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Published in:
Surface and Coatings Technology

Publication date:
2003

Document Version
Peer reviewed version

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Surface and Coatings Technology 174–175 (2003) 240–245
SURFACE & COATINGS TECHNOLOGY
www.elsevier.com/locate/surfcoat

Study of ZrN layers deposited by reactive magnetron sputtering

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Abstract

Zirconium nitride films are deposited onto borosilicate wafers by reactive magnetron sputtering. The films are analysed in situ by X-ray photoelectron spectroscopy (XPS). We have studied by XPS the effects of the nitrogen partial pressure (1–100%), the subtract temperature (ambient to 450 °C), and biasing (0–80 W) on the stoichiometry of ZrN films. The N1s peak is composed of three components at 397.2, 396.4 and 395.8 eV in binding energy. These components are correlated with the three existing phases of zirconium nitride (ZrN, Zr_3N_4 and ZrN_2). With an increase of the nitrogen partial pressure, a shift of the Zr3d line to the high binding energy and the increase of the N1s component at 395.8 eV are observed. These observations are explained by the charge transfer between Zr to N which increases with $P(N_2)$ as previously described for the Ti–N_2 system [1]. The bulk stoichiometry is calculated by Rutherford backscattering and nuclear reaction measurements. The resistivity of the films is measured by the four-point probes technique. The reflectivity of the films are recorded by a spectrophotometer in the IR–Vis range. A correlation between the reflectivity and the resistivity is observed. The roughness of the films is measured by atomic force microscopy. The bias voltage has a great influence on the surface roughness and on the reflectivity of the films. The dependence of the ZrN_x films structure and morphology with the discharge parameters is established.

Keywords: XPS; RBS; Reactive magnetron sputtering; ZrN

1. Introduction

The thermal insulation techniques of windows have been enhanced due to the development of thin films sputter deposition. ZrN is known to be a good reflective material in the IR wavelength range [2]. It is due to the metallic structure of the stoichiometric ZrN. This property is interesting for applications in thermal insulation coatings. Thin films are deposited by various methods: evaporation, spray pyrolysis, chemical vapour deposition and sputtering. In the present work, we study the sputtering of a zirconium target in a mixture of Ar/N_2 direct current magnetron discharges. X-ray photoelectron spectroscopy (XPS), Rutherford backscattering (RBS) and NRA are used to characterize the composition of the films. The resistivity is given by the four points probe technique. The reflectivity of the films are recorded in the IR–Vis range. The roughness of the films is measured by atomic force microscopy (AFM). We have correlated the shapes and positions of the XPS peaks with the stoichiometries of the ZrN_x films.

2. Experimental details

The ZrN films are deposited by d.c. reactive magnetron sputtering. The target–substrate distance is 15 cm. The substrate is a borosilicate glass of 1 cm^2 cleaned with a Balzers substrate cleaner 1 and 2. The experimental system is described elsewhere [3]. The low pressure is obtained by means of a turbomolecular–diaphragm pump combination. The ultimate vacuum pressure is approximately 10^{-7} Torr. The sputtering gas is an argon/nitrogen mixture and the pressure is regulated with a throttlevalve. The gas inlet is situated in front of the substrate holder. Two gas flow controllers maintain the argon and nitrogen flows in the chamber. A continuously variable power supply MDX 500 is used as the power source. The target current is set at 200 mA. The target voltage is fluctuating ($\approx$250 V) with the nitrogen partial flow. Zirconium disk (99.2% purity) of 1.3 inch in diameter is used as target. The deposition

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doi:10.1016/S0257-8972(03)00679-0

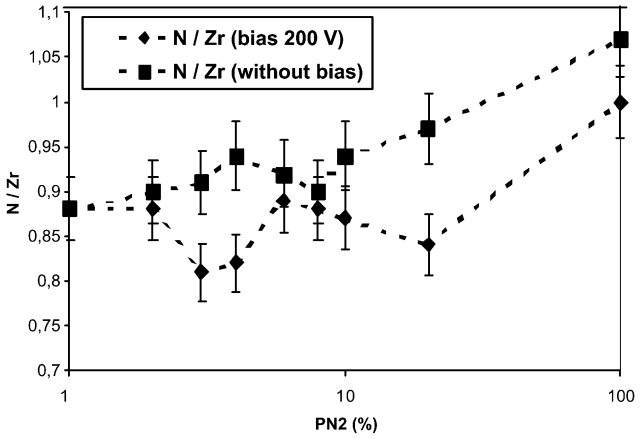

Fig. 1. Stoichiometry vs. P N_2.

