal organic chemical vapour deposition (MOCVD). The main reason is the low temperature needed for the preparation of protective layers on substrates which could easily deteriorate at high temperatures [6].

The purpose of this paper is the elucidation of the morphology and the chemical structure of alumina films deposited onto stainless steel substrate, type AISI 304, by MOCVD using aluminum-tri-sec-butoxide (ATSB).

Chemical composition as well as chemical elemental distribution in both the surface and the alumina/substrate interface region was evaluated by means of the combination of Auger Electron Spectroscopy (AES) and Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS). The microstructure of the films was investigated using both optical and Scanning Electron Microscopy (SEM).

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2 Experimental

Thin alumina films were deposited onto stainless steel, type AISI 304 (71% Fe, 18% Cr, 8% Ni, 2% Mn, 1% Si, 0.08% C). The substrate was cut from an electropolished metal sheet and ultrasonically cleaned in hexane and ethanol. The deposition process was carried out in the low temperature range of 220–230° C, by means of atmospheric pressure MOCVD using ATSB (Janssen Chimica) and dried nitrogen gas [2, 7].

In order to investigate the effect of thermal annealing on the chemical composition of alumina films, the samples deposited at 330° C were also exposed to a nitrogen atmosphere at 600 and 800° C, respectively, for 1 and 4 h.

AES measurements were performed using a PHI600 Scanning Auger Microprobe (SAM) system. The Auger spectra and Auger sputter profiles of alumina layers were recorded using the following experimental conditions: primary beam energy E_p = 10 kV, primary beam current I_p = 0.1 μA and a beam diameter Ø ≅ 0.4 μm. The resolution of the cylindrical mirror analyzer was set to 0.6%.

The argon ion beam with an energy of 3.5 kV was produced by a differentially pumped ion gun. The sputter rate was calibrated using a 100 nm thick Ta_2O_5 layer. All sputter rates given in this paper are derived from this sputter rate.

The sputter profiles were analyzed using the software package PC PHI-MATLAB (version 2.6/3.1).

During the deposition of thin alumina films on an AISI 304 substrate, the films cracked and delaminated at a critical thickness of 1 μm. In order to obtain a better insight into this phenomenon, we analyzed both the substrate and the alumina delaminated layers. For these samples, the

