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CHARACTERIZATION OF HARD Ti-W-N FILMS DEPOSITED BY REACTIVE D.C. MAGNETRON SPUTTERING

KARAKTERIZACIJA TRDIH TIWN PLASTI DEPONIRANIH Z REAKTIVNIM DC MAGNETRONSKIM NAPR[EVANJEM

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Ti-W-N films were de pos ited by re ac tive d.c. mag ne tron sput ter ing from a W-Ti (30 at.%) tar get in a mix ture of ar gon and ni tro gen onto steel and sil i con sub strates. The sub strates were placed at a dis tance of 50 mm from the tar get. The to tal pres sure prior to the ig ni tion of the dis charge was kept at 0.5 Pa, while the to tal gas flow was set to 50 sccm. The typ i cal de po si tion pa ram e ters were: sub strate tem per a ture 320°C, de po si tion rate 3 nm/s, film thick ness 3.5 µm, sub strate bias –100 V, and mean sub strate ion cur rent den sity 1.2 mA/cm^2. The crys tal struc ture, com po si tion and mi cro-hardness were stud ied as a func tion of de po si tion pa ram e ters, i.e., ni tro gen con tent in the work ing gas mix ture, sub strate ion cur rent den sity and sub strate bias. The films con tain ing less than 30 at.% ni tro gen were com posed of bcc W and, pos si bly, hcp Ti pha ses. The hard ness of these films in creased with in creas ing ni tro gen con tent from 25 GPa for 0 at.% N up to a max i mum of ap prox i mately 60 GPa for 25 at.% N. This was ac com pa nied by in creas ing microstrain, as re vealed by an anal y sis of the broad en ing of the X-ray re flec tions. The films with a ni tro gen con tent over 30 at.% were char ac ter ized by a mi cro-hardness of about 40 GPa and by X-ray re flec tions in dic a tive of an fcc phase.

Key words: TiWN films, mag ne tron sput ter ing, com po si tion, microstructure, hard ness, X rays analysis

TiWN plasti so bile deponirane z reaktivnim magnetronskim napr{evanjem iz W-Ti (30 at.%) tar~e v at mosferi iz du{ika in argona na sub strate iz jekla in silicija na oddaljenosti 50 mm od tar~e. Skupni pritisk pred za~et kom napr{evanja je bil 0.5 Pa, pretok plina pa 50 sccm. Zna~ilni parametri depozicije so bili: temperatura sub strata 320°C, hitrost depozicije 3 mm/s, debelina plasti 3.5 µm, bias sub strata –100 V in popre~ni ionski tok sub strata 1.2 mA/cm^2. Kristalna struktura, sestava in mikrotrdota so bile dolo~ene v odvisnosti od parametrov depozicije: vsebnost du{ika v atmosferi ter gostote ionske ga toka in biasa sub strata. Plasti z manj od 30 at.% du{ika so bile sestavljene iz bbc W in hcp Ti faz. Trdota teh plasti je ra stla z vsebnostjo du{ika od 25 GPa za 0% do maksimuma 60 GPa pri 25 at.% N. Pove~anje trdote je rastlo z mikrodeformacijami, ki so se pokazale s {irjenjem uklona X `arkov. Plasti z nad 30 at.% N so imele trdoto oko li 40 GPa, uklon X `arkov pa je bil zna ~ilen za neko fcc fazo.

Klju~ne besede: TiWN plasti, magnetronsko razpr{evanje, sestava, mikrostruktura, trdota, X `arki, a naliza

1INTRODUCTION

Considerable attention has recently been devoted to investigations of Ti-W-N films because of their use as diffusion barriers in the contacts of integrated circuits[1-4] These films were deposited by either r.f. or magnetron sputtering. The films were reported to consist of a mixture of phases of W and Ti and their nitrides. The exact phase composition was influenced mainly by the nitrogen partial pressure and the substrate bias. A crystal grain size of the order of 10 nm was determined[2,3]. The presence of ultrafine (sub-nanometer) particles was also suggested[3].

