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SCIENCE DIRECT

Thin Solid Films 494 (2006) 146 – 150

thin solid films

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Residual stresses in titanium nitride thin films deposited by direct current and pulsed direct current unbalanced magnetron sputtering

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Available online 21 September 2005

Abstract

This work presents a study on the effect of deposition parameters on the residual stresses developed in titanium nitride (TiN) thin films deposited onto cemented carbide (WC-Co) substrates. Depositions were conducted by reactive unbalanced magnetron sputtering of a single titanium target. Six different conditions were selected, varying parameters such as bias (0, −50 or −100 V), power applied to the target (direct current or pulsed direct current) and, in the cases where substrate bias was zero, substrate condition (ground or floating). Pulsed power was applied at a frequency of 50 kHz and with a reverse pulse time of 1 μs. Residual stresses were evaluated through X-ray diffraction, using the $\sin^2\psi$ method. Results confirmed the effect of substrate bias on the residual stresses of thin films. Additionally, it was possible to observe that by pulsing the power to the target, residual stress varies as a consequence of the increased ion energy.

Keywords: Stress; Plasma processing and deposition; Titanium nitride; Sputtering

1. Introduction

Pulsed magnetron sputtering (PMS) is a thin film deposition technique in which the magnetron discharge is pulsed from normal operating voltage and ground (unipolar pulsed sputtering) or from the negative operating voltage to positive during the pulse-off periods (bipolar pulsed sputtering) [1]. This technique has been mainly used for the deposition of highly insulating films, for which the pulsed discharge is able to reduce the amount of target poisoning and, consequently, the arcing events that result from the non-pulsed reactive sputtering. For highly insulating materials, arcing reduction with pulsed target power is able to significantly reduce the number of coating defects, thus allowing films produced by this physical vapor deposition technique to be suitable for applications where good mechanical [2] or optical [3,4] properties are required.

Besides the reduction of arcing in insulating films, pulsed target power is also known to affect the characteristics of the plasma developed inside the deposition chamber. Some authors [3,5] have demonstrated that this process resulted in an increased level of energetic particle bombardment. Since the characteristics of the ion bombardment may significantly affect the structure and, consequently, the properties of the film, PMS may also be considered a good candidate for the deposition of non-insulating materials, depending on the properties required for a given application.

The level of film residual stress presents one example of a film characteristic that may be altered due to differences in the plasma developed inside the deposition chamber. Among others [6–8], Mounier and Pauleau [9] discussed the evolution of compressive stresses generated on amorphous carbon films deposited onto biased substrates by conventional and unbalanced magnetron sputtering modes and Carrasco et al. [10] analyzed the effect of bias on TiN films deposited onto copper substrates. In both cases, results

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doi:10.1016/j.tsf.2005.08.214

indicated that an increase in substrate bias increased the level of compressive residual stresses, due to differences in the flux of ions to the substrate, including ion energy. In some cases, film residual stresses are capable of altering the behavior of thin films at a given application. For example, residual compressive stresses may improve the tribological behavior of wear resistant thin films [11], as long as the adhesion is not impaired [12].

The previous paragraphs indicate that the effect of substrate bias on film residual stresses has already been reported in the literature [6–10], and that a difference in the flux of atoms to the substrate, which alters film stresses, is expected depending on the type of target power selected during the depositions. However, it is possible to state that, currently, the effect of the type of target power on the level of film residual stresses has not been significantly quantified. In this work, a series of unbalanced magnetron sputtering depositions of TiN films was conducted to analyze the effect of substrate bias and type of target power (DC: direct current, or pulsed DC) on the level of residual stresses developed in a non-insulating film. In terms of bias, not only the value of the negative voltage was studied, but also different conditions (ground and floating) were analyzed in the cases where substrate bias was zero and target power was pulsed.

