

Influence of Al(Er) interlayer on the mechanical properties of AlN(Er) coatings

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Abstract

AlN(Er) thin films were deposited by sputtering on M2 steel (AISI) and Si substrates with different thickness of an Al(Er) interlayer. No significant variations were observed in the chemical composition and structure of the AlN(Er) films. The films in all cases presented excess nitrogen in relation to AlN stoichiometry. The diffraction peaks were strongly shifted to lower angles due to the presence of Er. The hardness of the films is approximately 32 GPa and does not change with the thickness of the Al(Er) interlayer. The cohesion and adhesion of the AlN(Er) films were improved with the inclusion of the Al(Er) interlayer; the cohesive and adhesive critical load values increased from 7 and 17 N to 15 and 27 N, respectively. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, AlN thin films have been successfully deposited by sputtering, with scope for their possible applications in many fields of industry, such as electronics, optics and acoustics [1–7]. Moreover, owing to its high hardness associated with high thermal and chemical stability, AlN is an excellent alternative for the protection of materials against wear and corrosion; a good example is the study carried out by Miao et al. [8] for the protection of organic photoconductor (OPC) materials. The doping of AlN with erbium allows for photoluminescence in the visible range, which makes it an interesting option for use as sensor [9]. Previously, AlN films doped with Er were deposited by sputtering [10] to try to produce a hard coating with luminescent properties for use as a sensor to evaluate the wear and corrosion in coated mechanical components. Besides obtaining luminescence, one very interesting result was that the Er doping led to an important increase in the hardness of AlN films [10]. Unfortunately, the coatings have only critical loads of 7 and 17 N for cohesive and adhesive failure, respectively [10], which makes them inappropriate for severe mechanical applications.

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The use of thin metal interlayers to promote the adhesion of thin films is well documented in the literature [11]. The aim of this work is to study the influence of an Al(Er) interlayer on the mechanical properties of a AlN(Er) film deposited on M2 steel (AISI) and Si substrates. The thickness of the interlayer was varied in the range 0–0.7 μm and the structure, hardness and scratch-test behaviour of the samples coated were studied.

2. Experimental details

The films were deposited by RF reactive magnetron sputtering from a 99.99% pure Al target (100 mm in diameter, 6 mm thick) as reported in a previous paper [10]. Silicon ([100]-oriented) and heat-treated M2 steel were used as substrates. Before the start of each deposition, both the target and the substrates were pre-sputtered in a high-purity argon (99.99%) atmosphere at 0.75 Pa for 20 min. A shutter was placed between the two electrodes to avoid cross-contamination. The incorporation of Er in the AlN films was achieved by partially covering the aluminium target with 2 erbium pieces (10 mm in diameter). All depositions were achieved with a discharge power of 600 W, $P_{\text{N}_2}/P_{\text{tot}} = 0.5$ and a total pressure of 0.74 Pa.

The structure of the as-deposited films was studied

Table 1
Chemical composition of AlN(Er) sputtered films

Sample	M2 substrate (at.%)				Si substrate (at.%)			
	Al	N	Er	O	Al	N	Er	O
Al(Er)	92.8	–	6.3	0.9	–	–	–	–
AlN(Er)	42.5	51.8	1.8	3.9	–	–	–	–
AlN(Er) 3 min	40.9	52.7	1.7	4.7	41.8	51.9	1.6	4.7
AlN(Er) 6 min	40.3	53.7	1.7	4.3	41.8	52.4	1.6	4.2
AlN(Er) 9 min	39.1	53.8	2.0	5.1	39.2	53.6	1.9	5.3

by glancing-angle X-ray diffraction using a Philips diffractometer with Co(K α) radiation. A Cameca SX 50 electron probe microanalysis (EPMA) instrument was used to determine the chemical composition of the coatings. The mechanical properties of as-deposited coatings were studied by ultramicrohardness and scratch tests. The hardness measurements were performed by the depth-sensing indentation technique using a Fischerscope H100. Each hardness value is the result of at least 10 indentation tests. The scratch tests were performed in a CSEM-Revetest fitted with an acoustic detector. A total of 10 scratches were made on each sample, measuring the load that gave rise to the first cohesive failure, L_{c1} , and the load that was responsible for the first adhesive failure, L_{c2} , for each scratch. Further details on the characterisation techniques can be found elsewhere [10].