rate is measured using a quartz microbalance. All the experiments have been performed under UHV, there is no air contamination of film surfaces before XPS analysis. The samples are transferred under UHV into an ESCA analysis chamber. XPS was performed on a VG-ESCALAB 220iXL spectrometer. The pressure in the analysis chamber was typically 8×10^{-11} Torr. Atomic composition were derived from peak areas by using photoionisation cross section calculated by Scofield [4], corrected for the dependence of the escape depth on the kinetic energy (KE) of the electrons (assumed to have the form $\lambda = KE^{0.6}$) and corrected for the analyser transmission function of our spectrometer. The diameter of the Al Kα X-ray beam is 250 μm. The scan number for each XPS area corresponding to all the film elements varies from 10 to 15. RBS and NRA measurements were performed on the Tandétron™ 2 MV (ALTAÏS) at the LARN. For RBS measurements, the energy of the incident particles ($^4He^{2+}$) is 2.0 MeV. This technique is suitable for the quantification of heavy atoms like Zr. Otherwise, for the NRA measurement, the energy of the incident particles is raised to 4.8 MeV. This technique is preferred for the quantification of light atoms like N or O. Simulated curves are compared to the experimental ones to quantify the atomic composition of the films. AFM measurements were performed on a Nanoscope IIIa microscope in the tapping mode. The root mean square (RMS) deviation are calculated from several pictures taken on each sample [10]. This measure is assimilated to the roughness of the film surface. The analysed surface is varied from 25 to 1 μm^2.

3. Results and discussion

3.1. Stoichiometry

We have studied ZrN coatings deposited at room temperature under different nitrogen partial pressure (1–100%). The total pressure is fixed at 8 mTorr. The ZrN films are synthesized with and without bias voltage of −200 V and analysed by XPS. Whatever the experimental conditions may be, oxygen traces are detected on the films surfaces (≈4% at.) and on the bulk films (≈2% at.). This low oxygen contamination of the films can be explained by the extreme reactivity of Zr in relation to H_2O still present as traces in the residual gas phase of the preparation and transfer chambers (10^{-7} Torr). The results are shown on Fig. 1. Without bias, the ratio N/Zr is under 1 until 15% of nitrogen and goes to 1.07 at 100%. The addition of a bias of 200 V induces a decrease of the ratio. It stays under 1 for all the nitrogen partial pressure. It is due to the preferential sputtering of the nitrogen in the growing film. We have realized an XPS depth profile of ZrN films synthesized with and without bias voltage and after air contamination (Fig. 2a and b). We can observe that the films synthesized without any bias are oxidised through all the bulk. The final stoichiometry reaches $ZrN_{0.5}O_{0.5}$. On the other hand, the films synthesized with bias contents only 6% of oxygen in the bulk. It is due to the porosity decrease of the films when bias is added during deposition. The oxygen diffusion in the bulk film is decreased.

The N1s XPS spectrum shows three components at 397.1 eV (1) in binding energy, 396.4 eV (2) and 395.8