2. Experimental details

2.1. TiN deposition

The substrates used in this work were commercial ISO P20 cemented carbide (WC-Co) triangular inserts with 16 mm edges, which were initially ultrasonically cleaned in acetone and ethanol. Depositions were conducted by reactive unbalanced magnetron sputtering of a 127 mm (5 in.) titanium target in a N_2+Ar atmosphere, and substrates were mounted such that the target/substrate distance was 127 mm. Prior to deposition, a base pressure lower than 5×10^{-4} Pa (4×10^{-6} Torr) was initially attained and substrates were sputter etched in argon at 8.7 Pa (65 mTorr) and 400 V for 20 min. Later, a titanium interlayer was deposited in all cases, as a result of a 2.4×10^{-1} Pa (1.8 mTorr) argon pressure and a 1000 W power applied to the titanium target for 1 minute. Six different deposition runs were initiated according to this procedure, followed by the deposition of TiN films, which was attained with a mixture of 30% N_2 and 70% Ar for 1 h and applying a 1000 W power to the titanium target. However, a different combination of bias and target power was selected in each case, as indicated in Table 1. For half of the specimens (DC0, DC50 and DC100), a DC power was applied to the target and different bias voltages were applied to the substrate. For the other half of the specimens, the 1000 W target power was pulsed at a frequency of 50 kHz in a bipolar mode with reversed pulse time of 1 μs and nominal positive voltage of 20% of the negative voltage. Table 1 indicates that a negative bias of 50 V was applied to the substrate in one of these cases (P50) and no bias was applied to the others. However, bias condition was also different in the latter, since the substrate was ground in one of the depositions (PG) and substrate potential was allowed to float in the other (PF).

Table 1
Type of power applied to the target and bias condition for the deposition of TiN coatings

Specimen	Target	Bias (V)	Coating thickness (μm)
DC0	DC	0, grounded	~1.2
DC50	DC	−50	~1.21
DC100	DC	−100	~0.33
PG	Pulsed	0, grounded	~0.95
PF	Pulsed	0, floating substrate	~1.23
P50	Pulsed	−50	~0.87

In the six deposition runs, a silicon substrate was also placed inside the chamber. Specimens with silicon substrates were fractured latter and analyzed in a scanning electron microscope (SEM), to provide the thickness of the TiN films obtained in each case (Table 1).

2.2. X-ray diffraction

X-ray analysis was conducted in a Philips diffractometer PW3710 using CuK_α radiation and a thin film attachment with a fixed divergence slit (1/12°). Considering that the thickness of the TiN films were in the range from 0.33 and 1.23 μm, the X-ray analysis was conducted using the grazing method with a low incident angle [13]. A small and constant incident angle α was used to fix the penetration of the X-ray beam in the coating and to reduce the effects of the substrate. The selected fixed incidence angle was $\alpha=2°$ in all cases, except for specimens DC100 and P50, for which $\alpha=1°$, for a better TiN peak resolution. The penetration depth was calculated to be 0.15 μm for $\alpha=1°$ and 0.31 μm for $\alpha=2°$. Voltage and current were set at 40 kV and 30 mA in the diffractometer, respectively, and a scan of 2θ angles from 30° to 90°, with a step of 0.03°, was considered in the analysis of specimens DC0, DC50, DC100, PF and P50. For specimen PG, the 2θ scan was restricted to angles close to the $\langle 111\rangle$, $\langle 200\rangle$, $\langle 220\rangle$, $\langle 311\rangle$ and $\langle 222\rangle$ reflections, with a scan step of 0.04°. In all cases, the counting time was 25 s per 2θ step, in order to give a clear peak profile and a better peak–background relation.

2.3. Method for determination residual stress through X-ray diffraction

According to the grazing method, for a given position ($2\theta_B$) of the diffraction peak, corresponding to the Bragg angle for a diffracting plane (*hkl*), the measured angle ψ can be calculated based on the normal to the surface of the sample and the normal to the diffracting plane (*hkl*). The relation $\psi=\theta_B-\alpha$ can thus be defined between the angle parameters. Therefore, for each angle ψ, the peak positions $2\theta_B$ were measured for each reflection (*hkl*) and peak fitting was conducted using software based on the Pseudo-Voigt functions [14]. The corresponding values for the lattice parameters a were determined for each reflection (*hkl*) from Bragg's law.