3. Results and discussion

Table 1 presents the EPMA results for the AlN(Er) films deposited with and without an Al(Er) interlayer on Si and M2 substrates. The chemical composition of the non-reactive Al(Er) interlayer deposited is also shown. No significant variations are detected, either among the Al–N films deposited on the same substrate, or the same film deposited on different substrates. Excess N is detected in all the films as a consequence of too high a N₂ partial pressure used in the deposition. For a similar gas-phase composition, Raveh et al. [6] found only a very small excess in nitrogen in their Al–N films, but working with higher deposition rates. On the contrary, other authors [2–5] have found that for N₂ partial pressures above a threshold value, the N content in the films was independent of the gas phase composition and the films were sub-stoichiometric in N (\approx AlN_{0.8}). A possible explanation for the discrepancies in these values is the type of analytical technique used for evaluation of the chemical composition. In the present work and that by Raveh et al. [6], EPMA and Auger electron spectroscopy (AES) techniques were used, respectively, whereas in the other works, X-ray photoelectron spectroscopy (XPS) was used as the analytical technique.

Oxygen contamination of approximately 4 at.% is usually found in sputtered films, originating from the residual atmosphere, particularly when elements with great affinity for O (as is the case for Al) are being deposited without substrate bias. The Er/Al ratio is higher in the non-reactive film than in AlN(Er) coatings (Table 1). Although no substrate bias was used during deposition, the growing film is bombarded by Ar neutrals reflected in the target. This bombardment induces a resputtering effect on the growing film, with species of lower atomic weight (in this case the Al) being preferentially ejected [12]. When the films are deposited in a reactive atmosphere, strong Al–N bonds are formed, making the preferential resputtering of the Al atoms more difficult. Thus, in a comparison between Al(Er) and AlN(Er) systems, a higher Al resputtering effect is expected in Al(Er) films, which can explain their higher Er/Al ratio.

All the films present a very compact cross-section morphology, with no changes observed for the deposition of the interlayer (Fig. 1a–d). The interlayer is also very compact, which contrasts with the columnar features observed in single Al films (Fig. 1e,f).

The presence of Er, probably replacing Al atoms in its lattice, leads to strong distortions of the lattice, inducing compressive stresses in the films. These stresses contribute to close the open morphology of Al films, making them more compact. This suggestion seems to be confirmed by the X-ray diffraction results (Fig. 2).

Firstly, Al(Er) films show a clear shift of the peaks position of the f.c.c. Al phase in relation to ICDD standard (card 85-1327) and to Al films. The shift to lower angles results from dilatation of the lattice (high interplanar distances) induced by the presence of the higher atomic-radius Er atoms. The high energetic nature of the sputtering process allows the incorporation of atoms into solid solution, even if this process is thermodynamically unfavourable. However, the distortion induced in the lattice leads to its mechanical instability, with the consequent tendency for the formation of an amorphous structure. As can be observed in Fig. 2b, the broad diffraction peaks (in comparison to single Al sputtered film) suggest a very low grain size. Higher contents in Er could lead to complete amorphisation of the films, as was previously observed in AlN(Er) sputtered films [10].

The X-ray diffractograms of the AlN(Er) films deposited on Si and steel substrates are shown in Fig. 3a,b, respectively. Only small changes are detected, either between the films deposited on different substrates, or among the films deposited on the same substrate. It was not possible to detect any systematic variation in the peak positions among all the films tested, regardless of the substrate or thickness of the interlayer used in the deposition. Taking into account the similar chemical

composition of the films, no changes in their residual stresses should be expected.

The films generally present a preferential growth orientation, as demonstrated by the much higher intensity of the (002) diffraction line in relation to (100) and (101), in contradiction to the ICDD standard for the close-packed hexagonal AlN phase (card 25-1133). For Al–N sputtered films deposited without substrate bias, the change in the orientation of the *c*-axis from perpendicular to parallel to the substrate is reported for discharge pressures over 1 Pa [3]. Thus, it would be expected that a preferential orientation following the [001] direction exists in the Al–N(Er) films. All the peaks are positioned with a strong shift in relation to the ICDD standard values, which was attributed to the presence of Er substitutions for Al in the AlN lattice. Although there are almost no references in the literature for the formation of the cubic AlN phase (ICDD card

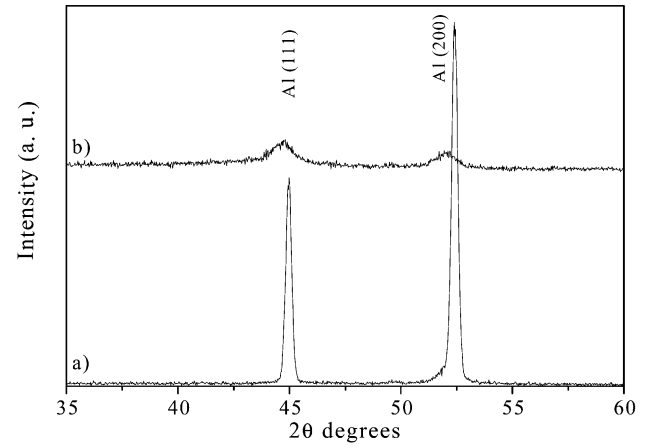


Fig. 2. X-Ray diffractograms of (a) Al and (b) Al(Er) sputtered films.

