

Structural stability of decorative ZrN_xO_y thin films

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Abstract

ZrN_xO_y thin films were prepared by rf reactive magnetron sputtering. The thermal stability of the coatings was tested in vacuum for an annealing time of 1 h in the temperature range 400–800 °C. Residual stresses originated by the deposition process were partially or almost completely released with the annealing, which is consistent with the X-ray diffraction results. Samples with low oxygen fraction ($0.10 < f_{O_2} < 0.22$) showed no significant changes in hardness after thermal annealing at 800 °C. For intermediate and high oxygen fractions, an initial decrease in hardness at 600 °C annealing is followed by an inversion at the highest temperatures (700 and 800 °C, respectively), resulting from possible oxide phases crystallization, defect annealing at high temperatures and some extended phase segregations. The increase in the oxygen fraction is followed by a decrease of hardness in the as-deposited samples towards the values of “pure” ZrO_2 . No significant changes in colour were observed with the annealing.

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1. Introduction

Decorative thin films for high-quality consumer products, such as eyeglass frames, wristwatch casings and wristbands, are gaining increasing commercial importance. The investigations in these materials are very specific since the films are supposed to provide both scratch-resistance and protection against corrosion, while enhancing their appearances with attractive surface colouring. The available knowledge is yet far from being complete and requires further investigations. Important findings in terms of colour change are clearly insufficient to go straight forward into the use of these materials in real conditions. In fact, beyond colour, thermal stability is also seen as fundamental for any coating material for industrial use and the comprehensive understanding of its relationships with physical/mechanical properties such as hardness is an important goal in modern materials science.

Thermal stability of a thin film system is actually the motive of several research activities since a low thermal stability of the coating strongly limits their industrial use. Therefore, it is required to produce thermally stable films that keep their main properties constant up to relatively high temperatures. However, to our knowledge, only very few attempts have been made to systematically investigate the stability of coloured thin films and the details of phase transition/formation have not been well characterized [1]. Our study addresses these open questions, trying to evaluate the film property evolution.

2. Experimental

The ZrN_xO_y films were deposited by reactive rf magnetron sputtering, from a high purity Zr target onto polished high-speed steel (AISI M2) and stainless steel (AISI M316) substrates. Depositions were carried out in a mixed $Ar+(N_2+O_2)$ atmosphere in an Alcatel SCM650

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apparatus, with the substrates rotating at 60 mm over the target at a constant speed of 4 rpm. The base pressure in the deposition chamber was about 10^{-4} Pa and rose to about 4×10^{-1} Pa during depositions. A pure zirconium adhesion layer with a thickness of about 3×10^{-7} m was deposited on each sample to improve adhesion. Films were prepared with variation of the gas flow (N_2+O_2) from 0 to 6.5 sccm, at a constant temperature of 300 °C and bias voltages ranging from -75 V up to ground state. Argon flow was kept constant at 100 sccm. Two sets of samples were prepared: a group with variation of the oxygen fraction, keeping constant the bias voltage (-50 V); and a second group with variation of the bias voltage keeping constant the reactive gas flow at 4.3 sccm (although using a constant flow, some changes in the oxygen fraction were obtained [2]). In order to study the thermal stability of the coatings, a vacuum furnace with a base pressure of 10^{-4} Pa was used, with a heating thermal cycle of 1 h up to the desired temperature annealing for 1-h cooling (“free cooling”). The samples were annealed at temperatures ranging from 400 up to 800 °C. The chemical composition of the films was determined by Rutherford backscattering spectrometry (RBS), using a 1.4 MeV $^1H^+$ beam. The crystallographic structure was investigated by X-ray diffraction (XRD), using monochromatic Cu $K\alpha$ radiation. Film colour was computed using a commercial MINOLTA CM-2600d spectrophotometer. Hardness experiments were carried out in a Fischerscope H100 ultramicrohardness tester. Residual stresses, σ_r , were obtained from the substrates curvature, using Stoney equation [3]. Surface morphology was investigated by optical microscopy (OM).