In order to calculate the residual stresses in the films, it was considered that the stress state was biaxial in the TiN coating.

Table 2
Elastic constants for TiN [15]

Crystalline orientation	$2S_1$ (T Pa^{-1})	½S_2 (T Pa^{-1})
⟨111⟩ ⟨222⟩	−1.06	2.06
⟨200⟩ ⟨400⟩	−0.68	1.52
⟨220⟩	−0.96	1.92
⟨311⟩	−0.86	1.77

In this case, Eq. (1) is valid for the measured lattice parameter a and the residual stress σ [13], where ψ corresponds to the diffraction angle for planes (hkl) and a_0 is a stress-free lattice parameter for the coating. The X-ray elastic constants $2S_1$ and ½S_2 for the TiN film are reported in Table 2 for different crystalline orientations ⟨hkl⟩ [15].

$$a = a_0(\sigma f(\psi) + 1) \qquad f(\psi) = \frac{1}{2}S_2^{hkl}\sin^2\psi + 2S_1^{hkl}. \tag{1}$$

Thus, once the values of the lattice parameters a, measured for each plane (hkl), were plotted as a function of $f(\psi)$, the intercept with the ordinate axis provides a_0 and with the slope to the curve it is possible to obtain the stress σ.

Additionally, for each (hkl) peak, the full width at half maximum (FWHM) was measured and the grain size (GS) was determined from the Scherrer relation (Eq. (2)), where λ is the X-ray wavelength and θ is the Bragg's angle.

$$GS = \frac{0.9\lambda}{\cos\theta FWHM}. \tag{2}$$

3. Results and discussion

Table 3 presents the values of lattice parameter, residual stress, FWHM and grain size calculated for each specimen analyzed in this work. The lattice parameters calculated for all samples are close to the theoretical value of 0.42417 nm, [16], which indicates that the ratio between nitrogen and titanium atoms does not differ significantly from unity [17]. High values of compressive residual stresses were calculated for all specimens.

As expected, results in Table 3 also indicate an increase in the level of film residual stresses as the bias applied to the substrate was increased (Fig. 1). This fact is probably associated with the increase in impinging ion energy, which results in more point defects in the structure of the growing film [6]. In addition to the relation with more compressive residual stresses, the increase in point defects may also provide additional preferential sites for nucleation, which may be associated with the decrease in grain size shown in Fig. 2, also characterized by the broadening of the peaks (values of FWHM in Table 3).

Figs. 1 and 2 also allow a comparison between the residual stresses and grain sizes obtained with DC and pulsed unbalanced magnetron sputtering. These results clearly indicate that stresses became more compressive, and grain size decreased, when the pulsed option was selected. Explanations for these results probably rely on the fact that pulsed power may not only increase the impinging atom energy, but also may increase the ion current densities [3,5]. Therefore, the tendency for the increase in point defects in film structure is increased, which increases the compressive residual stresses and reduces the average grain size.

Table 3
Lattice parameter (a_0), residual stress (σ), full width at half maximum (FWHM) and average grain size of TiN deposited by DC and pulsed DC unbalanced magnetron sputtering at different substrate bias conditions

Specimen	a_0 (nm)	σ (GPa)	FWHM$_{hkl}$ (°)	GS$_{hkl}$ (nm)
DC0	0.42456±0.00010	−3.69±0.23	(111) 0.576	14.5
			(200) 0.753	11.3
			(220) 0.984	9.4
			(311) 1.219	8.1
DC50	0.42496±0.00017	−6.61±0.70	(111) 0.645	12.9
			(200) 0.901	9.4
			(220) 1.145	8.1
			(311) 1.267	7.8
DC100	0.42478±0.00045	−10.29±1.88	(111) 1.178	7.1
			(200) 1.073	7.9
			(220) 1.572	5.9
			(311) 2.132	4.6
PG	0.42423±0.00026	−5.65±0.94	(111) 0.590	14.2
			(200) 0.797	10.7
			(220) 1.098	8.4
			(311) 1.662	6.0
PF	0.42461±0.00009	−5.15±0.37	(111) 0.653	12.8
			(200) 0.975	8.7
			(220) 1.018	9.1
			(311) 1.265	7.8
P50	0.42451±0.00012	−11.32±2.12	(111) 1.279	6.5
			(200) 1.093	7.8
			(220) 1.576	5.8
			(311) 2.134	4.6