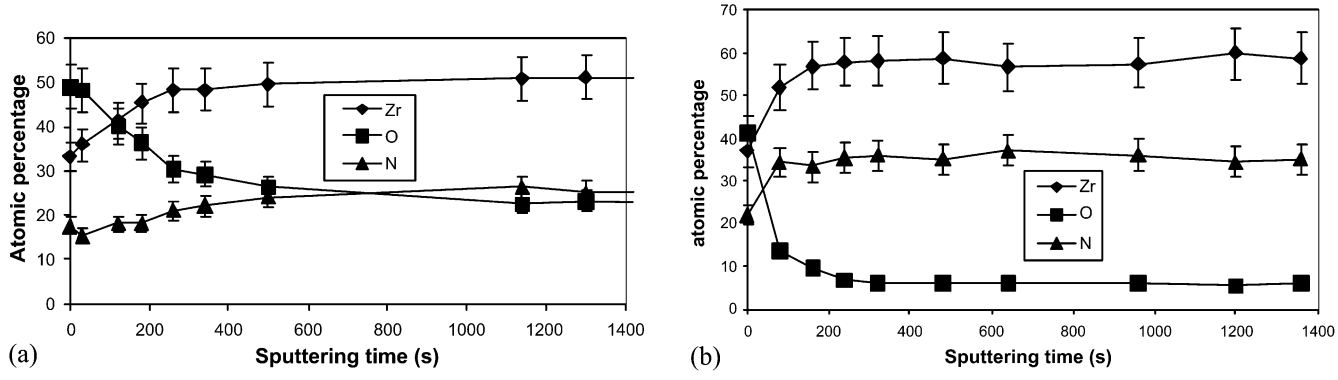

Fig. 2. (a) ZrN without bias, profile, after air contamination; (b) ZrN with bias, profile, after air contamination.

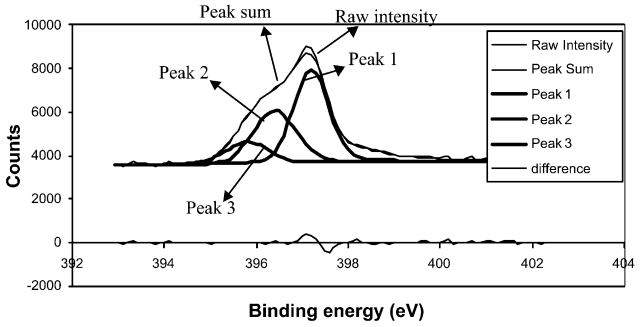

Fig. 3. N1s peak fit.

eV (3) (Fig. 3: at 4% N2, −200 V bias). In some papers [1,2], the component (1) is attributed to the ZrN stoichiometry while the component (2) is attributed to zirconium oxynitride [5]. But in an other paper [6], the component (2) corresponds to the Zr_3N_4 stoichiometry. The component (3) could be attributed to an over-stoichiometry like ZrN_2. We have followed the evolution of these three components areas with the increase of the nitrogen partial pressure in films synthesized with bias and without bias (Fig. 4a and b, respectively). These evolutions are quite different depending on whether the deposition is done with or without bias voltage. In both cases, the area of the component (1) is higher than the others until a nitrogen partial pressure of 40%. On the other hand, the area of the component (2) increases only with bias voltage. At 100% of nitrogen, the ratio between area (3) and (1) is almost 3 with bias while it is under 2 without bias. The components (2) and (3) correspond to phases which appear when the sputtered atoms arriving on the film surface receive an energy supply thanks to the bombardment of the growing film by positive ions (Ar^+, N_2^+). These two components could correspond to the over-stoichiometric metastable phases of the ZrN_x (Zr_3N_4 and ZrN_2). A chemical shift to the high binding energy of the Zr3d XPS peak with the nitrogen partial pressure increases has been observed (Fig. 5). The Zr3d peak goes from 179.6 eV at 1% of nitrogen partial pressure to 180.6 eV at 100%. These kind of shift has already been observed for TiN films sputtered by N_2^+ ions [1]. The absence of the oxyde components in the Zr3d peaks (located at 182.2 eV and 184.6 eV in binding energy) turns down the oxynitride hypothesis. From the XPS results, zirconium nitride films synthesized with bias voltage are made of over stoichiometric metastable phases (Zr_3N_4, ZrN_2). But the atomic composition derived from peak areas (calculated by the method describes at point 2) shows that nitrogen/zirconium ratio is always lower than 1. In order to understand this result, the stoichiometry of the films has been measured using another techniques, RBS and NRA [7]. The combination of these techniques gives the stoichiometry of the films which varies from ZrN to ZrN_2 when the N_2 percentage increases from 1 to 100% (Table 1).

