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Control of morphology (ZrN crystallite size and SiN_x layer thickness) in Zr–Si–N nanocomposite thin films

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Abstract

DC reactive magnetron sputtering was used for the deposition of Zr–Si–N thin films. Four series of samples have been deposited at various substrate temperatures T_S: 300 K, 510 K, 710 K and 910 K. Depending on T_S, different N_2 partial pressures p_{N2} were required to obtain nearly stoichiometric ZrN films. Si content (C_{Si}) was varied in each series by changing the power applied on the Si target, whereas the power on the Zr target was kept constant. The microstructure of the coatings was examined by XRD and in cross-section by transmission electron microscopy (TEM). Depending on T_S and p_{N2}, the deposition rate showed significant variations from 0.04 to 0.18 nm/s. The correlation between film morphology (preferential orientation of crystallites, grain size, column dimensions, thickness of the SiN_x layer covering ZrN crystallites) and the deposition conditions (power applied on Si target, temperature, nitrogen partial pressure and deposition rate) provides useful information for optimizing the deposition process.
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Keywords: Nanocomposite; Zirconium nitride; Morphology

1. Introduction

Nanocomposite coatings are materials that derive their unique properties from a subtle interplay between phase equilibrium, the crystalline grain size and morphology and the nature of phases present in these nanocomposites. Thus, the unusually high hardness values of MeN-Si_3N_4 coatings, observed at approximately 5–10 at.% of Si, are the result of an optimized microstructure in which nanocrystallites of MeN (nc-MeN) having sizes smaller than 20 nm are surrounded by a thin amorphous layer of Si_3N_4 (a-SiN_x) [1–15].

In our previous papers we have reported the results of our investigations into the physical and mechanical properties of thin films prepared by reactive magnetron sputtering for many systems, such as Ti–Si–N, Ti–Ge–N, Cr–Si–N, Nb–Si–N and Zr–Si–N [8–11]. Based on their common nanostructural modification due to the addition of the third element, a 3-step model was proposed for the film formation in Me–X–N ternary compounds deposited by reactive magnetron sputtering. Three distinct concentration regions have been identified concerning the evolution of films morphology with increasing X content: 1 — the solubility region (X substitute Me atoms in the MeN lattice), 2 — the region of formation of the amorphous layer covering MeN crystallites, 3 — the region of reduction of the crystallite size by increasing the surface to volume ratio of the nanocrystallites,

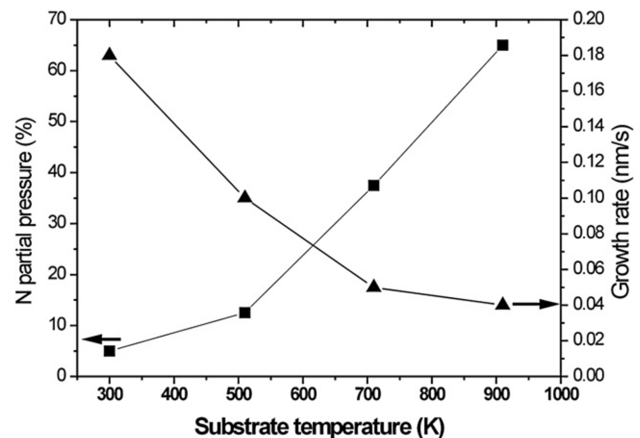

Fig. 1. N_2 partial pressures p_{N2} and growth rate vs. deposition temperature T_S.

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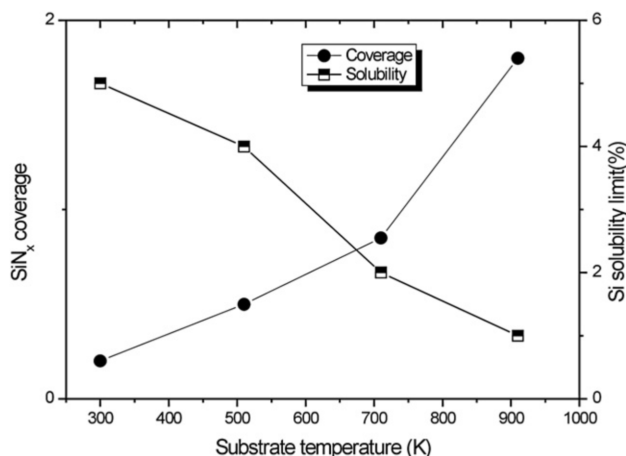

Fig. 2. Zr–Si–N films morphology: SiN_x coverage thickness and Si solubility limit for different temperature T_S.

whilst keeping the "amorphous" layer thickness constant [9]. The presence of a SiN_x coverage layer at the grain boundaries and its constant thickness in the 3rd region have been confirmed from optical and electrical measurements [12,13]. These results are different from those reported in some publications [5,16] in which the authors claimed that the thickness of the Si_3N_4 layer on TiN crystallites can be monitored by varying only the Si content in the films. We should mention that these papers rely on calculated values for the Si_3N_4 layer thickness, derived from volume fraction and crystallite size considerations, and not experimental results [5,16].