Recently, a number of papers have appeared reporting on nano-composite films consisting of basically two or more phases with small crystal grains. These multiphase films possess high hardness, in excess of the hardness of the single phase films, often over 40 GPa, i.e., in the domain of super-hardness[5,6]. Considering these studies on superhard nano-composite films, the reported properties of Ti-W-N films and the intrinsic high hardness of both TiN and W, it is clear that it is interesting to investigate the Ti-W-N films with respect to their application as hard protective coatings. Indeed, the microhardness of sputter-deposited Ti-W-N films was measured by Cavaleiro et al.[7]. They observed hardness of 38 GPa for fcc Ti-W-N films with a nitrogen concentration of 44 at.%.

The aim of the present paper is to investigated in detail the microhardness of sputter-deposited Ti-W-N films as a function of the deposition parameters, particularly partial nitrogen pressure p_{N_2}, substrate temperature T_s, negative substrate bias U_s and substrate ion current density i_s, and to correlate it with the film composition and crystal structure.

2 EXPERIMENTALDETAILS

The Ti-W-N films were deposited by unbalanced planar d.c. magnetron reactive sputtering of a W-Ti (30 at.%) target of diameter 100 mm. The films were deposited onto Si monocrystal plates and steel discs with a diameter of either 18 or 25 mm and a thickness of 5 mm. The substrates were ultrasonically cleaned in isopropyl alcohol and dried before clamping to the

substrate holder. A substrate-to-target distance of 50 mm was used throughout the experiments. The vacuum chamber was pumped down to a base pressure below 10^{-3} Pa. Then the mixture of argon and nitrogen, both of 99.999% purity, was leaked in at a typical total flow rate of 50 sccm and a total pressure of 0.5 Pa (i.e., prior to the discharge ignition). The partial pressure of nitrogen was varied from 0 to 0.3 Pa. The substrate holder was electrically floating (floating potential was about –25 V) or negatively biased up to U_s=-350 V. A pre-sputter conditioning for 10 min, with a shutter over the substrate, was used to clean the target and to achieve steady state conditions. The discharge was run at a current of 1.5 A, resulting in a typical deposition rate of 3 nm/s. A typical film thickness was about 3.5 μm which demanded a typical deposition time of 20 min. The substrate ion current density was about i_s=1.2 mA/cm^2. In one experiment i_s was varied from 0.25 mA/cm^2 to 2 mA/cm^2 by variation of the magnetron magnetic field.

The substrate temperature was measured by a CrNi-Ni thermocouple clamped to the surface of a dummy substrate located close to the actual substrate. The substrate temperature was increasing during the deposition due to the energy flux from the plasma carried by electrons, ions, and energetic neutrals. A combination of substrate holder heating before the deposition was started and cooling by water and compressed air during the deposition was used to achieve a stable temperature during the deposition. In this way, a stable substrate temperature was achieved in 1-2 min after the start of the deposition. A typical substrate temperature was about 320°C, however depositions at 240°C and 430°C were performed for comparison, too.

Film thickness was measured with a stylus-type surface profiler (Tencor Alpha-Step 500). The chemical composition of the films was investigated by an electron microprobe (JEOL JXA733). The microhardness was measured using a Fischerscope H-100. The crystal structure of the films was determined by XRD using a Bragg-Brentano powder diffractometer HZG 3, rotating anode Rigaku RU 300, and $CuK_{\alpha 12}$ radiation monochromatized by a Johannsonn monochromator in the diffracted beam. The XRD patterns were fitted with the Pearson function including α_{12} splitting. Various characteristics of the peaks, such as the position of the peak, integral width and integral intensity were determined from the fit.

3 RESULTS

The films were deposited at various nitrogen partial pressures, substrate biases, substrate currents and deposition temperatures. Among those parameters varied within the ranges indicated in the previous section the film properties were most sensitive to the partial pressure of nitrogen p_{N_2}. The composition of the films as a function of p_{N_2} is shown in **Fig. 1**. The nitrogen concentration is steadily increasing with increasing p_{N_2} with a tendency to saturate for p_{N_2}>0.2 Pa. The maximum nitrogen content in the films is about 50 at.% for 0.3 Pa. At the same time, the atomic ratio of Ti/W is increasing too, starting from 0.14 at p_{N_2}=0 and approaching 0.4 for large p_{N_2}, a value slightly lower than the target composition of Ti/W=0.43. In other words the films are always deficient in Ti, when compared to the composition of the target.

