Thin Solid Films 517 (2009) 6635–6641

Contents lists available at ScienceDirect

Thin Solid Films

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

Compositional and structural evolution of sputtered Ti-Al-N

Li Chen [a,b,*], Martin Moser [a], Yong Du [b], Paul H. Mayrhofer [a]

[a] Department of Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Leoben, 8700, Austria
[b] State Key Laboratory of Powder Metallurgy, Central South University, Changsha Hunan, 410083, China

ARTICLE INFO

Article history:
Received 13 March 2009
Received in revised form 21 April 2009
Accepted 22 April 2009
Available online 3 May 2009

Keywords:
Physical vapour deposition (PVD)
Ti-Al-N
Reactive sputtering
Composition

ABSTRACT

The compositional and structural evolution of Ti-Al-N thin films as a function of the total working gas pressure (p_T), the N_2-to-total pressure ratio (p_{N2}/p_T), the substrate-to-target distance (ST), the substrate position, the magnetron power current (I_m), the externally applied magnetic field, and the energy and the ion-to-metal flux ratio of the ion bombardment during reactive sputtering of a $Ti_{0.5}Al_{0.5}$ target is investigated in detail. Based on this variation we propose that the different poisoning states of the Ti and Al particles of the powder-metallurgically prepared $Ti_{0.5}Al_{0.5}$ target in addition to scattering and angular losses of the sputter flux cause a significant modification in the Al/Ti ratio of the deposited thin films ranging from ~1.05 to 2.15.

The compositional variation induces a corresponding structural modification between single-phase cubic, mixed cubic-hexagonal and single-phase hexagonal. However, the maximum Al content for single-phase cubic $Ti_{1-x}Al_xN$ strongly depends on the deposition conditions and was obtained with $x = 0.66$, for the coating deposited at 500 °C, $p_T = 0.4$ Pa, ST = 85 mm, and $p_{N2}/p_T = 17\%$. Our results show, that in particular, the N_2-to-total pressure ratio in combination with the sputtering power density of the $Ti_{0.5}Al_{0.5}$ compound target has a pronounced effect on the Al/Ti ratio and the structure development of the coatings prepared.

1. Introduction

Magnetron sputtering of thin films is a major field of physical vapor deposition (PVD) technologies [1–5], where various material combinations and compounds are accessible. In general, compound films can be prepared by reactive sputtering, where in addition to the sputtered target material a reactive gas like N_2 is introduced to the PVD chamber, or by sputtering of a compound target itself [6–9]. Due to the massive move in industry and research from binary to ternary and further towards multinary systems, compound target development became a major field for PVD [10–17]. While it is noticed that the composition of the coating can vary from that of the corresponding target [18–22] depending on the deposition conditions used, such as gas flow, sputtering power, substrate bias, etc., little is understood on the origin of these influences. In order to benefit from these effects of deposition-parameters-induced variations in coating composition, with respect to the corresponding compound target, we use a model-system, Ti-Al-N, for detailed studies of their compositional and structural evolution as a function of specific parameters during unbalanced magnetron sputtering.

Ti-Al-N hard coatings with cubic NaCl (c) structure, where Al substitutes for Ti in the TiN based structure (i.e., $Ti_{1-x}Al_xN$), are widely used for wear resistant applications like cutting tools, due to their unique properties, such as high temperature oxidation resistance and age-hardening abilities [23–29]. The chemical composition of Ti-Al-N thin films depends to a great extent on the deposition parameters, which basically determine their structure and properties [30–33]. Single phase cubic Ti-Al-N films with high Al contents exhibit excellent mechanical properties and oxidation resistance. For Al contents exceeding the cubic solid solubility, which is reported with x being in the range of 0.65-0.75, a mixed cubic-NaCl and hexagonal-ZnS (h-AlN) structure is formed, which results in reduced film properties, e.g., decreasing hardness, bulk-, elastic-, and shear-moduli, as well as wear resistance [11,26–33]. Therefore, the compositional variation of Ti-Al-N films, arising from the deposition parameters, influence their structure evolution and mechanical properties. Extensive studies of the correlation between film composition, structure and performance of Ti-Al-N films deposited by magnetron sputtering have already been reported [10–17]. However, only little is known and understood on the correlation between deposition parameters during reactive sputtering of a compound target and the resulting film composition and structure.