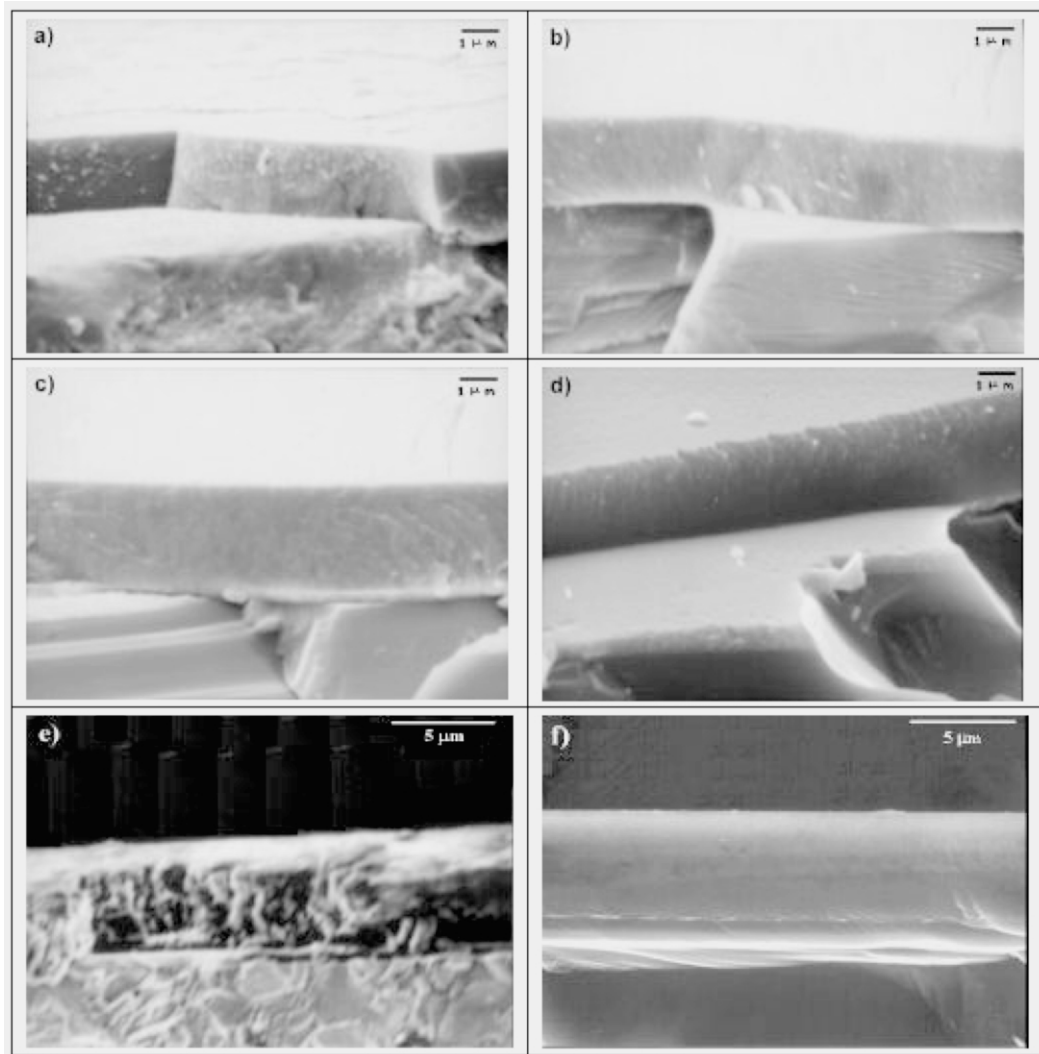


Fig. 1. SEM images of the cross-section morphology of sputtered films: AlN(Er) (a) without; (b) with 3-min; (c) with 6-min; and (d) with 9-min Al(Er) interlayer; (e) Al and (f) Al(Er) films.

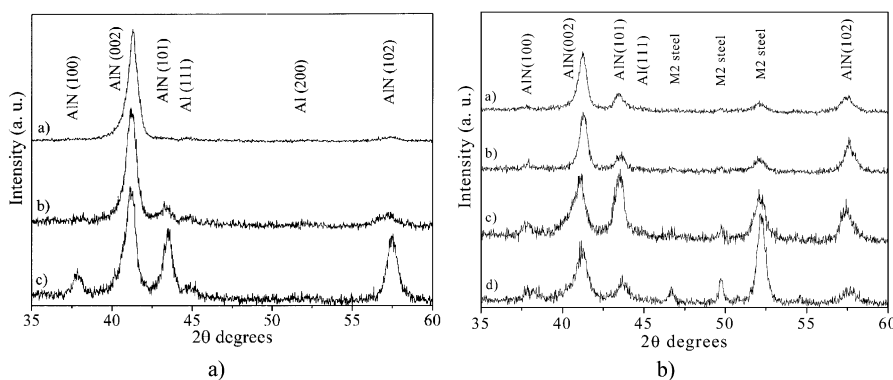


Fig. 3. X-Ray diffractograms of AlN(Er) sputtered films deposited on (a) Si and (b) M2 substrates.