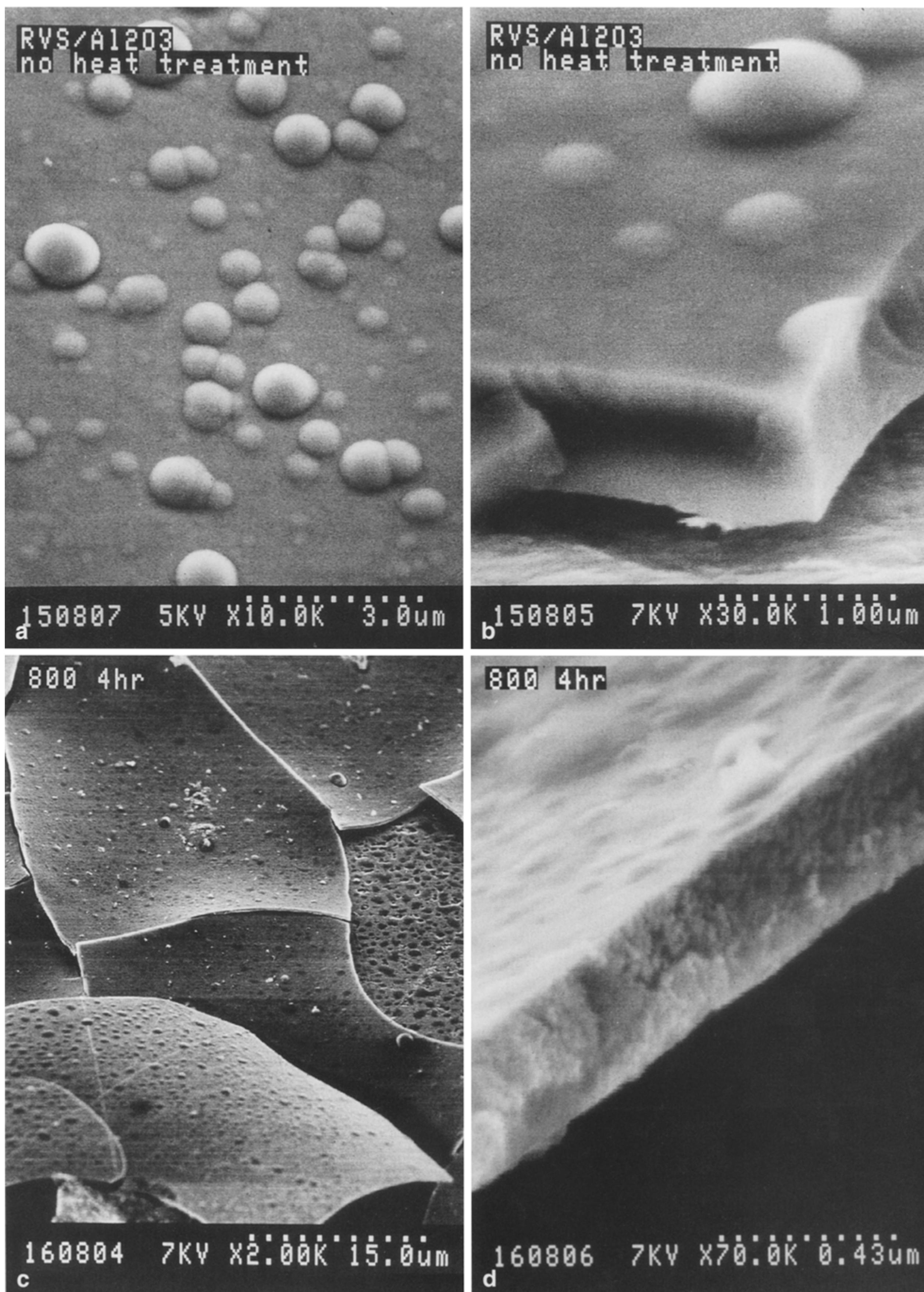

Fig. 1 a–d. Scanning Electron Microscope images of alumina film deposited by MOCVD on stainless steel, type AISI 304, at 330°C, **a** surface, **b** fracture surface, **c** delaminated surface, **d** fracture surface, after annealing 4 h at 800°C

Auger spectra were recorded using E_p = 3 kV and I_p = 0.05 µA.

XPS and ARXPS experiments were carried out in a Kratos XSAM 800 system controlled by a PDP 11 microcomputer. A Mg Kα radiation source was used for excitation. The spectrometer was calibrated and its linearity checked by measuring the $Ag3d_{5/2}$ peak and the X-ray-induced Ag MNN Auger peak on a clean sputtered silver sample. The position of the C 1s peak, relative to its normal position at 285.1 eV, was used to correct the measured binding energies (BE) for electrostatic charging of the alumina samples. The spectra were analysed using a DS 800 software package. For the synthesis 100% Gaussians were used.

Scanning electron microscopy (HITACHI S800) was applied for the analysis of the microstructure of the alumina films.

3 Results and discussion

3.1 SEM/AES/XPS analysis of alumina film surfaces

Figure 1a–d shows SEM images of alumina films deposited on AISI 304 at 330°C without (Fig. 1a, b) and with (Fig. 1c, d) annealing at 800°C. The annealed film shows delamination.

Figure 1a, b shows the morphology of the surface and fracture surface (the picture of the fracture indicate amorphous structure). Figure 1c, d shows the delaminated surface and the fracture surface (the picture of the fracture indicate crystalline structure) [2].

The Auger spectrum of the alumina film deposited at 330°C is presented in Fig. 2a. It reveals O and Al. Annealing of the sample at 600° for 1 h (Fig. 2b) resulted in the appearance of C and Si. Carbon could still be detected after annealing for 4 h at 800° (Fig. 2c).

The chemical composition of the alumina film surface was also analyzed by means of ARXPS. In Fig. 3a two XPS spectra of the Al 2p peak measured on the alumina film deposited at 220° are shown, taken at electron take-off angles of 0° and 30°. The deconvoluted spectra of Al 2p at 30° take-off angle for alumina films deposited at 220° and 330° are presented in Fig. 3b, c, respectively. The lines a and b represent the Al 2p peaks of AlO(OH) and γ-Al_2O_3, respectively. The sum of these Al lines is given as the envelop of the spectrum.