Table 1
Bulk stoichiometries of the ZrN films obtained by RBS and NRA

Ech.	PN2 (%)	Bias (V)	Zr (%)	N (%)	O (%)	Stiochio princ
1	1	250	46	46	7	ZrN
2	3	250	50	47	2	ZrN
3	50	250	43	51	4	$ZrN_{1,2}$
4	100	250	30	57	13	ZrN_2
5	1	0	36	34	30	ZrNO
6	3	0	36	32	32	ZrNO
7	50	0	36	60	4	ZrN_2
8	100	0	35	60	5	ZrN_2

The under-estimated stoichiometry results obtained by XPS can be explained by the approximation of the electron mean free path to $KE^{0.6}$ from the universal curve (at 1 KE, strong variations of λ depending on the nature of the analysed components), the sensitivity factor used (Scofield rather than Wagner). This point has still to be improved.

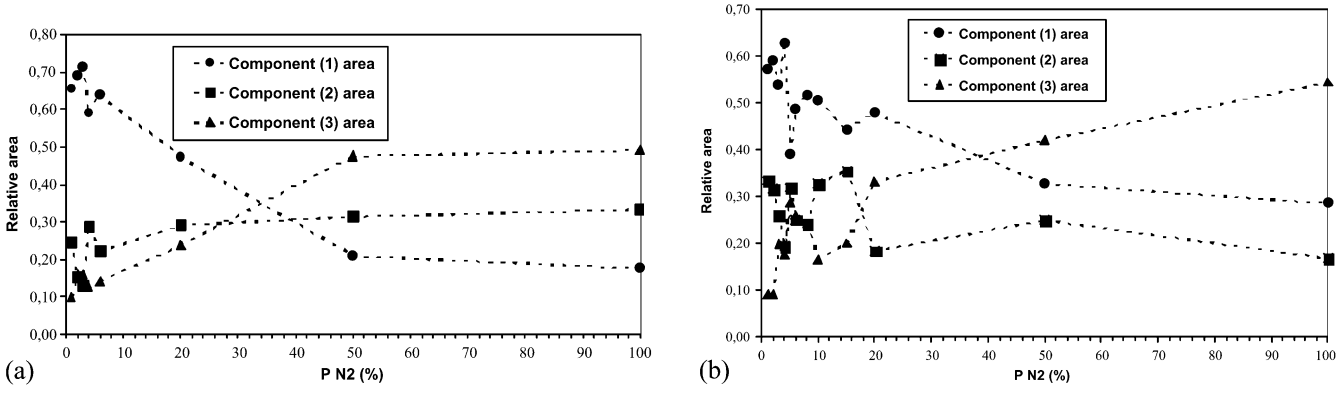

Fig. 4. (a) Quantification of the N1s XPS peak, film synthesized with bias; (b) quantification of the N1s XPS peak, film synthesized without bias.

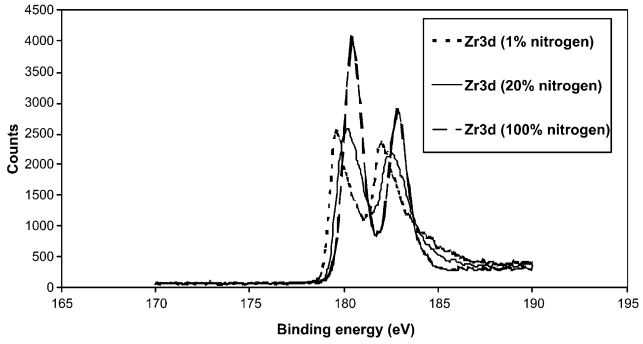

Fig. 5. Chemical shift of the Zr3d XPS peak with nitrogen.

A correlation between the bulk stoichiometries of the films and the Zr3d and N1s XPS peaks shapes and positions has been observed. We can also conclude that the component (1) of the N1s peak is correlated to a ZrN stoichiometry. The component (3) is correlated to a ZrN_2 stoichiometry. Otherwise, the component (2) is not yet well defined.

