Vacuum 158 (2018) 52–59

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Effect of energy on macrostress in Ti(Al,V)N films prepared by magnetron sputtering

M. Jaroš*, J. Musil, R. Čerstvý, S. Haviar

Department of Physics and NTIS – European Centre of Excellence, University of West Bohemia, Univerzitní 8, CZ-306 14, Plzeň, Czech Republic

ARTICLE INFO

Keywords:
Ti(Al,V)N films
Energy
Mechanical properties
Macrostress
Film cracking
Magnetron sputtering

ABSTRACT

The article reports on the effect of the energy $\mathscr{E}$ delivered into the growing film on its macrostress, microstructure, mechanical properties and resistance to cracking of Ti(Al,V)N films. The Ti(Al,V)N films were deposited on Si(111) and Mo substrates by magnetron sputtering in a mixture Ar + N_2 gases using a dual magnetron with closed magnetic field and equipped with TiAlV (6 at.% Al, 4 at.% V) alloy targets. It is shown that the compressive macrostress σ in sputtered films can be reduced either by the pulsed bipolar bias voltage U_{sp} with alternating negative and positive pulses or the electron and ion bombardment during overshoots in the pulsed magnetron sputtering. All sputtered films with high ratio $H/E^* \geq 0.1$, compressive macrostress ($\sigma < 0$), and non-columnar microstructure exhibit an enhanced resistance to cracking; here H is the hardness and E^* is the effective Young's modulus. The high compressive macrostress in the film is not the necessary condition for the formation of the films with an enhanced resistance to cracking.

1. Introduction

There is a huge number of papers devoted to the investigation of relationships between the deposition parameters of the film and its structure [1–12], microstructure [8–26], phase and elemental composition [2–5,15–20], macrostress [4–9,18–25], physical and functional properties [1–31]. Despite these facts, it is very difficult to sputter in different deposition chambers with different magnetrons, and different power supplies (DC, pulsed) the films with reproducible properties. It is due to the fact that different combinations of deposition parameters, different magnetrons (single, dual, etc.) and different arrangement of substrate holders (stationary, rotating) result in different energies $\mathscr{E}$ delivered into the growing film. It means that the main parameter controlling the properties of the film is the energy $\mathscr{E}$ [32–42]. Therefore, the knowledge of correlations between the energy $\mathscr{E}$ and the film properties is very important.

In deposition of films using an ion plating process, i.e. in the case when the substrate on which the film is deposited is held on a negative substrate bias U_s, the most important is the energy $\mathscr{E}_{bi}$ delivered to the film during its growth by bombarded ions. In the simplest case of a collision-less, fully ionized plasma the energy $\mathscr{E}_{bi}$ can be expressed in the following form [42].

$$\mathscr{E}_{bi}\ [\mathrm{J/cm^3}] = |U_p - U_s| \times i_s/a_D \quad (1)$$

Here, U_p is the plasma potential, U_s is the substrate bias, i_s is the substrate ion current density and a_D is the deposition rate of the film. Under the assumption that $|U_p| \ll |U_s|$, which is well fulfilled in many experiments, Eq. (1) can be simplified in the following simple form

$$\mathscr{E}_{bi}\ [\mathrm{J/cm^3}] \approx (|U_s|\, i_s)/a_D \quad (2)$$

Eq. (2) shows that the energy $\mathscr{E}_{bi}$ delivered to the growing film by bombarding ions can be easily calculated from measured deposition parameters (U_s, i_s) and the film deposition rate $a_D = h/t_d$ calculated from the measured film thickness h and the deposition time t_d.

Recently, it was demonstrated that, the Ti(Al,V)N films with enhanced resistance to cracking are created at high energies $\mathscr{E}_{bi} > 1.7\ \mathrm{MJ/cm^3}$ [43]. However, the intensive ion bombardment generates high compressive stresses (up to -3 GPa to −5 GPa) in sputtered films [44]. Such films easily delaminate from the substrate and crack. Therefore, it is necessary to decrease the compressive macrostress σ but simultaneously to deliver to the film sufficiently high energy $\mathscr{E}_{bi}$ necessary to sputter the film with dense, non-columnar microstructure exhibiting no delamination from substrate and an enhanced resistance resistance to cracking.