87-1053) [1], in all the spectra, the shoulder on the left of the (002) peak is close to the (111) peak of this phase. Vestiges of the (111) peak for the Al(Er) interlayer can be detected in the X-ray diffractograms, particularly in the coated Si samples. Finally, it should be remarked that in spite of the glancing angle of incidence, diffraction peaks of the M2 substrate can be observed. As would be expected, their intensity is lower for thicker Al(Er) interlayers.

In agreement with the similar characteristics for films deposited with and without an Al(Er) interlayer, no significant changes were observed in the hardness values (Table 2).

Lee et al. [7] found a decrease in the hardness of their AlN films when deposited on a Al interlayer. However, this decrease was attributed to the influence of the soft Al layer. In fact, the comparison was carried out between a 200-nm-thick AlN film and a Al (100 nm) + AlN (100 nm) film. For other type of films (e.g. TiC [13]), a significant increase in hardness was measured when a Ti or Cr interlayer was used in the TiC deposition. However, no explanations were presented for this effect. In comparison to the literature values for AlN films [6,7], the hardness of AlN(Er) films is significantly higher, a fact attributed to the distortion effect of Er in the AlN lattice [10].

Fig. 4 presents the cohesive and adhesive critical loads determined by scratch-testing for the coated sam-

ples. Tensile cracking and interfacial, shell-shaped spallation are congruent to the failures previously observed for this type of coating [10]. Two distinct effects were detected when an Al(Er) interlayer was incorporated into the film: for the cohesive critical load, a great increase in its value was observed. However, the thickness of the interlayer has no influence on the values of the critical load. It seems that the more compliant Al(Er) layer allows a more efficient adaptation of the deformation induced by the indenter, retarding the cracking of the AlN(Er) film.

On the other hand, a progressive increase in the adhesive critical load is registered with increasing Al(Er) thickness. This effect can arise either from the improvement of the adhesion forces between the AlN(Er) film and the interlayer (similar to the improvement in adhesion that Lee et al. [7] obtained for Al/AlN films), or to the increase in the global thickness of the coating. For the same external applied load, the shear stress at the interface film/substrate decreases with increasing thickness. Thus, to reach the critical stress for adhesive failure, a higher external applied load is necessary in thicker films. The adhesive failure seems to occur at the interface between the AlN(Er) film and the interlayer, as shown in Fig. 1d. The interlayer is

Table 2
Hardness of AlN(Er) sputtered films

Sample	Hardness (GPa)
Al	1.7 ± 0.1
Al(Er)	4.6 ± 0.3
AlN(Er)	33.1 ± 2.1
AlN(Er) 3 min	33.6 ± 1.2
AlN(Er) 6 min	34.2 ± 2.6
AlN(Er) 6min (Si)	33.0 ± 1.8
AlN(Er) 9 min	32.8 ± 2.0

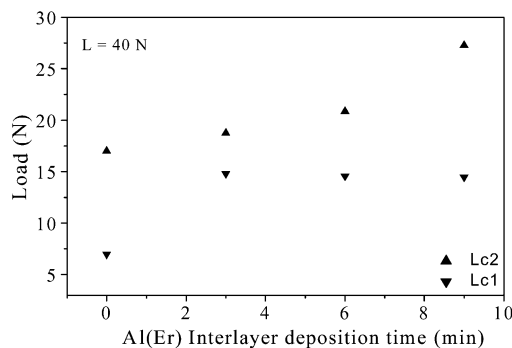


Fig. 4. Critical loads determined by scratch-testing for AlN(Er) sputtered coatings.

strongly attached to the substrate, whereas spalling of the AlN(Er) film is observed during preparation of the samples for cross-sectional observation. Similar results have been obtained in other systems. For example, for TiAlN films, Lii et al. [14] observed an increasing value for the adhesive critical load with increasing thickness of the AlTi interlayer. However, a maximum value was reached for a 1- μ m-thick Ti–Al interlayer, with values decreasing for thicker films.

4. Conclusions

AlN(Er) thin films were deposited by sputtering on Si and M2 steel substrates coated with an Al(Er) interlayer of different thickness. No significant changes in their chemical composition and cross-sectional morphology were detected. The films showed the AlN hexagonal structure. The hardness obtained was very high (>32 GPa) and did not vary among the different samples. Both cohesive and adhesive scratch-test critical loads increased with increasing thickness of the Al(Er) interlayer.

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