

2.9 g/cm³ and 3.9 g/cm³ [4]. In this work, the density, ρ , and the thickness, d , obtained by GIXR are used to determine the Young's modulus, E , by SAWS for TiO₂ films with a thickness of 280 nm and 500 nm deposited by reactive evaporation (RE) and ion plating (IP). E is of the order of 65 to 100 GPa for RE and 150 GPa for IP layers, correlating strongly with film density. Since there is another strong correlation between the refractive index, n , and the density, ρ , of the films, it may be possible to detect the elastic properties of thin films by the measurement of the refractive index. The validity of this findings for TiO₂ and other oxides has to be proven in future investigations. Annealing of amorphous titania films induces a transition to the crystalline state of anatase, which causes an increase of the Young's modulus by 40 GPa, but no changes in the density.

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Characterization of interfaces of alumina – high alloyed steels by SST and AES depth profiling

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Abstract Thin alumina films, deposited at 280°C on several high alloyed steels by low pressure metal-organic chemical vapour deposition (LP-MOCVD), were annealed at 0.17 kPa in a nitrogen atmosphere for 2, 4 and 17 h at 600 and 800°C. The effect of the annealing process on the adhesion of the thin alumina films was studied using a scanning scratch tester (SST)

and Auger electron spectroscopy (AES). The best adhesion properties were obtained with commercial oxide dispersion strengthened (ODS) high temperature alloys, especially type PM 3030. From the “normally” high alloyed stainless steels, type AISI-321 showed the best properties. The other stainless steel – alumina combinations showed after a thermal treatment a decrease of the critical load, L_c . Using ODS alloys as the substrate resulted in an increased L_c . AES-studies revealed that the increased L_c can be explained by 1) the presence of sulphur trapping elements, avoiding segregation of sulphur near the interface which could have a detrimental effect on scale adherence, and 2) titanium and carbon enrichment at the interface resulting in a beneficial effect on the adherence between the oxide and the substrate.

1 Introduction

The mechanical properties of thin oxide films are characterized commonly using microhardness and scratch test adhesion measurements [1, 2, 3]. The aim of this study was to investigate the effect of substrate composition and annealing on the adherence of thin alumina films.

2 Experimental

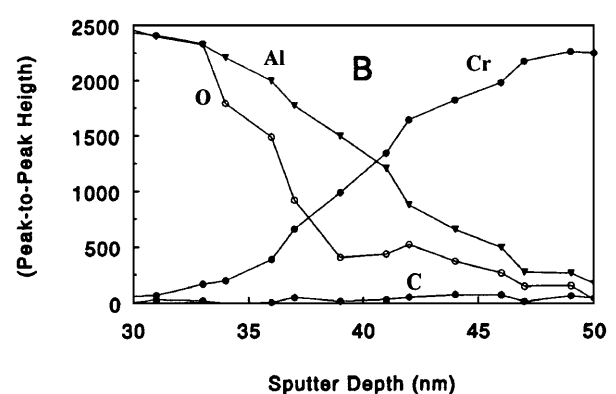
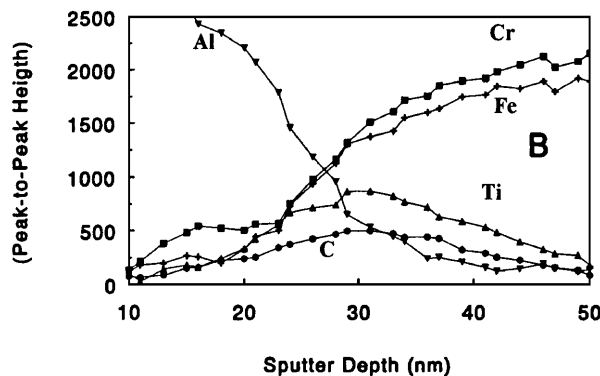
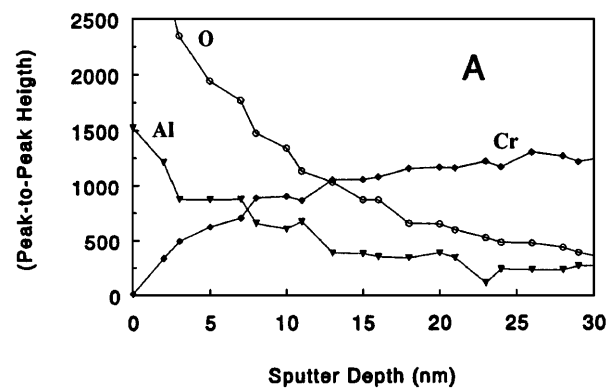
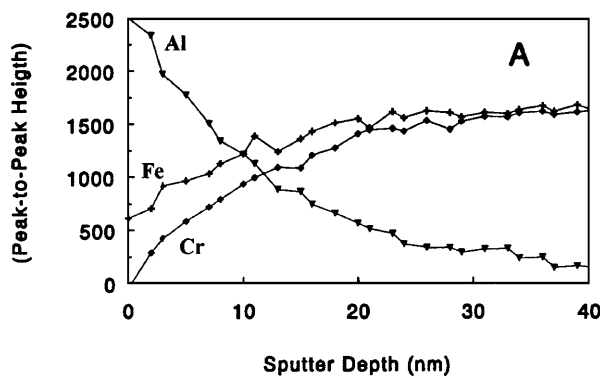
The nominal compositions of the substrate alloys used in this investigation are shown in Table 1. The Al₂O₃ was deposited