An additional observation in the data presented in Figs. 1 and 2 refers to a comparison between specimens PF (floating substrate) and PG (ground substrate), which were prepared with pulsed power and with no external bias applied to the substrate. The residual stress and grain size values calculated for these two specimens did not vary as significantly as the difference observed between DC and pulsed plasmas. Once again, using the residual stresses as an indication of both impinging ion energy and ion current density, these results are in agreement

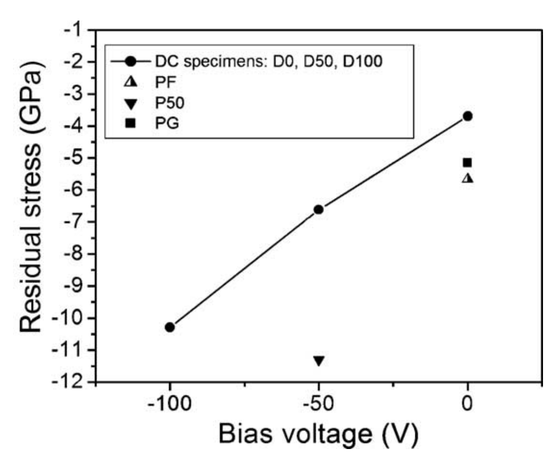

Fig. 1. Residual stress as a function of bias voltage of TiN films deposited by DC and pulsed DC unbalanced magnetron sputtering at different substrate bias conditions.

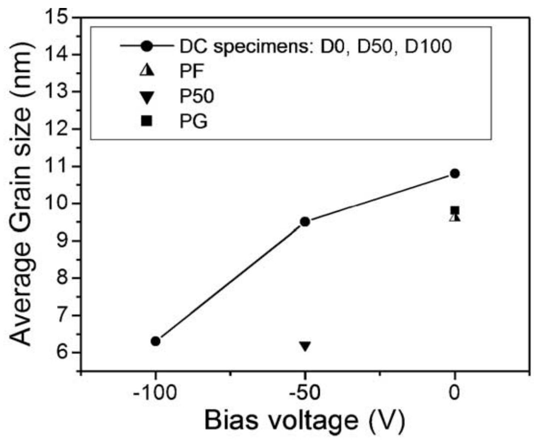

Fig. 2. Average grain size as a function of bias voltage of TiN films deposited by DC and pulsed DC unbalanced magnetron sputtering at different substrate bias conditions.

with the theory presented by Bartzsch et al. [5], who described that: (i) both floating and grounded substrates will acquire a negative potential with respect to the plasma, a self-bias voltage, which accelerates the plasma ions towards the substrate and (ii) the ion current density mainly depends on the characteristics of the plasma itself and cannot be influenced by bias techniques.