To study the effect of various deposition parameters on the composition and structure of Ti-Al-N thin films we varied the total working gas pressure (p_T), the ratio of the N_2-partial pressure (p_{N2}) to total pressure (p_{N2}/p_T), the substrate-to-target distance (ST), the substrate position with respect to the center of substrate holder (SP), which is above the center of the parallel aligned target, the magnetron power current (I_m), the externally applied magnetic field (B_{ext}), the ion energy (E_i), and the ion-to-metal flux ratio (J_{ion}/J_{me}).

2. Experimental details

Ti-Al-N films were deposited onto Si substrates ($20 \times 7 \times 0.3$ mm^3) by unbalanced magnetron sputtering from a powder-metallurgically

* Corresponding author. Tel.: +43 3842 402 4236; fax: +43 3842 402 737.
E-mail address: li.chen@unileoben.ac.at (L. Chen).

0040-6090/$ – see front matter.
doi:10.1016/j.tsf.2009.04.056

Table 1
Total working gas pressure (p_T), N_2-to-total pressure ratio (p_{N2}/p_T), substrate-to-target distance (ST), distance of the substrate to the center of the substrate holder (SP), magnetron power current (I_m), externally applied magnetic field (B_{ext}), applied substrate bias potential (V_b), and ion energy (E_i) used during deposition.

p_{N2}/p_T (%)	p_T (Pa)	ST (mm)	SP (mm)	I_m (A)	$\pm B_{ext}$ (G)	$-V_b$ (V)	E_i (eV)
0–100	0.4	85	32	1.5	−40	60	43
17	0.4–2.24	85	32	1.5	−40	60	43
17, 23	0.4	57–85	32	1.5	−40	60	43
0, 17, 100	0.4	85	0–80	1.5	−40	60	43
27	0.4	85	32	1.5–4.0	−40	60	43
17	0.4	85	0	1.5	−120–+120	30–86	30
17	0.4	85	0	1.5	−40	37–112	20–95
0, 100	4	85	32	1.5	−40	60	43

Chen et al.

prepared $Ti_{0.5}Al_{0.5}$ compound target (diameter of 152 mm and purity of 99.9%, PLANSEE) in a mixed $Ar+N_2$ (both of 99.999% purity) glow discharge. More details on the magnetron sputtering system used are described in Ref. [34]. Prior to the deposition with a constant substrate temperature (T_s) of 500 °C and a base pressure ≤0.8 mPa, the substrates were etched for 20 min using an Ar^+ glow discharge with ~1250 V and 25 mA, at a pressure of 3.0 Pa. Before loading the chamber, the polished Si substrates were ultra-sonically cleaned in acetone and ethylene. The total working gas pressure p_T was varied between 0.4 and 4 Pa, the N_2-to-total pressure ratio p_{N2}/p_T was varied between 0 and 100%, the substrate-to-target distance ST was varied between 57 and 85 mm, the substrate distance to the center of the substrate holder SP was varied between 0 and 80 mm, the magnetron power current I_m was varied between 1.5 and 4.0 A, and the ion energy E_i was varied between 20 and 95 eV.

The externally applied magnetic field (B_{ext}) using a pair of Helmholtz coils was varied between −120 and +120 G. This notification refers to a broadening (−) or concentration (+) of the sputtering zone at the target surface and the plasma zone at the substrate holder by influencing the permanent magnetic field of the planar magnetron.

The plasma characteristics like ion flux J_{ion} and plasma potential V_p, were determined by Hiden ESP Langmuir wire probe measurements following the procedures described in Refs. [35,36]. The metal flux J_{me} was estimated from the deposition rate (R), which itself was calculated from the film thickness, measured by the ball crater method, deposition time, and assuming a theoretical density for cubic $Ti_{1-x}Al_xN$ [37–39]. The ion energy can be estimated from the difference between the plasma potential (V_p) and the substrate bias potential (V_b) with $E_i=e(V_p-V_b)$ [40]. Details on the deposition parameters are presented in Table 1, and the schematic of the substrate holder and target arrangement is given in Fig. 1.

The chemical composition of the films was determined using energy dispersive X-ray analysis (EDX) with an Oxford Instruments INCA EDX unit attached to a scanning electron microscopy (SEM) operated with 25 kV. Structural investigations were conducted by X-ray diffraction (XRD) with CuK_α radiation using a Bruker D8 in Bragg/Brentano mode.