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Table 1 Nominal composition of the commercially available alloys

Alloy	Fe	Ni	Cr	Al	Ti	Si	Mn	C	S	Y ₂ O ₃	Other
MA 956	Bal.	–	19.8	4.6	0.3	–	0.09	0.04	0.004	0.52	–
MA 754	0.33	Bal.	19.6	0.2	0.3	–	0.002	0.04	0.0007	0.57	–
Inc. 800H	Bal.	31.7	19.9	0.38	0.7	0.5	0.7	0.08	0.006	–	–
AISI-316	Bal.	10.68	16.62	–	–	0.28	1.15	0.044	0.016	–	P: 0.03 Mo: 2.01
AISI-304	Bal.	8.88	17.39	–	–	0.70	1.27	0.044	0.017	–	P: 0.033
AISI-321	Bal.	10.13	17.45	–	0.40	0.52	1.55	0.048	0.003	–	P: 0.037
PM 2000	Bal.	–	20	5.5	0.3	–	–	0.01	–	0.5	–
PM 3030	–	Bal.	17	6	–	1.0	–	0.05	–	1.1	Mo: 2.0 W: 3.5

**Fig. 1a, b** AES depth profiles of alumina – PM 2000, a) before annealing, b) after annealing for 17 h at 800°C**Fig. 2a, b** AES depth profiles of alumina – PM 3030, a) before annealing, b) after annealing for 17 h at 800°C

by pyrolysis of aluminium-tri-sec-butoxide (ATSB, Janssen Chimica) in a LPCVD-system at 280°C [16]. After deposition the samples were annealed in nitrogen at 600 and 800°C, for 2, 4 and 17 h. The oxygen partial pressure in the LPCVD-system during the annealing period was high enough to keep the alumina stable. Adhesion was evaluated with a Shimadzu SST-101 scanning scratch tester which expresses the adhesion as critical load, L_c . The principles of the tester are explained in [4]. The films and interfaces were analysed using a Perkin-Elmer PHI 600 scanning Auger multiprobe. The Auger spectra and sputter profiles were recorded with a primary beam energy $E_p = 10$ kV, primary beam current $I_p = 0.5$ μ A, angle of incidence with the surface normal = 30°. Depth profiling was performed using an argon ion beam with an energy of 3.5 kV. The etching rate was 33 nm/min; just before the interface the etching rate was reduced to 3.3 nm/min. The sputter rate was calibrated using a 100 nm thick Ta₂O₅ layer.