3. Results

RBS composition determination using the RUMP code simulations [4] revealed that although oxygen is extremely reactive in comparison with nitrogen [5], a large range of oxygen contents were obtained. The oxygen fraction (f_{O_2}) was determined by the ratio of the oxygen content and the sum of both oxygen and nitrogen contents: $f_{O_2} = C_O / (C_O + C_N)$. Further details on the samples composition and thickness can be found elsewhere [2].

RBS composition determination after the annealing experiments revealed that no significant changes in composition were obtained. From these results it can be concluded that the films are very stable, although it is not possible to conclude about the particular arrangement of the different species, in terms of the correspondent compounds or location (e.g. grain boundaries, lattice positions, etc.). Nevertheless, structural characterization by XRD revealed that all films, as-deposited and thermal annealed, exhibited a face centred cubic δ -NaCl structure-type, with a strong (200) texture. Fig. 1 shows the diffraction patterns for a sample with an oxygen fraction, $f_{O_2} = 0.22$.

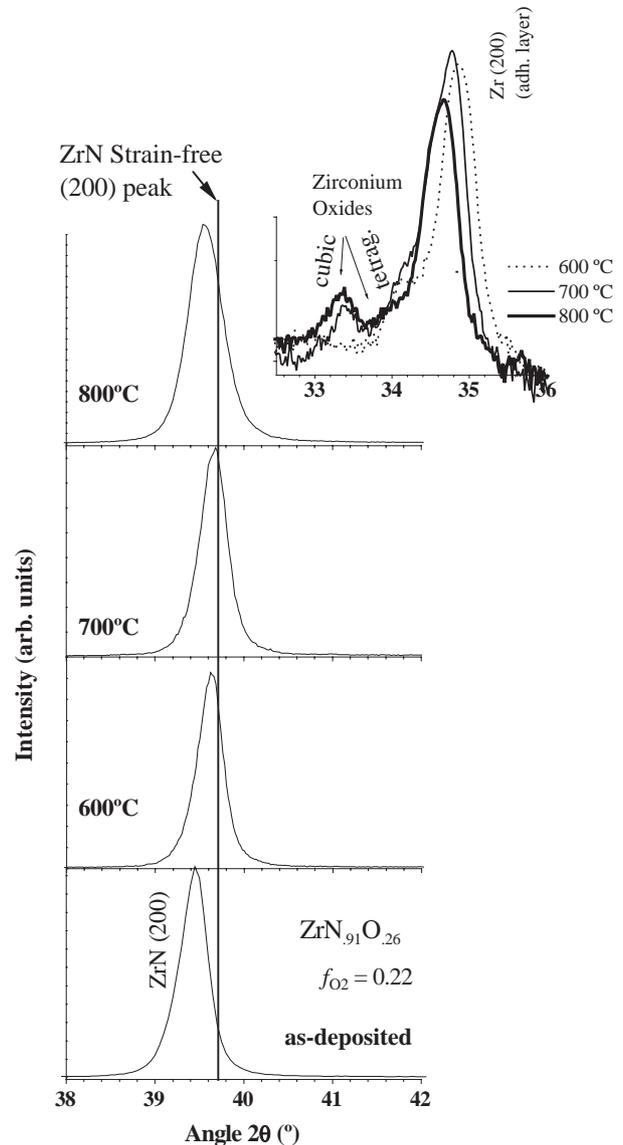


Fig. 1. XRD patterns of ZrN_xO_y films for the as-deposited sample and annealed in vacuum at different temperatures, for a particular sample with an oxygen fraction of $f_{O_2} = 0.22$.

Detailed analysis of the XRD patterns with the thermal annealing, allows the detection of important structural changes at different temperatures. In the first group of samples (variation of oxygen fraction) there was some tendency for the diffraction peaks to shift continuously towards the Zr–N strain-free position for annealing temperatures up to 700 °C. The simulation of the diffraction peaks using Fourier analysis [6] revealed, in the case of the sample with $f_{O_2} = 0.22$, grain sizes in the range of 19–20 nm for the as-deposited and 600–700 °C annealed films, which changed to about 15 nm at 800 °C. Anyway, this unusual decrease of grain size might not be real since this could be not a single peak but a mixture of both O-doped nitride, Zr–N–O (solid solution), and undoped Zr–N phases, as it was claimed recently [2] and reported by R. Roch et al. [7]. Similar behaviour has been

extensively analysed and reported for the Ti–Si–N system [8–10].