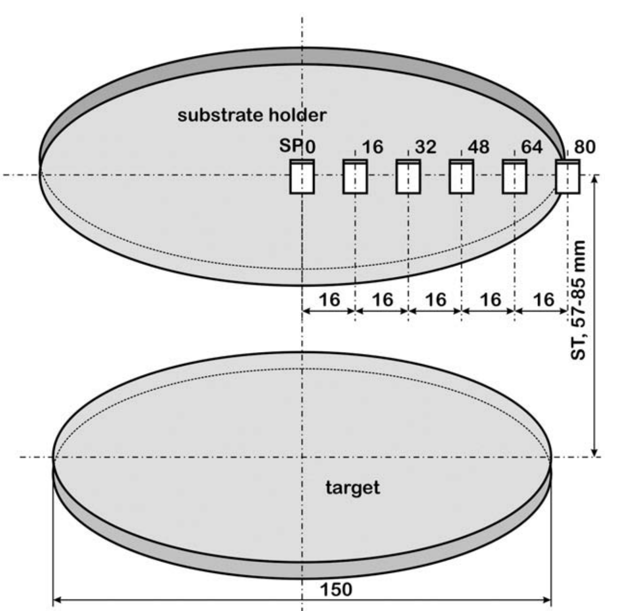

Fig. 1. Schematic of the substrate and target arrangement with indicated substrate-to-target distance ST and substrate position SP. Dimensions are given in mm.

3. Results and discussion

3.1. Plasma characteristics and deposition rate

Increasing the N_2-to-total pressure ratio p_{N2}/p_T from 0 to 100% at a constant total pressure of 0.4 Pa induces a reduction in deposition rate from 59 to 9 nm/min. The strong change in the dependence of the deposition rate on the N_2-to-total pressure ratio suggests a change in sputtering mode from metallic towards poisoned in the p_{N2}/p_T range 17–23%, see Fig. 2a. However, J_{ion}/J_{me} almost continuously increases from 0.5 to 5.0 and V_p increases from −15.8 to −20.2 V when increasing p_{N2}/p_T from 0 to 100%, respectively. The sputtering yields for Ti, Al, TiN, and AlN are ~0.5, 0.9, 0.1, and 0.2 using argon ions with an energy of 500 eV [21]. Consequently, nitridation of the target is responsible for a decrease in deposition rate. The degree of the target nitridation determined by the partial pressure of reactive gas N_2 plays a significant role in deposition rate. As shown in Fig. 2a, initially the deposition rate strongly decreases to 20 nm/min with increasing p_{N2}/p_T to 15%, which indicates a transition of the target surface from metallic to nitridic. With increasing p_{N2}/p_T to 23% the deposition rate only slightly decreases from 20 to 17 nm/min suggesting that the target is still in transition mode. For a further increase in p_{N2}/p_T the deposition rate initially decreases more pronounced and then approaches to an almost constant value of ~10 for $p_{N2}/p_T \geq 60\%$, indicating a poisoned target surface, in agreement with Ref. [18,41]. Consequently, we have chosen a p_{N2}/p_T ratio of 17% (within the transition mode) as the standard value for further investigations.

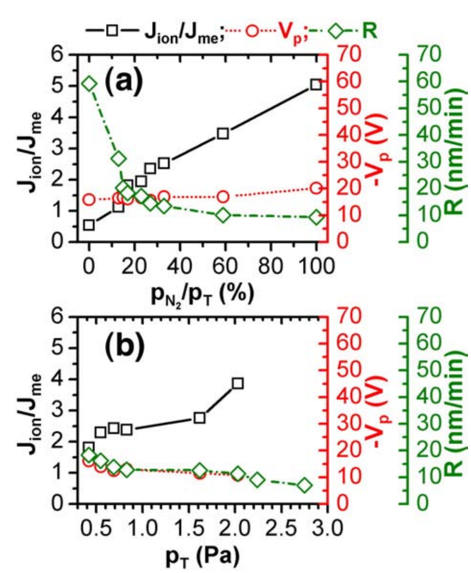

Fig. 2. Dependency of the incident ion-to-metal flux ratio (J_{ion}/J_{me}), plasma potential (V_p), and deposition rate (R) on the (a) N_2-to-total pressure ratio (p_{N2}/p_T) for $p_T=0.4$ Pa, and the (b) total working gas pressure (p_T) for $p_{N2}/p_T=17\%$. The additional deposition parameters used were kept constant: $T_s=500$ °C, ST = 85 mm, SP = 32 mm, $I_m=1.5$ A, $B_{ext}=-40$ G, and $E_i=43$ eV.