The present paper focuses on the formation of the nanostructures in Zr–Si–N thin films as a function of the deposition temperature. Because the phase segregation is a diffusion-controlled mechanism, the deposition temperature is a key parameter for the segregation, atomic diffusion and self structuring mechanisms in these materials. The purpose of this paper is to correlate qualitatively the deposition conditions with the morphology of the nanocomposite films.

2. Experimental

The deposition of Zr–Si–N films was carried out by DC reactive magnetron sputtering of Zr and Si targets in an Ar+ N_2 atmosphere. The residual pressure in the reactor was less than 3×10^{-5} Pa. During the deposition, the total pressure was kept constant at 0.5 Pa for all Zr–Si–N films. Four series of samples have been deposited at various substrate temperatures T_S: 300 K, 510 K, 710 K and 910 K. Depending on T_S, different N_2 partial pressures were required to obtain nearly stoichiometric ZrN films. The nitrogen partial pressure was kept constant for each series at 5%, 12.5%, 37.5% and 65%, respectively. The power applied on the Zr target was kept at 100 W, whereas the power on the Si target was varied between 10 and 100 W. The diameter of the targets was 5 cm. The substrates were polished silicon wafers, oxidized silicon wafers and WC-6%Co strips. The film thicknesses, measured by profilometry, were between 0.9–1.2 µm. The microstructure of the films was examined in cross section by TEM on a Philips CM20 (2.8 Å point resolution and Cc 1.2 mm) and Philips CM300 (1.7 Å point resolution and Cc 1.2 mm). Details concerning XRD and electron probe microanalysis measurements are given in [10].

3. Results and discussions

For depositing nearly stoichiometric zirconium nitride film it was necessary to significantly increase the N_2 partial pressure with increasing substrate temperature T_S (Fig. 1). Details concerning the chemical composition of Zr–Si–N films are given in [10]. At a fixed power applied on Zr target the film growth rate has 4.5 times decreased (Fig. 1). The reduction of the growth rate can be explained by the reduction of the sputtering rate due to the nitrogen poisoning of the Zr target with increasing p_{N2} and by the increase of resputtering probability of the atomic species from the substrate with increasing substrate temperature. Also, the lower sputtering efficiency of N ions compared with Ar can be considered. Consequently, the film morphology is affected by the modification of the growth kinetics. The thickness of the SiN_x layer surrounding the ZrN nanocrystallites has increased by 9 times and the Si solubility limit decreased by 5 times upon changing the deposition conditions from 300 K to 910 K (see Fig. 2). Various models exist to explain the formation of the nanostructure. One model explains the phase segregation in Ti–Si–N as being a consequence of spinodal decomposition during deposition [2,17] (thermodynamic approach), while another model uses purely kinetic arguments for the nanostructure formation [18]. In our case we observed that the increase of the

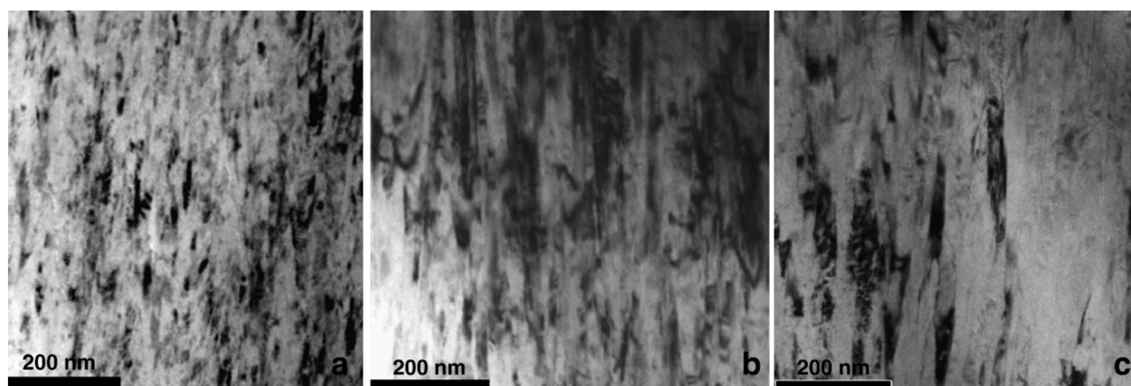

Fig. 3. TEM bright field images in cross-section of Zr–Si–N films: at ~1% Si for different temperatures: a) T_S=300 K, b) T_S=510 K and c) T_S=910 K.

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