From these results one can conclude that the annealing had an effect on the stress relief by structural relaxation of the films related to processes such as the annihilation of dislocations, effusion of interstitials, such as those of nitrogen or oxygen from the Zr–N lattice, among other structural defects [11,12]. The relaxation of large compressive stresses is a well-known process and extensively reported in literature, such as the case of TiN for temperatures from 450 up to 700 °C [1,19], leading to significant film hardness decrease.

These features are illustrated in Fig. 2a, where the variation of residual stresses is presented as a function of the annealing temperature for three different samples of this same group. In this plot it is clearly observed that the above mentioned stress relaxation occurs in a sample with an oxygen fraction of $f_{O_2}=0.19$, but already at 400 °C. Furthermore, Fig. 1 shows in the upper right diffractogram an insert where the appearance of “new” diffraction peaks at

700 and 800 °C is revealed, corresponding to cubic (JCPDS card n° 51–1149), tetragonal (JCPDS card n° 42–1164) or even to cubic oxynitride zirconium (JCPDS card n° 49–949). The increase in zirconium oxide formation with the increase in the annealing temperatures [14] and the consequent increase in the tendency for oxide crystallizations (increase in local density), together with the referred increase in oxygen segregation from “doped” nitride lattices to form crystalline oxides (increase of molar volume), could also result in an increased tendency for compressive stress relaxations [15–18], and thus an increasing tendency for film cracking in these highest temperatures (Fig. 2a). The sample with an oxygen fraction of $f_{O_2}=0.29$ is an evidence of this fact, revealing significant stress relaxation at the highest temperatures. Another factor that might be important for this behaviour is the diffusion of substrate elements and the plastic deformation of substrate. With the increase of the oxygen fraction, as revealed by the sample with an oxygen fraction of $f_{O_2}=0.32$ (Fig. 2a), the stress levels become significantly lower and the relaxation is more difficult to be observed.

Regarding the group of samples prepared with variation in bias voltage, similar results were observed (Fig. 2b). The samples with the highest bias voltages (–50 and –66 V) revealed again extensive stress relaxations at the first annealing temperature (400 °C), while the sample with low stress levels (unbiased sample) revealed almost no variation in its very low stress level. A tendency to stress reduction at the highest annealing temperatures was observed for the sample with the highest ion bombardment conditions (–66 V). Nevertheless, no cracking was observed in this sample after all the annealing process (Fig. 2b). We should keep in mind that the oxygen content decreased as the ion bombardment increase during sample preparation [2] due to the so-called preferential re-sputtering [5]. This effect together with the mentioned phase segregation that might occur at the highest annealing temperatures, leading to the formation of a nanocomposite-type structure, where nanocrystalline zirconium nitride grains are embedded in amorphous zirconium oxide tissue, nc-ZrN/a-ZrO_x, similar to that of nc-TiN/a-Si₃N₄ [18], suggest that oxygen and its structural positioning are important factors to explain, not only the film properties, but also the observed cracking. Only samples with intermediate and high oxygen fractions ($f_{O_2}>0.20$) revealed cracking, starting already at 700 °C.