Quantitative evaluation and deconvolution of Al 2p spectra, obtained for alumina films deposited in the temperature range of 220 to 330°, revealed two peaks at BE ranging between 73.7 and 73.9 eV and between 74.2 and 74.4 eV. Comparing these results with the BE reported earlier for alumina compounds, we can confirm the coexistence of γ-Al_2O_3 [8, 9] and AlO(OH) (boehmite) [8–10] in the surface region of these alumina films. On the basis of the results of fitting procedure (Fig. 3b, c) it was possible to calculate the ratio of the X-ray photoelectron Al 2p-peaks areas of the AlO(OH) and γ-Al_2O_3 species on alumina films deposited at different temperature. The results, given in Table 1, clearly show that the concentration of AlO(OH) is more pronounced within the region close to the surface (see results obtained at take-off angle 30°). With an increase in the deposition temperature, the AlO(OH)/γ-Al_2O_3 ratio decreased. This means that at higher temperature, the boehmite partly decomposes to alumina and water by dehydroxylation [2].

3.2 AES/XPS analysis of the alumina/AISI 304 interface region

The alumina/AISI 304 interface region has been analyzed in two ways: (i) multiple-point argon ion-sputtering Auger depth profiles have been measured on well-deposited

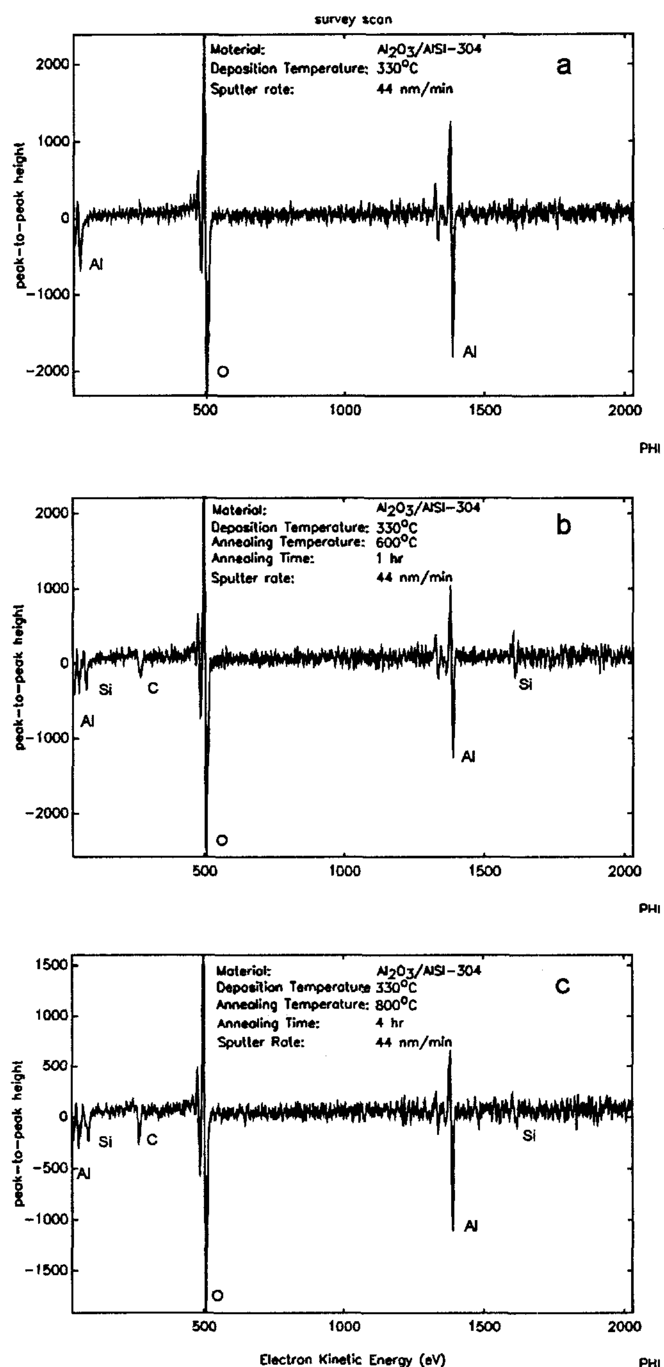

Fig. 2a–c. AES survey scan analysis of the alumina film on AISI 304, deposited at 330°C; **a** without annealing, **b** after 1 h annealing at 600°, **c** after 4 h annealing at 800°

