Residual stresses in titanium nitride thin films obtained with step variation of substrate bias voltage during deposition

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Abstract

In this work, a series of depositions of titanium nitride (TiN) films on M2 and D2 steel substrates were conducted in a Triode Magnetron Sputtering chamber. The substrate bias was either decreased or increased in a sequence of steps. Residual stress measurements were later conducted through the grazing x-ray diffraction method. Different incident angles were used in order to change the penetration depth and to obtain values of residual stress at different film depths. A model described by Dolle was adapted as an attempt to calculate the values of residual stress at each incident angle as a function of the value from each individual layer. Stress results indicated that the decrease in bias voltage during the deposition has produced compressive residual stress gradients through the film thickness. On the other hand, much less pronounced gradients were found in one of the films deposited with increasing bias voltage.

Introduction

The deposition of thin films on substrates is usually inherently associated with the development of residual stresses[1,2]. In general, Physical Vapor Deposition (PVD) processes result in compressive stresses on the order of a few GPa[3,4]. Data in the literature[5,6] indicate that compressive stresses can improve the wear resistance of coated systems, but can also increase the possibility of film detachment during system use in tribological applications[5,6]. In theory, one could think that the imposition of a stress gradient in the film could be beneficial. Lower levels of compressive residual stresses at the film/substrate interface would decrease the tendency for film detachment and a gradual increase in compressive values towards the surface would improve wear resistance. The idea of gradient film stresses was already presented in the literature[7,8]. However, one of the challenges associated with such idea is to verify if the deposition procedure was successful in imposing the stress gradient and also to determine the residual stress values in such gradients using a non-destructive technique.

Several authors have studied film stress and strain gradients through grazing incidence x-ray diffraction (GIXD) techniques, where the penetration depth was varied by changing the incident angle of the beam. These x-ray methods are usually employed to determine stresses in thin films produced with constant deposition parameters. Little work has been conducted in order to verify if the variation of the parameters selected during deposition results in stress gradients. Exceptions may be found[7], but stress gradients were measured in combination with stepwise removal of the film layers by mechanical polishing.

The objectives of this work are to verify the possibility of imposing stress gradients in thin films by changing the process parameters during deposition and to adapt a model available in the literature[9] in order to evaluate these gradients using a non-destructive technique.

Experimental details

TiN films were deposited on steel substrates. A hybrid duplex treatment was carried out in all cases, in a home built hybrid reactor, where pulsed plasma nitriding and triode unbalanced reactive magnetron sputtering are conducted in the same cycle[10]. Three types of specimens were produced in this work (Table 1): Specimens with films deposited (i) without variation of substrate bias voltage during deposition (S1, S2, S3, S4 and S5), (ii) with increasing substrate bias voltage (G1D2 and G3M2), and (iii) with decreasing substrate bias voltage (G2D2 and G4M2).

Table 1: Deposition conditions for TiN thin films

Sample	Substrate material	Layer	Time (min)	Bias (V)	Film thickness (µm)
G1D2	AISI D2	1	45	-20	≈ 2.4
		2	45	-40	
		3	45	-100	
		4	45	-150	
		5	45	-200	
G2D2	AISI D2	1	45	-200	≈ 2.0
		2	45	-150	
		3	45	-100	
		4	45	-40	
		5	45	-20	
G3M2	AISI M2	1	45	-20	≈ 1.4
		2	45	-40	
		3	45	-80	
		4	45	-100	
G4M2	AISI M2	1	45	-100	≈ 1.4
		2	45	-80	
		3	45	-40	
		4	45	-20	
S1	AISI D2	1	120	-20	≈ 1.5
S2		1	120	-40	
S3		1	120	-100	
S4		1	120	-150	
S5		1	120	-200	

In this work, the GIXD method was used and S_1^{hkl} and $½S_2^{hkl}$, the X-ray elastic constants, were calculated for the different lattice planes (*hkl*) using procedures defined in the literature[11-13]. In the analysis, different angles of incidence (α) were selected in order to measure the residual stresses at different beam penetration depths. Measurements were conducted part at LNLS - Brazilian Synchrotron Light Laboratory and part in a Rigaku RINT Ultima+ diffractometer.