Fig. 3 shows the hardness values measured in the films. The two plots represent, as previously, three samples from each of the two sets of samples. The annealing led to a mixed behaviour that is characterized by both increase and decrease in hardness, which in fact was already observed for other systems [1,13,19]. In the first set of samples (Fig. 3a), the most notorious feature is the nearly constant values of hardness obtained for films with low oxygen fractions ($0.10 < f_{O_2} < 0.22$), up to 800 °C annealing temperature. These low oxygen content samples are also those who present highest hardness, even higher than that of “pure” ZrN (~26 GPa [2]). The increase in the oxygen

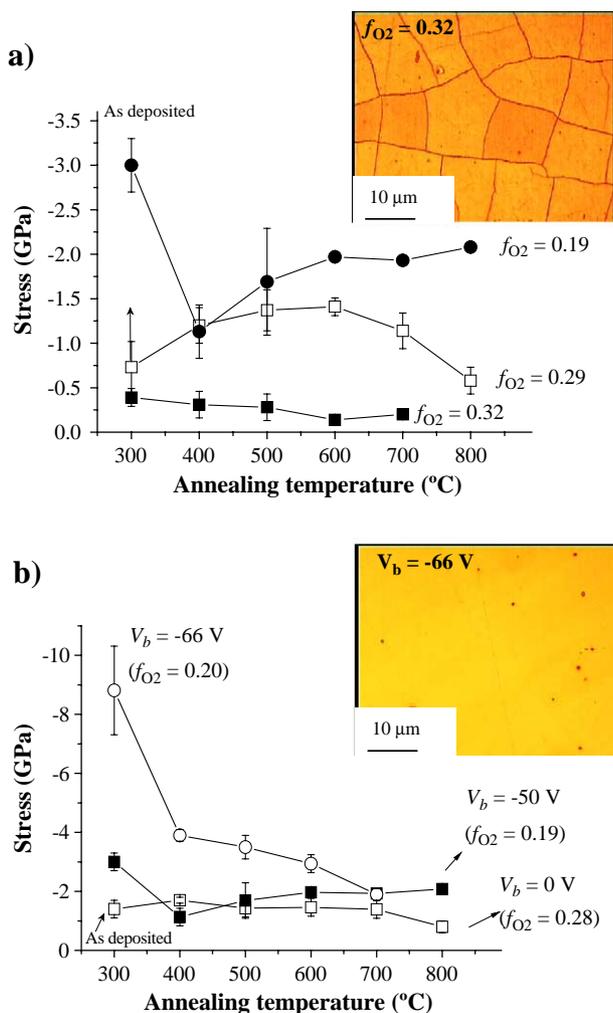


Fig. 2. Residual stresses of sputtered ZrN_xO_y, a) prepared with different oxygen fractions and b) prepared at different bias voltages, as a function of annealing temperature.

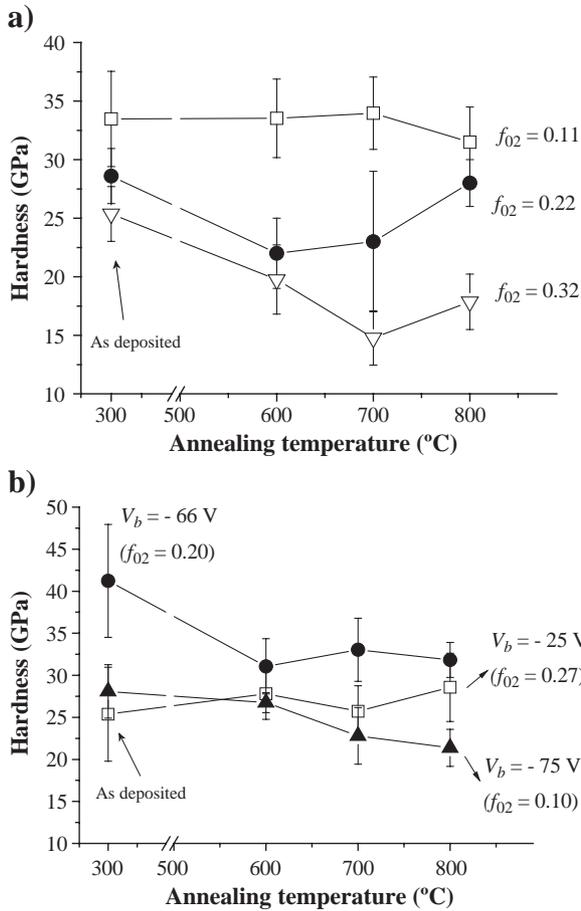


Fig. 3. Hardness of sputtered ZrN_xO_y films a) prepared with different oxygen fractions and b) prepared at different bias voltages, as a function of annealing temperature.

fraction is followed by a systematic decrease of hardness in the as-deposited samples [2]. In these intermediate and high oxygen fractions, a decrease in hardness at lower annealing temperatures is followed by an inversion at higher temperatures.