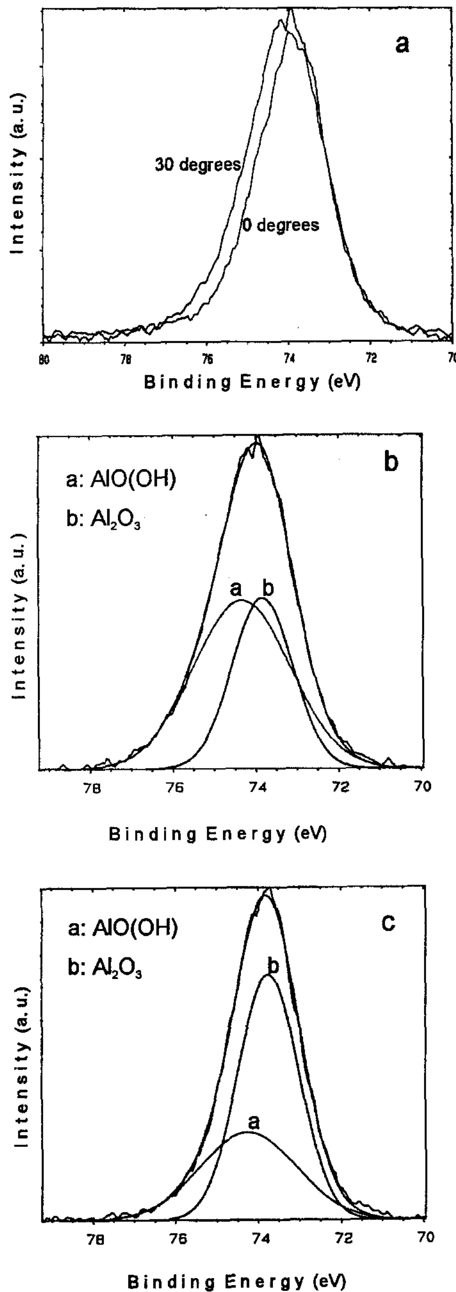

Fig. 3 a–c. Al 2p XPS peaks of alumina film, deposited at 220° C, at photoelectron take-off angles of 0° and 30° (**a**). Simulation of Al 2p XPS spectra at 30° take-off angle for alumina films deposited at 220° and 330° is presented in **b** and **c**, respectively

alumina films, (ii) Auger survey scan spectra have been taken at different parts of the delaminated alumina coating.

Auger depth profiles of the alumina film (550 nm thick) deposited at 330° C are shown in Fig. 4a. The scaled peak-to-peak heights of the O KLL, Al KLL, Fe LMM, Cr LMM and Ni LMM have been plotted as a function of sputter depth. The sputter rate was ≅ 44 nm/min. The influence of different heat treatments on the course of Auger depth profiles is presented in Fig. 4b (700 nm thick alumina film after 1 h annealing at 600°) and Fig. 4c (400 nm thick alumina film after 4 h annealing at 800° C). It can be seen (Fig. 4c) that a certain

Table 1. Ratios of X-ray photoelectron Al 2p-peak intensities of the boehmite (AlO(OH)) and γ-Al_2O_3 species at two different angles of incidence for alumina films deposited at different temperatures

Deposition temperature (° C)	R[a]	
	Take-off angle 0°	Take-off angle 30°
220	0.68	1.44
250	0.64	0.91
280	0.57	0.98
330	0.45	0.50

[a] R = [Al 2p (AlO(OH)) peak area]/[Al_2O_3) peak area]

