

Microstructure and mechanical properties of Al–Si–N transparent hard coatings deposited by magnetron sputtering

A. Pélisson*, M. Parlinska-Wojtan, H.J. Hug, J. Patscheider

*Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Nanoscale Materials Science,
Überlandstrasse 129, CH-8600 Dübendorf, Switzerland*

Available online 6 June 2007

Abstract

Motivated by the success of transition metal nanocomposite hard coatings, a new optically transparent coating based on the Al–Si–N ternary system was developed. Al–Si–N thin films were deposited by reactive DC magnetron co-sputtering of Al and Si targets in an Ar/N₂ atmosphere at 200 °C and 500 °C sample temperature. The structure and mechanical properties of the coatings were investigated by XPS, XRD, TEM, nanoindentation and mechanical profilometry. The chemical composition was varied from pure AlN to Al–Si–N with 23 at.% of Si. The films are crystalline with the hexagonal AlN structure up to 12–16 at.% of Si as found from XRD and TEM analyses. A shift of X-ray diffraction peaks indicates a substitutional incorporation of silicon in the h-AlN lattice up to a solubility limit identified at 6 at.% of Si. By further increasing the silicon content, a nanocomposite *nc*-Al_{0.44}Si_{0.06}N_{0.5}/*a*-SiN_x is formed. From TEM analysis it follows that the crystalline material consists of columnar grains composed of crystallites with a (002) texture. The mean crystallite size decreases from 60 nm to about 5 nm upon addition of silicon, as revealed by XRD. Hardness measurements show a diffuse hardness maximum exceeding 30 GPa around 10 at.% of Si. At this value a negligible residual stress in the coating is measured.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Al–Si–N; Nanocomposite; XRD; TEM; Hardness

1. Introduction

Since the nineties, superlattice and nanocomposite coatings with greatly improved mechanical properties are used as wear protection coatings of industrial drilling and cutting tools. Among them, hard and superhard nanocomposite coatings based on *nc*-TMN/*a*-SiN_x (TM=Ti, Cr, Zr etc., i.e. a transition metal) are extensively investigated [1–4]. However, such coatings are optically opaque due to their metallic nature and cannot be used in applications which require optical transparency. The combination of group III nitrides, as the crystalline constituent of a transparent hard nanocomposite, together with amorphous SiN_x as the matrix material, could lead to a new class of transparent hard coatings.

Among group III nitrides AlN has the widest bandgap (6.2 eV), shows good optical, mechanical and anti-oxidation properties and

can easily be deposited by sputtering techniques [5–7]. According to the existing ternary phase diagram for the Al–Si–N system [8], AlN and Si₃N₄ are moreover expected to be immiscible. However, some authors found that the co-deposition of AlN and Si₃N₄ at high temperature may lead to an Al–Si–N solid solution [9–10] whereas others suggested the formation of a two phase composite [11]. From available data, a co-deposition at low substrate temperature is hence expected to lead either to an *nc*-AlN/*a*-SiN_x nanocomposite, or to an Al–Si–N solid solution [12]. Up to now, Al–Si–N films were only investigated for potential application in field emission devices [9], UV light emitters [10], anti-oxidation coatings [11] or optical films with tailored refractive indices [13]. We propose here to explore the suitability of Al–Si–N coatings for new oxidation resistant hardness-enhanced optically transparent coatings with a hardness exceeding that of Al₂O₃.

In this publication, we report the structural and mechanical studies of Al–Si–N thin films that can be prepared at low deposition temperatures by reactive magnetron sputtering.

* Corresponding author. Tel.: +41 44 823 4349; fax: +41 44 823 4034.

E-mail address: aude.pelisson@empa.ch (A. Pélisson).

2. Experimental procedures

2.1. Deposition conditions

The films were deposited by DC unbalanced magnetron sputtering from confocally arranged Al and Si targets in an Ar/N₂ reactive atmosphere at a total pressure of 0.3 Pa. The base pressure of the deposition chamber at room temperature was about 10^{−6} Pa. Si (100) substrates were mounted face-down on a heated substrate holder rotating 12 cm above the 5 cm diameter targets. The composition of the coatings was varied from pure AlN to Al–Si–N with 23 at.% of Si by keeping the power applied to the Al target constant and progressively increasing the power on the Si target. No substrate bias was applied. The argon and nitrogen flows were set at 15 sccm and 7 sccm respectively for all depositions. Three series of samples were prepared, using different power values on the Al target (100 W and 200 W) and two different deposition temperatures (200 °C and 500 °C). The deposition parameters used are given in Table 1. For the sake of simplicity the conditions coding A, B, and C from Table 1 are used throughout this paper. The film thickness is in the 1–2 µm range for all samples.