The remarkable constancy of hardness with annealing temperature (even increasing slightly in some cases) for the low and intermediate oxygen content samples (Fig. 3a and b), clearly indicates that the relatively high hardness values are not only due to high compressive stresses (they relax at the first annealing temperatures), but to structural modifications in the films. Among these, the crystallization processes that will induce the appearance of some oxide and/or other nitride/oxynitride phases are possible mechanisms to take into account. Fig. 4 shows the influence of residual stresses in hardness, where stress relaxations are accompanied by a decrease in hardness. Anyway, a closer look to this figure reveals that both samples show an increase in hardness in the temperature range 600–700 °C, although the residual stresses decrease slightly. These facts show that beyond residual stresses, the structural features play an important role. Similar conclusions were drawn for the as-deposited samples, where low stress films (<1.5 GPa) revealed hardness values varying

from 15 to more than 30 GPa [2]. The observed decrease in the hardness at the lowest annealing temperatures for samples with intermediate and large oxygen fractions, Fig. 3a, and the –66 V sample in Fig. 3b, can be related again to some defect annealing in the film structure.

Regarding colour behaviour with annealing procedures, the first note that should be pointed out is the significant constancy of colour coordinates for all the samples, which means no significant colour change with the thermal treatment and thus a significant thermal stability in these films.

4. Conclusions

Thin films within the Zr–N–O ternary system were prepared by rf reactive magnetron sputtering. RBS composition determination after the annealing experiments revealed that no significant changes in composition were obtained. XRD showed that all films, as-deposited and thermal annealed, were face centred cubic δ -NaCl structure-type, with a strong (200) texture. Structural characterization of annealed samples revealed that the annealing had an effect on the stress relief by structural relaxation of the films. Stress measurements confirmed this tendency as well as the influence of structural recovery of the films with annealing experiments.

Regarding hardness, low oxygen content samples show no significant changes in the hardness values after thermal annealing at 800 °C, which might induce the conclusion that the high hardness values are not due to high compressive stresses, but to particular structural arrangement of these films. The same effect can be related to the constancy of hardness values at –25 and –75 V samples. The increase in the oxygen fraction is followed by a systematic decrease of hardness in the as-deposited samples towards the values of “pure” ZrO₂. In these intermediate and high oxygen fractions, an initial decrease in hardness is followed by an inversion at the highest temperatures (700 and 800 °C,

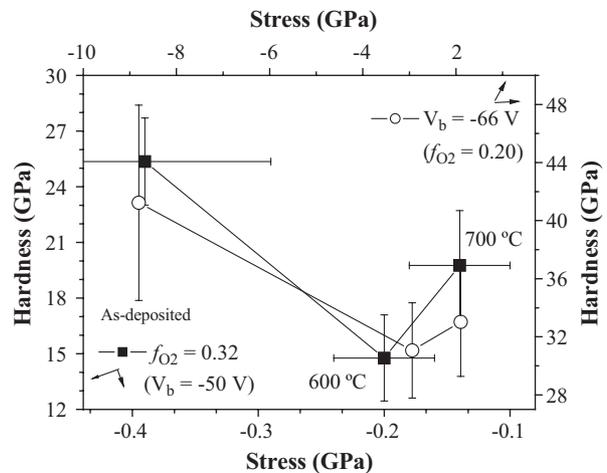


Fig. 4. Hardness as a function of residual stresses for two samples studied in this work.

respectively). The decrease in the hardness for these samples as well as that prepared at -66 V in the lowest annealing temperatures can be related to the recovery of film structure such as, annihilation of dislocations, grain growth and other structural defects.

No significant colour changes were observed with the increase of annealing temperatures.

Acknowledgments

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