3 Results and discussion

The Auger depth profiles of ODS alloys (Figs. 1 a, b, 2 a, b, 3 a, b, 4 a, b) show that the sharpness of the interface was not affected by annealing, while in non-ODS alloys (Figs. 5 a, b), Cr had penetrated the film. The results of ODS alloys show that Ti and C segregated to the interface after annealing. In the case of non-ODS alloys, S, Mn, C, Si, or Ti were segregated at the interface, depending on the composition of the alloys. In the figures, which do not include the elements Ti, C, or S, no peaks were detected above the background level of the equipment.

Results of the scratch testing are shown in Fig. 6. In non-ODS alloys, L_c was reduced after annealing (Fig. 6 a, b, c, d) [2]. In general the ODS alloys showed an increase in L_c after annealing (Fig. 6 e, f, g, h). The extent of spalling was significantly lower than the non-ODS alloys. The results of non-ODS

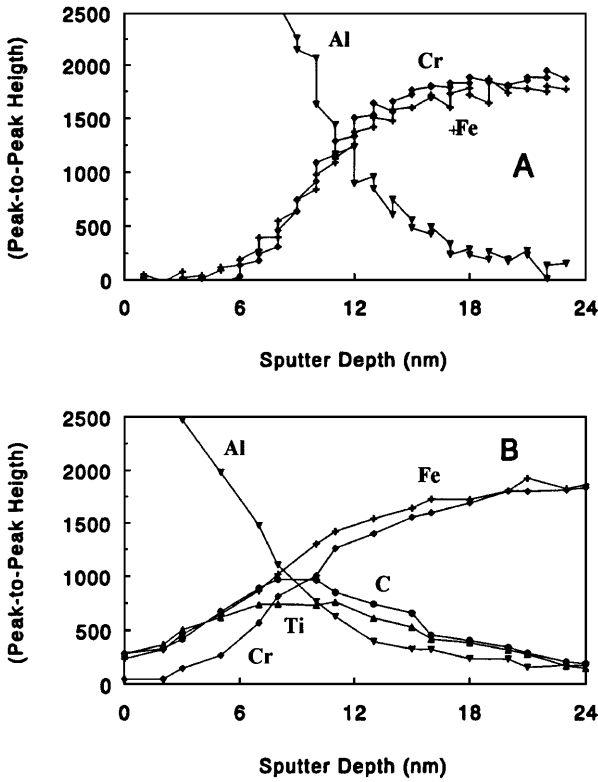


Fig. 3a, b AES depth profiles of alumina – MA 956, a) before annealing, b) after annealing for 17 h at 800°C