2.2. Characterization techniques

The atomic composition of the samples was determined by XPS using a PHI Quantum 2000 microprobe. A mild pre-sputtering (3 keV Ar⁺ for 90 s) was used to remove the surface oxide layer on the samples. The texture of all films was investigated by recording conventional θ – 2θ X-ray diffractograms using Cu K α radiation on a Siemens D5000 diffractometer. The crystallite size was estimated from the integral width of the diffraction peaks (here the (002) peaks) using the Scherrer formula with $K=1$ and assuming negligible strain broadening. Such a treatment gives access to an effective crystallite dimension L_{hkl} , that is a volume-averaged crystallite dimension normal to the (hkl) reflecting planes, independent on the crystallite shape or symmetry [14]. Cross-sections of selected samples were prepared by mechanical polishing followed by ion milling to electron transparency. Then both conventional and high resolution TEM on a Philips CM30 microscope was performed. The hardness and the elastic modulus of the films were determined from nanoindentation tests with a MTS Nanoindenter[®] XP using a Berkovich tip and following the Oliver Pharr method [15]. A maximum load of 2 mN was applied on all samples that resulted in indentation depths of about 50–70 nm ($\leq 10\%$ of the coating thickness). The thickness and the internal residual stress in the coatings were determined using a Tencor[®] P-10 mechanical profilometer. The biaxial residual stress was

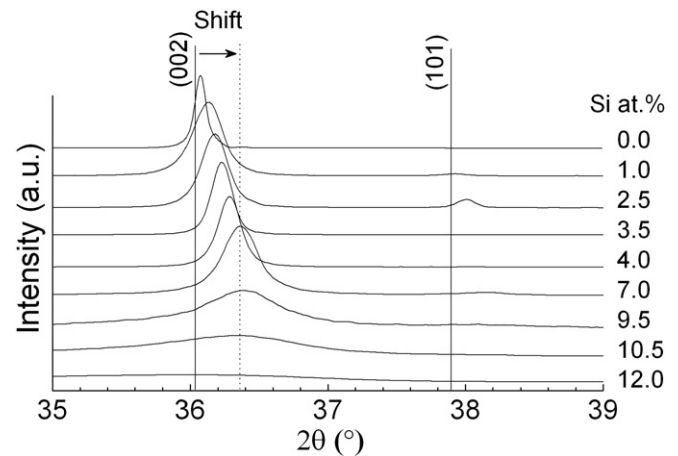


Fig. 1. XRD patterns obtained for Al–Si–N films of series B, representative for all three series, using Cu K α radiation. The silicon atomic content corresponding to each film is given on the left hand side of the diffractograms. The solid vertical lines represent the peak positions in pure h-AlN (wurtzite). The intensity was normalized on diffractograms corresponding to Si content from 0 to 9.5 at.%, so that peaks present comparable amplitudes. The same intensity scale was used for diffractograms corresponding to Si content ≥ 9.5 at.% of Si.

calculated using the Stoney's equation after measuring the spherical deflection of samples deposited on silicon [16].

3. Results

3.1. Chemical analysis

The total composition of the films was determined in terms of Al, Si, N and O atomic contents. The nitrogen content was found to be constant and equal to 50 ± 2 at.%. Since the measurement accuracy of XPS is usually considered as 10% of the atomic content, we can consider that the (Al+Si+O)/N composition ratio was ≈ 1 in all films. The mean oxygen content of the samples after pre-sputtering was found to be about 4 ± 2 at.%.

3.2. Structural analysis

3.2.1. XRD analysis: texture, bond length and phase separation

The X-ray diffractograms measured on the samples of series B, being representative for all three series reported here, are given in Fig. 1. The samples are crystalline up to about 12 at.% of Si with the crystallographic structure of hexagonal AlN (wurtzite) and a (002) texture in the growth direction. Above 12 at.% of Si the films become X-ray amorphous. However, the existence of small crystallites in the films up to about 16 at.% of Si is revealed by TEM, as shown in the next section.

A remarkable feature of the diffractograms is the progressive shift of the (002) diffraction peak toward higher 2θ angles with increasing Si content. It corresponds to a diminution of both the c -axis lattice parameter and the bond length d between Al and N atoms in the h-AlN lattice, related to each other by $d=3/8c$. The bond length decreases linearly with increasing the Si content up to 6 at.% and then remains constant for higher Si contents (see Fig. 2). At low Si content, the observed decrease can be explained by a substitution of Si atoms in tetragonal sites of the

Table 1
Deposition conditions for three series of Al–Si–N samples

Series	Deposition temperature (°C)	Power on Al (W)	Power on Si (W)	Deposition rate (nm/h)
A (○)	200	100	0–100	95–190
B (■/□)	200	200	0–150	245–595
C (▲/△)	500	200	0–170	265–680

Download English Version:

<https://daneshyari.com/en/article/1661682>

Download Persian Version:

<https://daneshyari.com/article/1661682>

[Daneshyari.com](https://daneshyari.com)