The solution of this quite difficult task is the subject of this article. It is shown that the films with an enhanced resistance to cracking and a low compressive macrostress $|\sigma| \leq 1$ GPa can be formed in the case

* Corresponding author.
E-mail address: jarosm@kfy.zcu.cz (M. Jaroš).

https://doi.org/10.1016/j.vacuum.2018.09.038
Received 4 April 2018; Received in revised form 7 August 2018; Accepted 17 September 2018
Available online 18 September 2018
0042-207X/

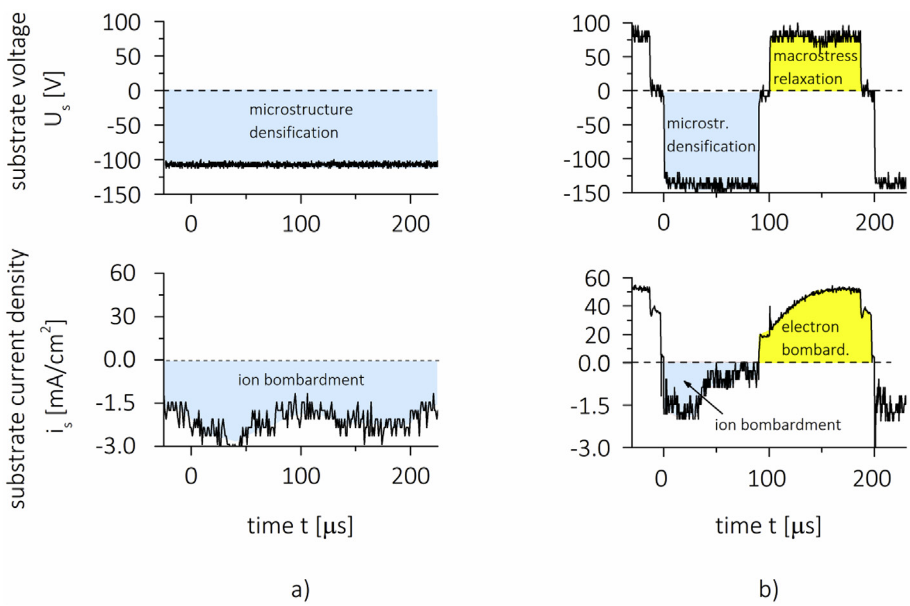

Fig. 1. Comparison of DC and pulsed substrate bias used in deposition of Ti(Al,V)N films by DC dual magnetron discharge generated at $I_d = 1$ A, $T_s = 500\,^{\circ}C$, $d_{s-t} = 60$ mm, $p_T = p_{Ar} + p_{N2} = 0.8 + 0.2 = 1$ Pa. (a) Continuous ion bombardment and (b) alternating ion/electron bombardment of the growing Ti(Al,V)N film by ions and electrons produced by DC bias ($U_s = -100$ V) and pulsed bias ($U_{sp} = -130/+70$ V, $f_r = 5$ kHz), respectively. Here, U_{sp} is the pulsed substrate bias U_{sp} and i_{sp} is the pulsed substrate current density.

Table 1
Physical and mechanical properties and compressive macrostress ($\sigma < 0$) in the Ti(Al,V)N films sputtered by DC dual magnetron operated at $I_d = 1$ A, $T_s = 500\,^{\circ}C$, $d_{s-t} = 60$ mm, $p_T = p_{Ar} + p_{N2} = 0.2 + 0.8 = 1$ Pa on the substrate held at (i) DC substrate bias voltage $U_{s\,DC}$ and (ii) pulsed substrate bias voltage U_{sp} with repetition frequency of pulses $f_r = 5$ kHz. The bending test was performed on the films sputtered on the Mo strip and the indentation test on the films sputtered on the Si substrates.

bias voltage	f_r [kHz]	U_{sp} [V]	i_s [mA/cm^2]	h [nm]	a_D [nm/min]	τ_e/τ_i	$\mathcal{E}_{bip}$ [MJ/cm^3]	σ [GPa]	H [GPa]	E* [GPa]	W_e [%]	H/E*	ε_{cr} [%]	L_{cr} [N]	structure	texture
DC	0	−40	1.0	2100	36.0	0	1.6	−1.7	28.4	282	70	0.10	–	0.25	crystaline	(200)+(220)
DC	0	−100	1.8	1100	37.5	0	3.7	−4.0	30.7	220	81	0.14	> 2.0	> 1	crystaline	(220)
pulsed	5	−100/+70	0.9	1000	33.0	1.3	1.6	−0.8	19.1	175	68	0.11	1.3	0.75	XRA	

$\mathcal{E}_{bip}$ is the average energy of ions during the negative pulse of pulsed substrate bias U_{sp}, and XRA is X-ray amorphous.