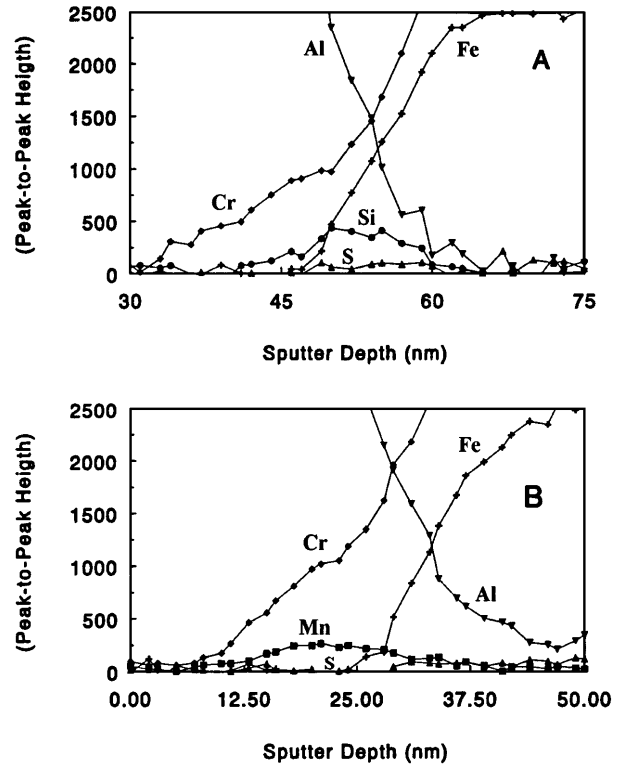


Fig. 5a, b AES depth profiles of a) alumina – AISI 304 after annealing for 17 h at 800°C, and b) alumina – AISI 316 after annealing for 17 h at 800°C

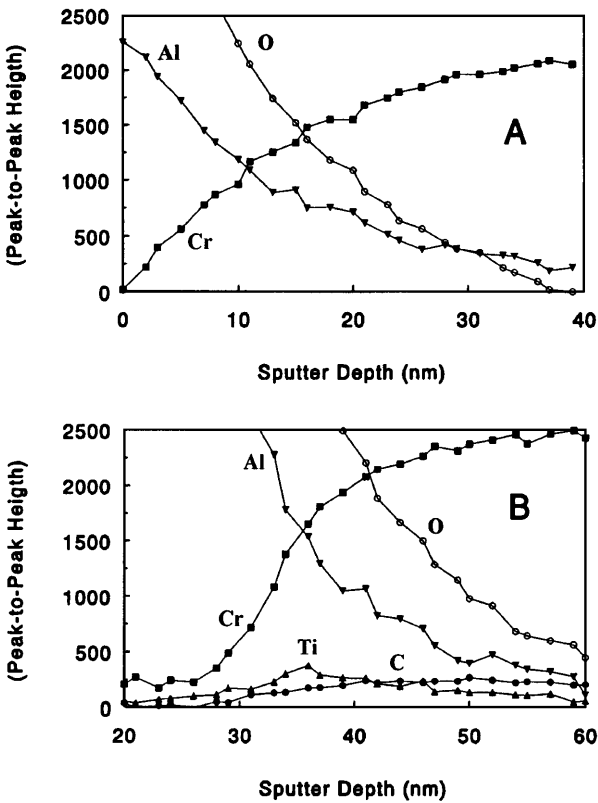
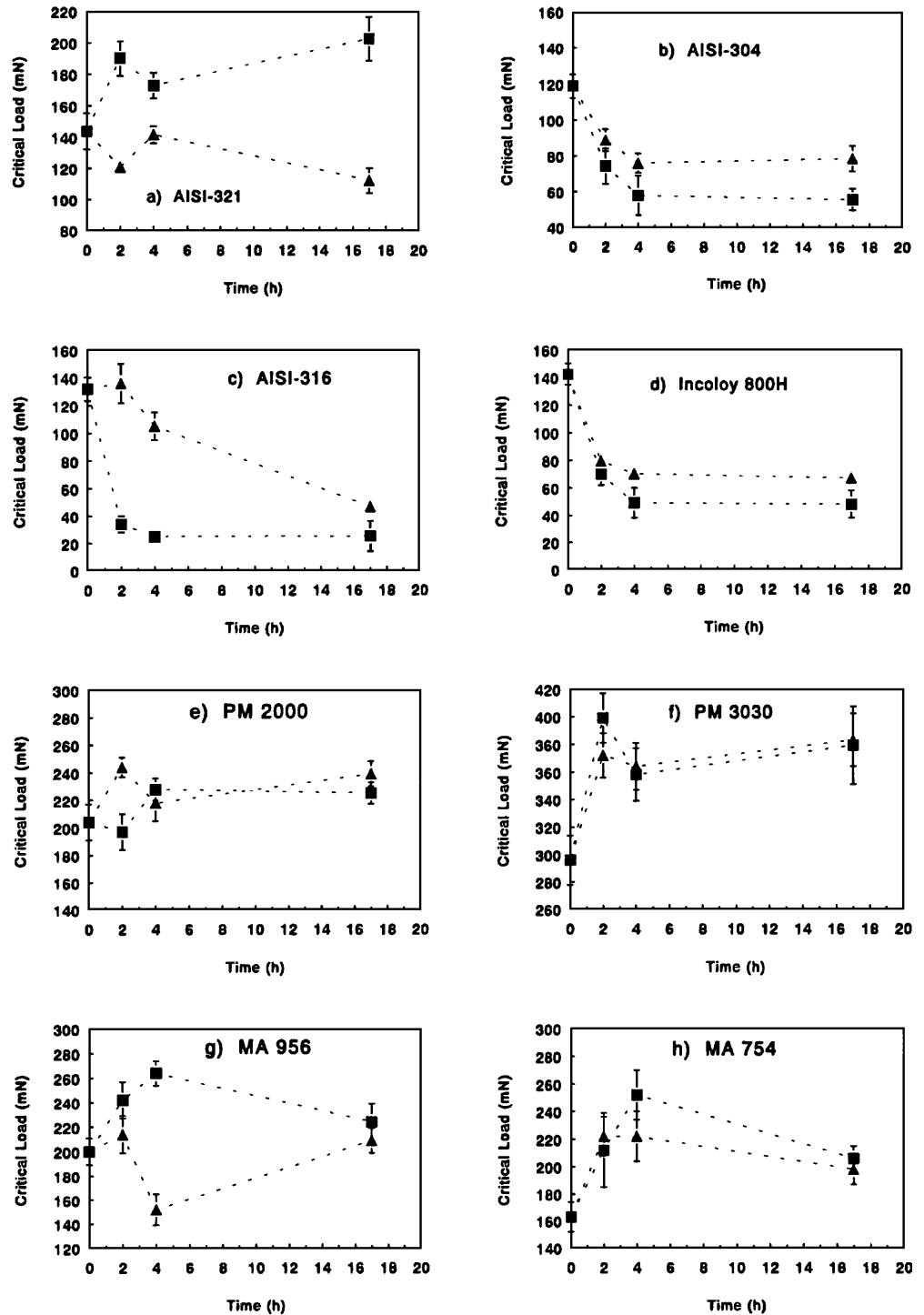