3.2. Resistivity

We have studied the influence of the bias voltage and the substrate temperature on the films resistivity. The nitrogen partial pressure is fixed at 3.5% to stay in the ZrN stoichiometry. The total pressure is 8 mTorr and the target current is fixed at 200 mA. The DESIGN-EXPERT® software has been used to reduce the experiments number [8]. It is a statistical tool that allows us to calculate the dependence of the resistivity on different parameters (temperature, bias voltage). The ranges of studied temperatures and bias are (80–450 °C) and (−50 to −450 V). The isoresistivity curves are shown on Fig. 6. This statistical tool pointed the strong influence of the bias on the resistivity. A theoretical minimum of 70 μΩ cm has been located at −350 V and 380 °C.

3.3. Reflectivity

The relative reflectivity (the reference sample is a silver film of 50 nm deposited onto borosilicate) of ZrN films has been measured on the same samples used for the resistivity measurements. We have investigated the influence of the bias voltage and substrate temperature on the film reflectivity. The wavelength range is (300–2000 nm). Fig. 7 shows an example of the results. The sample 13 has been synthesized at −350 V and 350 °C, the sample 1 at −200 V and 80 °C and the sample 5 at −90 V and 260 °C. Afterwards, we have measured the reflectivity of the films at 1500 nm. The results have been analysed by the DESIGN-EXPERT® software. Theoretical isoreflectivity curves has been calculated by the software. A maximum of reflectivity at 1500 nm has

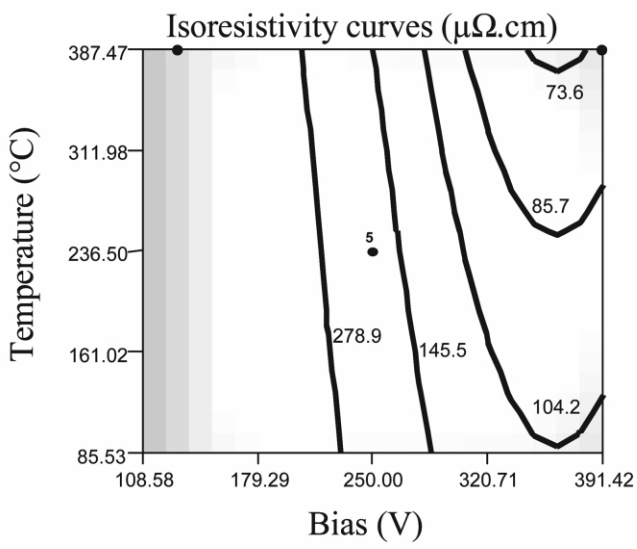

Fig. 6. Isoresistivity curves obtained by DESIGN-EXPERT®.

been located at approximately −370 V and 390 °C. It corresponds approximately to the minimum of resistivity. It confirms the relation of Hagen–Rubens for the reflectivity and resistivity of metals [9].

3.4. Roughness

Finally, the samples have been analysed by AFM. All the pictures are quite similar (Fig. 8). The RMS deviation are calculated from several pictures taken on each sample [10]. Here again, the results are treated by the DESIGN-EXPERT® software. With the theoretical isoroughness curves (Fig. 9), we can observe that the bias voltage has a great influence on the roughness. An optimal bias appears at approximately −360 V. On the opposite, the roughness seems to be quite indifferent to the substrate temperature. The fact that the roughness is increasing after a critical value of bias voltage is explained as follows. The negative bias voltage of the

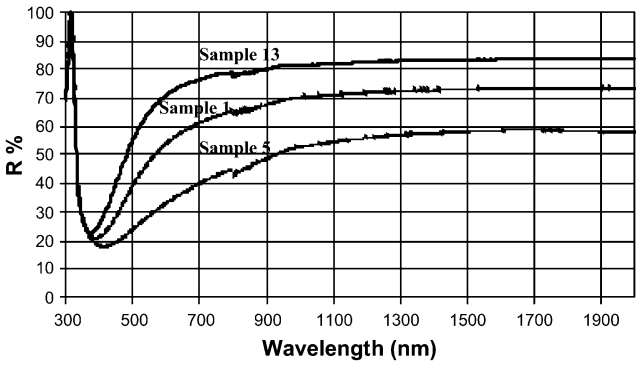

Fig. 7. Reflectivity of ZrN films.