In X-ray diffraction, the intensity of the incident beam is attenuated exponentially by the specimen due to absorption. Therefore, if the specimen stress changes with the distance from the surface, the measured value is affected not only by the variation of the stress but also by any change in the penetration depth. Dolle[9] described a method to calculate the mean value of residual stress over a depth *x* based on the depth profile of stress $\sigma(x)$, assuming it is a continuous function. However, in the case of multilayered coating systems, or films deposited with step variation of bias voltage, the method must be corrected to consider that $\sigma(x)$ is not continuous[14]. Adjusting the model by Dolle and assuming that the procedure has succeeded in producing a step distribution of residual stresses, a system composed of N_L layers will have a mean stress over a depth *x*, at a given angle of incidence (α_i), given by:

$$\sigma(\alpha_i) = \sum_{n=1}^{N_L} I_n(\alpha_i)\sigma_n \tag{1}$$

where σ_n is the mean residual stress of layer *n*, *t* is the thickness of the film, and τ is the mean penetration depth. Furthermore, $i=1,2,\ldots,N_\alpha$, is the number of the angle of incidence that is considered and

$$I_n(\alpha) = \frac{\int_{t_{n-1}}^{t_n} e^{-x/\tau}\,dx}{\int_{o}^{t} e^{-x/\tau}\,dx} \tag{2}$$

Since the values of σ_n are unknown, the values of stress measured in the films deposited at constant bias voltage (S1 to S5) were used to calculate the mean stress at each angle of incidence.

In this work, Eq. 1 was also used in an attempt to calculate the residual stress value in each layer based on the average residual stresses obtained in a given specimen at each of the angles of incidence. Thus, based on an optimization algorithm, Eq. 1 was used to find the values of σ_n that would best provide the N_α values of $\sigma(\alpha_i)$ obtained experimentally for a given specimen.

Results and discussion

The residual stress values calculated for specimens S1 to S5, deposited with constant bias voltage, initially increased as the bias voltage increased. This behavior has been previously reported in several works regarding thin films deposited by sputtering. Some authors have found that the stresses reach a maximum value as the negative bias substrate increases[2,15], which was observed in this work.

Fig. 1 shows a comparison between the experimental results of specimens deposited with variation of bias voltage, and the values of stress over a depth at each angle of incidence, calculated using the model in Eq. (1). In specimens G2D2 and G4M2, which were deposited with decreasing bias voltage, Fig. 1 indicates smaller compressive residual stress levels near the surface and higher residual stresses closer to the film/substrate interface. This behavior was expected since lower stresses should be associated with lower bias. In terms of specimens G1D2 and G3M2, in which the bias voltage was increased during deposition, high compressive stresses were expected at the surface and smaller stresses were expected at the interface, as previously obtained by Fischer and Oettel[7]. However, in specimen G1D2 the difference found in residual stress level between the surface and the interface was not significant. In specimen G3M2 a difference of 1 GPa was observed between the interface and the surface. In general, Fig. 1 shows that the trend in residual stress values predicted by the model is in agreement with the experimental results, although some discrepancy can be observed in terms of the absolute values.