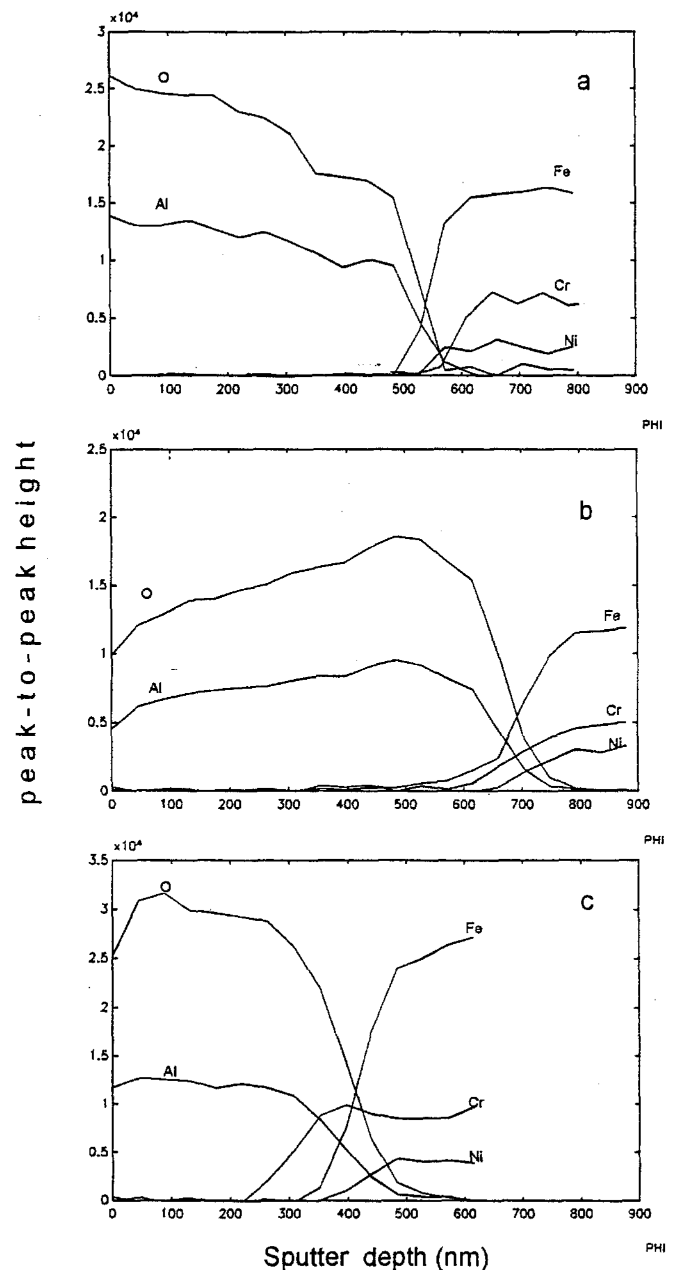

Fig. 4 a–c. AES depth profile analysis of the alumina film on AISI 304, deposited at 330°; **a** without annealing, **b** after 1 h annealing at 600°, **c** after annealing at 800°