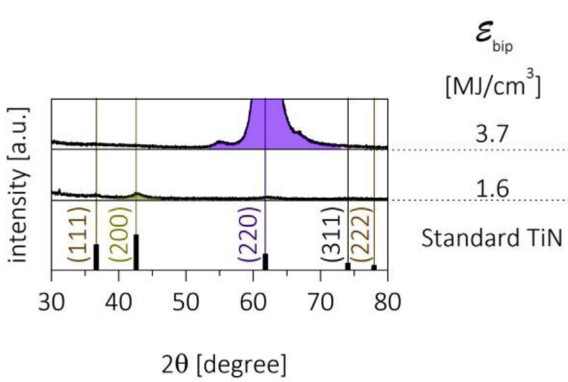

Fig. 2. Comparison of the structure of the Ti(Al,V)N film sputter deposited at (i) DC substrate bias $U_{s\,DC} = -100$ V and a high energy $\mathcal{E}_{bi} = 3.7$ MJ/cm^3 and (ii) the pulsed substrate bias U_{sp} and a low energy $\mathcal{E}_{bip} = 1.6$ MJ/cm^3.

when σ generated in sputtered film is relaxed by bombardment of electrons during its growth. Two methods are described in detail: (1) the DC sputtering with pulsed bipolar bias with alternating negative and positive pulses and (2) the pulsed sputtering with electron bombardment of the film during overshoots at the end of each pulse. Both methods efficiently reduce the compressive macrosrostress ($\sigma < 0$) in sputtered films. It was demonstrated in sputtering of the Ti(Al,V)N nitride films.

2. Experimental

The Ti(Al,V)N nitride films were reactively sputter deposited on Si (111) and Mo substrates at substrate temperature $T_s = 500\,^{\circ}C$ and substrate-to-target distance $d_{s-t} = 60$ mm by a dual magnetron with closed magnetic field equipped with TiAlV (6 at.% Al, 4 at.% V) alloy targets of diameter ∅ = 50 mm in a mixture of Ar + N2 sputtering gases. The magnetrons were tilted at angle 20° to the vertical axis [45] and supplied by an Advanced Energy Pinnacle Plus+ 5/5 kW power supply operated either in the DC or pulse mode. The Ti(Al,V)N films deposited by a dual magnetron powered by DC power were sputtered at $I_d = 1$ A results in $W_t = I_d U_d/S \approx 16$ W/cm^2, and the substrate held either at constant negative bias U_s or at pulsed bipolar positive/negative bias. The Ti(Al,V)N films deposited by a dual magnetron powered by pulsed power were sputtered at the repetition frequency of pulses f_r ranging from 100 kHz to 350 kHz, τ/T = 0.5 and I_d ranging from 1.6 to 2 A resulting in the target power density $W_t = I_{dp} U_{dp}/S < 16$ W/cm^2 and the substrate bias held at the floating potential U_{fl} or at the constant negative bias; here I_{dp} and U_{dp} is the discharge current and voltage during pulse-on time, respectively, and S is the total area of the sputtered target. All Ti(Al,V)N_x films were sputtered in the nitrogen-rich atmosphere at $p_{N2}/p_T = 0.8$. The films sputtered under these conditions were almost stoichiometric (x = N/(Ti + Al + V) ≈ 1) and their stoichiometry x varied in a very narrow range from 0.98 to 1.09 only. The Si plates (20 × 20 × 0.64 mm^3) were used for of X-ray diffraction patterns and the Si strips (30 × 5 × 0.64 mm^3) were used for the measurement of the macrostress σ in the sputtered films. The Mo substrates (80 × 15 × 0.20 mm^3) coated by sputtered films were used for the assessment of the film resistance to cracking in bending. A pre-