Fig. 4a, b AES depth profiles of alumina – MA 754, a) before annealing, b) after annealing for 17 h at 800°C

alloys can be explained by: 1) the presence of thermal stresses in the films, 2) changes in the interfacial structure and/or composition. The AES analyses suggest that segregation of S at the interface and Cr penetration into the film reduces adhesion, while Ti and C segregation at the interface improves adhesion. The mechanism of S segregation near the interface and the effect of TiC on the improvement of the adhesion can be found in the literature [2–12]. Recent publications [8–10] showed that sulphur favours formation of voids, cavities, and separations at oxide/metal interfaces by decreasing the surface energy at newly formed surfaces. Tosa et al. attributed the effect of TiC to an anchoring mechanism [5]. The concentration gradient of TiC near the interface can also relax the thermal stress. A third mechanism suggests Al-O-Ti bonding between the film and the TiC [5]. Moreover, the Ti-carbide or Ti-oxycarbide can act as a 'graded seal' between alumina and the metal phase, since its lattice constants can be fit, depending on its oxygen content, to obtain good epitaxy at both interfaces [10–12]. Segregation of C as graphite is not beneficial to the adhesion. The results suggest that the diffusion of Cr will also have a detrimental effect on the adherence. A local volume expansion of the oxide at the interface could result in a higher stress which makes the oxide scale more susceptible for cracking and delamination.