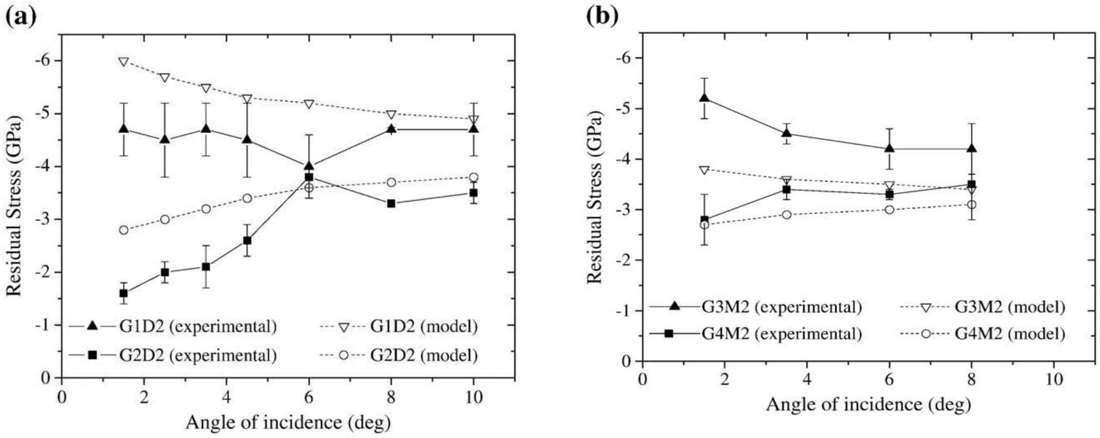

Fig. 1: Comparison between the experimental values of residual stress of specimens deposited with variation of bias voltage, and the results of stress over a depth calculated using the model of (a) specimens deposited on AISI D2 substrates, and (b) specimens deposited on AISI M2 substrates.

The results of the optimization method are shown in Fig. 2. In this figure, the open squares represent the values of residual stress calculated for films deposited at constant bias voltage. In terms of the values that were obtained, the results of the optimization procedure presented in Fig. 2b) suggest that, although differences exist in terms of the maximum residual stress value and the voltage at which the residual stresses reach the maximum, the trend was similar to that of the specimens deposited with constant bias voltage. Fig. 2a presents the optimization procedure for specimens produced with increasing bias In this case, although the optimization values for specimen G3M2 suggest that the differences in experimental and predicted results were due to the layer stress values used in Eq. (1), the optimization results suggest that no stress gradient was obtained for specimen G1D2. At this point, no reason was found to explain why such differences may occur for the two films produced with increasing bias, especially when one considers that the differences were basically regarding the substrate and film thickness.

Conclusions

A model described by Dolle was adapted to calculate the residual stresses as a function of beam penetration depth for the cases where deposition was conducted to impose a step variation in residual stresses along the film thickness. The values of stress measured in the films deposited at constant bias voltage were used in the calculations. The results were compared with the experimental ones, providing good qualitative agreement in all cases.

An optimization procedure was later conducted to analyze the individual layer values that would provide the best agreement with the experimental values calculated as a function of penetration depth. The results suggest that, in most cases, a step variation in residual stresses may have been obtained, and that the differences between experimental and predicted results are due to the stress value selected for each layer. The optimization procedure suggested that no step variation in residual stresses was obtained for one of the specimens produced with increasing bias.

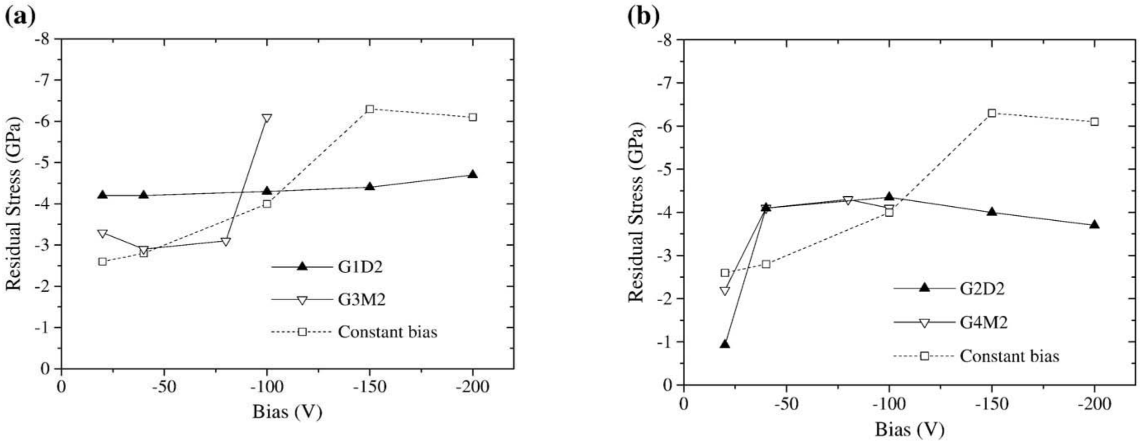

Fig. 2: Values of mean stress of each layer obtained using an optimization procedure for specimens deposited with a) increasing substrate bias voltage and b) decreasing substrate bias voltage.

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