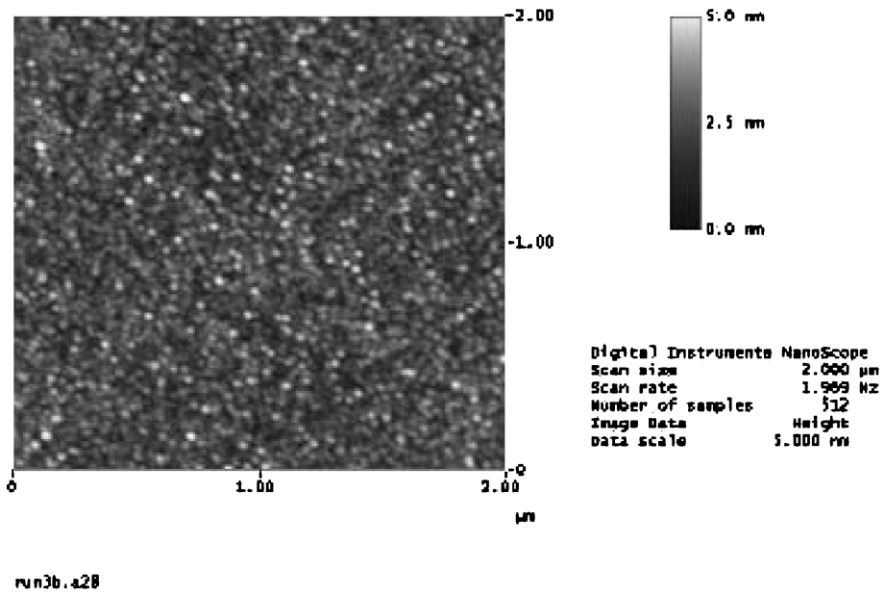

Fig. 8. AFM picture of ZrN film.

substrate induces a bombardment of the growing film by the positive ions of the plasma. The collisions smooth the film surface and the roughness decreases. However, when the ions energy is too high, the film surface starts to be sputtered and the roughness increases again.

4. Conclusions

We have correlated the shapes and the positions of the XPS peaks with the stoichiometries of the ZrN_x films thanks to the combination of XPS, RBS and NRA techniques. The positions of the N1s and Zr3d peaks corresponding to the ZrN and ZrN_2 stoichiometries have been defined.

The measurements of the roughness, resistivity and reflectivity of the ZrN films have pointed a substrate temperature and bias voltage limits. Over these limits, these three parameters deteriorate. We have observed that a substrate temperature of approximately 350 °C and a bias voltage of −350 V allows us to obtain a ZrN film with optimum features.

For industrial applications of these results, the optimum conditions in bias voltage and substrate temperature must be adjusted to the real coating equipment and all coating conditions.

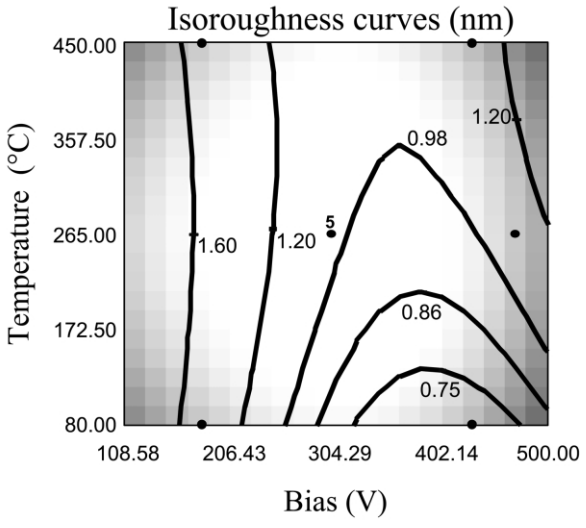

Fig. 9. Isoroughness curves obtained by DESIGN-EXPERT®.

Acknowledgments

M. Del Re thanks the Fonds pour la Recherche dans l'Industrie et l'Agriculture (FRIA, Brussels) for financial support.

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