In ODS alloys, after annealing, the interface was enriched with Ti and C, probably as TiC. There was low S concentration at the interface because of low S content in the matrix. Another reason is the trapping of S by Y which was proposed by Smeggil et al. [13, 14]. Yttria dispersions had a beneficial effect on the adherence of alumina layers. An overview of the trapping of S is reported in literature [15]. The increased adherence in ODS alloys can be explained as follows 1) low S content of the alloy, 2) presence of S trapping elements, 3) retardation of migration of Cr into the film and 4) formation of TiC near the interface.

Fig. 6 Critical load (L_c) of alumina films as a function of the annealing time and annealing temperature ($\blacktriangle = 600^\circ\text{C}$, $\blacksquare = 800^\circ\text{C}$)



4 Conclusions

Segregation of S or C at the interface oxide/substrate can reduce the L_c . On the other hand, TiC probably influenced the adherence beneficially. Using ODS alloys as the substrate material for alumina layers resulted in an increased L_c . This is probably due to the presence of S trapping elements and TiC segregation near the interface.

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Characterization of the stoichiometry of coevaporated FeSi_x films by AES, EDX, RBS, and electron microscopy

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Abstract The composition of FeSi_x films on Si coevaporated from separate sources of Fe and Si was analyzed comparatively by AES, EDX, RBS, and electron microscopy. Cross-checks between EDX and RBS reveal systematic errors originating from the spectra background subtraction in RBS and from the thickness correction of the EDX signals. PCA (principal component analysis) assisted AES was successfully applied to the characterization of different Si bonding states in nonstoichiometric FeSi_x films. For the growth of β-FeSi₂ films by means of molecular beam epitaxy (MBE) the adjustment of the atomic beam intensities is reported in order to illustrate the capabilities of the various techniques.

1 Introduction

Thin films of semiconducting silicides have attracted increasing interest for device applications in the field of thermoelec-

trics, optoelectronics, and photovoltaics [1]. Especially the orthorhombic β-FeSi₂, which has a direct optical gap at about 0.87 eV [2], is regarded as a potential constituent of silicon based photovoltaic cells [3]. The main task of current research on FeSi₂ is the preparation of thin films with stoichiometric composition for which optimized semiconducting and photoelectric properties are to be expected [1, 3]. Therefore, any progress in the film deposition technology is closely linked to the possibilities of the stoichiometry characterization. Here the composition analysis of coevaporated FeSi_x films by energy dispersive x-ray spectroscopy (EDX), Rutherford backscattering spectroscopy (RBS), Auger electron spectroscopy (AES) and scanning electron microscopy (SEM) is discussed. These techniques are used to adjust the component beam intensities of the evaporating sources, the most critical parameter of the codeposition methods.

2 Experimental

The FeSi_x films were grown on Si substrates by two different methods of coevaporation. Type 1 samples were deposited in a high vacuum chamber (pressure of the order of 10⁻⁶ mbar) by coevaporation from two off-center placed sources onto a substrate which was not moved during deposition [3]. This resulted in a FeSi_x film with a composition gradient along a connection line between the evaporation distribution maxima of the Fe and the Si evaporators. Cutting the wafer along this direction a set of samples with x = 1.9 to 2.3 became available. Type 2 samples were MBE films grown under UHV conditions (basic pressure below 10⁻¹⁰ mbar) [2]. Before deposition, the substrate was covered with a 50 nm Si buffer layer and a FeSi₂ template of a few nm thickness. The β-FeSi₂ film was deposited on the rotating substrate held at 660°C by coevaporation of Fe and Si.

A HITACHI S-4100 scanning electron microscope, equipped with a field emission cold cathode and a Si-Q-Detector Pioneer Ultra of NORAN, was used for EDX analysis and film morphology investigations. For EDX Si-K and Fe-L lines were selected and monitored at an acceleration voltage of 6 keV and a take-off angle of 30°. The signal correction was calculated by the Proza method. A stoichiometric β-FeSi₂ single crystal platelet with a specially prepared surface was used as a reference. RBS

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