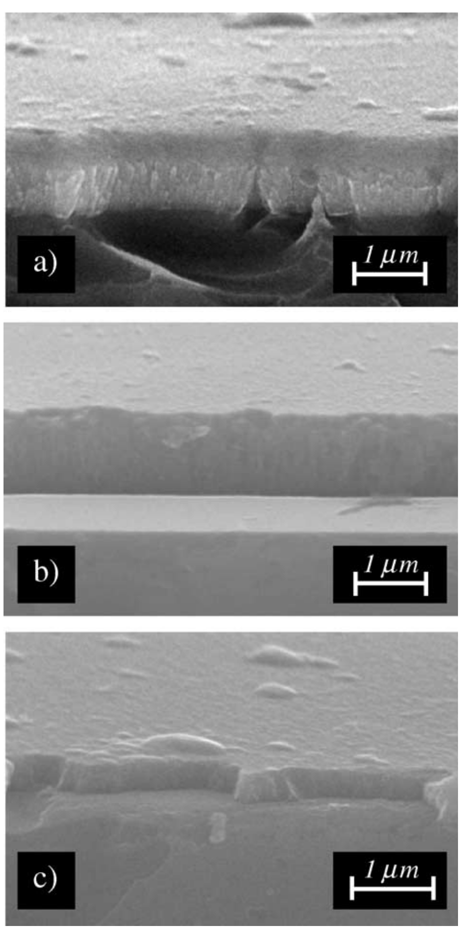

Fig. 3. Secondary electron images of the films produced by DC unbalanced magnetron sputtering at different substrate bias conditions: (a) bias = 0, (b) bias = – 50 and (c) bias = – 100 V.

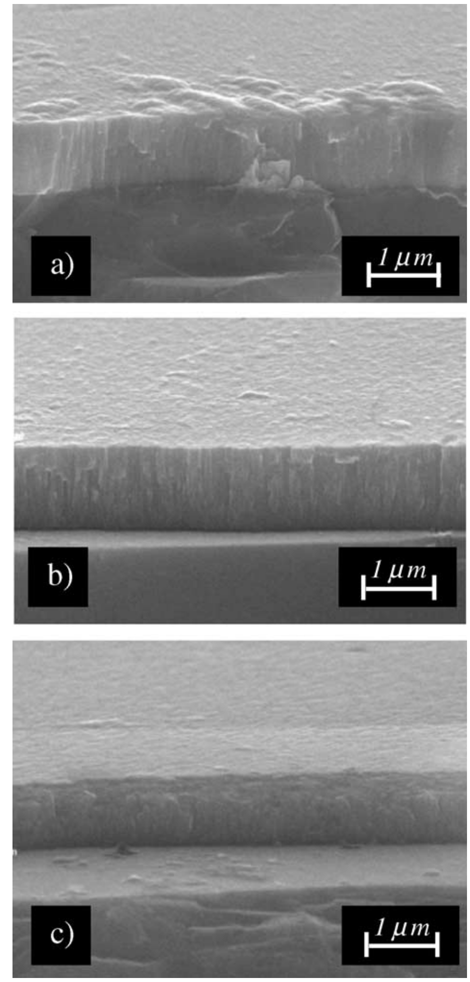

Fig. 4. Secondary electron images of the films produced by pulsed DC unbalanced magnetron sputtering at different substrate bias conditions: (a) bias = 0, (b) bias = – 50 and (c) bias = – 100 V.

Fig. 3 presents SEM micrographs of the cross-sections of films deposited by DC unbalanced magnetron sputtering on silicon substrates and Fig. 4 presents similar results for the specimens deposited by pulsed magnetron sputtering. All specimens presented columnar structures but different grain sizes (column width) were observed.

Since all depositions were conducted for 1 h, Figs. 3 and 4, and Table 1, allow a comparison in terms of the deposition rates attained in each run. Results indicated a tendency for the decrease in deposition rate as the negative bias applied to the substrate was increased. This observation was possible both in specimens DC100 and P50, but the decrease in deposition rate was more pronounced in specimen DC100. One of the possible reasons for this decrease in deposition rate is related to the re-sputtering of film atoms by the ions that impinge at the substrate during film growth.

4. Conclusions

Results presented in this work provide further evidence that the use of pulsed power results in changes in the plasma generated inside the deposition chamber and, consequently, in the microstructure and level of residual stress of the films.

As previously reported in the literature, higher compressive residual stresses, and lower average grain sizes were observed with an increase in the negative bias applied to the substrate.

The use of pulsed power resulted in higher residual stresses and in a decrease in average grain size, which is in agreement with the expected increase in impinging ion energy and ion current density in pulsed depositions. It is possible to expect the selection of pulsed power to be beneficial for some of the mechanical characteristics of the film, such as hardness and wear resistance.

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