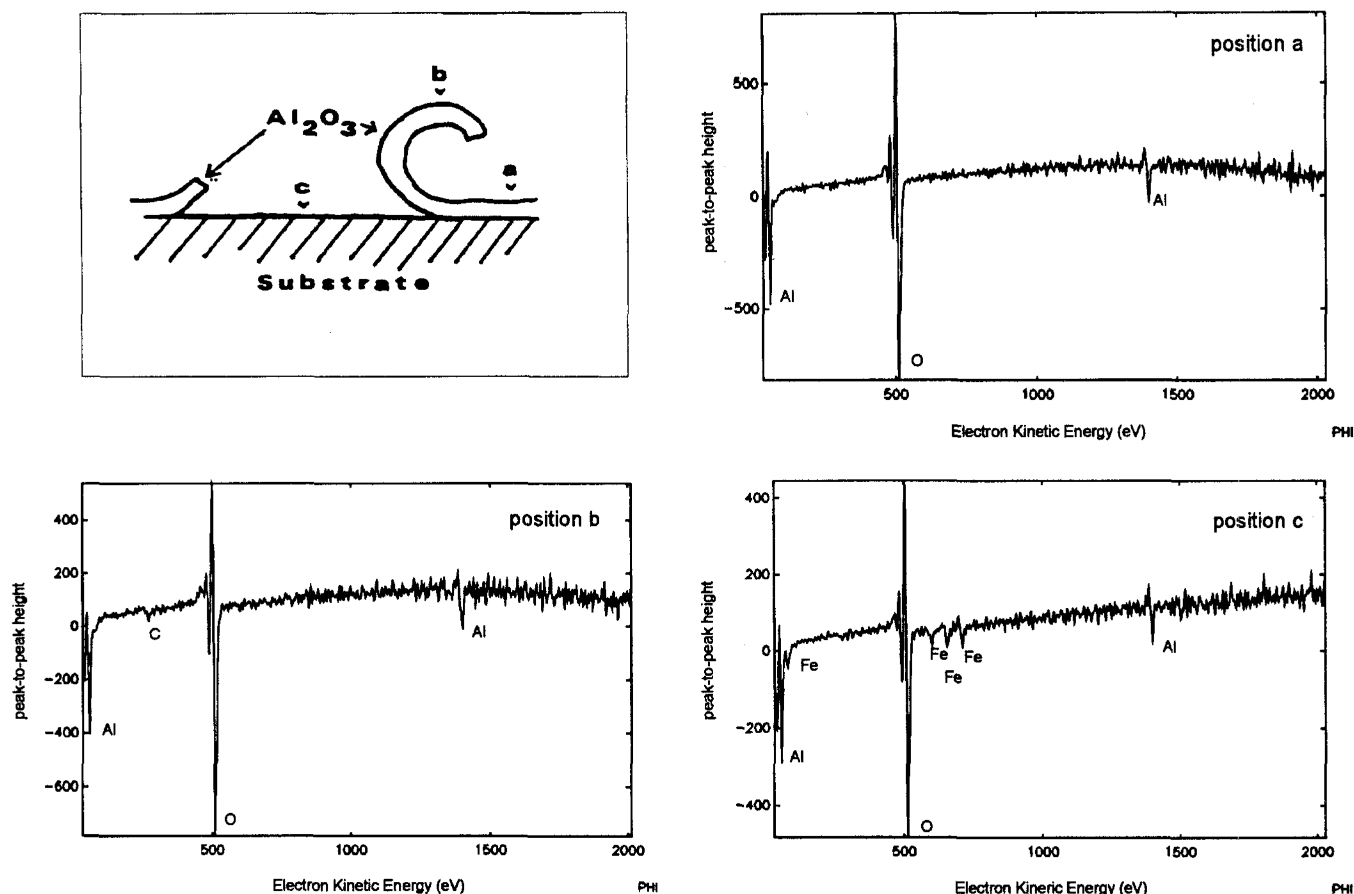

Fig. 5. Model and AES survey spectra for different positions of a delaminated alumina film deposited at 330°

amount of chromium penetrates into the alumina film due to prolonged annealing at higher temperature. Also small amounts of carbon appear (surface contamination). However, after one sputtering cycle no carbon was found anymore (and therefore not presented in the graphs). The nickel and iron profiles seem to be unaffected by the thermal treatment. The nature of chromium interaction with alumina is rather complex and was already discussed [1] in terms of the structure of γ-alumina and the expected complete miscibility of Cr_2O_3 and Al_2O_3 with a substitution of Al by Cr in the oxide forming within the Al_2O_3/AISI 304 interface region.

As it was mentioned above, alumina films thicker than 1 μm underwent delamination during deposition procedure. The delaminated alumina coating was investigated by SAM. AES spectra at different parts of the surface are shown in Fig. 5. Only Al and O were detected on the surface of the alumina film at the gas side (position a). Small amounts of C appeared in addition to Al and O on the alumina film near the film/substrate interface (position b). Al, O and Fe were the main components on the surface of the substrate after delamination of the alumina layer (position c).

Delamination of the alumina film was also observed after a long period (4 h) high-temperature (800° C) annealing. The XPS analysis of delaminated alumina film, in this way, revealed, apart from Al, Fe, O and C, small amounts of Ca and S. The S 2p spectrum disclosed the existence of the XPS peak at BE = 168.6 eV which can be attributed to sulfate-groups [8–10]. Thus some $CaSO_4$ [11], $Fe_2(SO_4)_3$ [12] or $FeSO_4$ [13] impurities resulting from the preparation or the annealing procedure were probably detected.

4 Conclusions

SEM analysis revealed that cracks and pores are present on alumina films deposited at low temperature.

The presence of boehmite (AlO(OH)) in the surface region of Al_2O_3 film was detected by ARXPS. Concentrations of AlO(OH) decreased with increase of deposition temperature.

Carbon was not detected above the background level of the AES and XPS spectra for alumina films deposited at 330°.

Prolonged high-temperature annealing of alumina films deposited on AISI 304 substrates results in migration of Cr into "Al-O" layer as shown by the AES-depth-profile.

Carbon was detected on both the delaminated and the annealed alumina surfaces.

Small amounts of sulfate-groups were detected on delaminated alumina film surfaces after prolonged high-temperature annealing.

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