The examination of films by XRD, shown in **Fig. 2**, revealed two different phase compositions for p_{N_2} lower and higher than 0.1 Pa. For the films deposited in the argon atmosphere without nitrogen, the dominant phase was bcc W. The remaining reflections, after leaving out those due to the substrate, could be ascribed to the hcp Ti phase, though not all the reflections of this phase were present. The identification of this phase is hindered by the fact that the strongest reflections of the bcc W phase (110) and the hcp Ti phase (101) are practically overlapping. By adding nitrogen to the working gas mixture at partial pressures lower than 0.1 Pa, the XRD pattern simplifies to basically bcc W (110), (211) and (220) reflections, with other reflections close to bcc W (110) and its second order (220) present, which are probably hcp Ti (101) and (202). Simultaneously, the peaks become wider.

The XRD patterns at p_{N_2}>0.1 Pa are completely different from the pattern at low p_{N_2}. Only a single fcc phase can be identified. All other peaks in these patterns are due to the substrate or due to the CuK_{β} radiation, which is not completely filtered out and may appear when a very strong CuK_{α} reflection is present. The lattice constants were a=0.423 nm, 0.424 nm, 0.428 nm and 0.426 nm for p_{N_2}=0.12 Pa, 0.15 Pa, 0.2 Pa and 0.3 Pa, respectively. The possible phases are TiN (a=0.424 nm) or W_2N (a=0.412 nm). The crystal grains are strongly textured in the (100) direction with the exception of the film prepared at p_{N_2}=0.3 Pa, for which the XRD pattern is close to the TiN powder pattern.

The Williamson-Hall plot revealed a large microstrain in the films, which prevented determination of the grain size. The maximum strain was found in the film deposited at p_{N_2}=0.08 Pa, i.e., in the film with the maximum nitrogen concentration where the dominant phase is bcc W, see **Fig. 3**. With respect to the grain size, it was possible to determine only its lower limit, which was about 40 nm for the film prepared in argon and 10 to 20 nm for the films with nitrogen.

The hardness of the films deposited without nitrogen was about 22 GPa. All the nitride films were harder. The hardness as a function of p_{N_2} reached its maximum of 54 GPa at p_{N_2}=0.08 Pa **(see Fig. 4)**, i.e., at the point where there was a maximum in the microstrain and the dominant phase in the film was the bcc W. The films with the fcc phase were less hard, but still the hardness of some of them exceeded 40 GPa. This value is close to

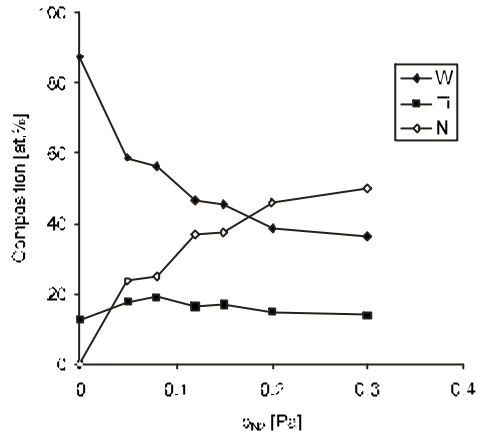

Figure 1: Composition of the Ti-W-N films as a function of the partial pressure of nitrogen. Total pressure 0.5 Pa, discharge current 1.5 A, substrate bias – 100V

Slika 1: Sestava TiWN plasti v odvisnosti od parcialnega pritiska du{ika. Skupni pritisk 0.5 Pa, tok razelektritve 1.5 A, bias substrata – 100V

the microhardness of 38 GPa measured in fcc Ti-W-N films in Ref. 7.

The nitrogen partial pressure p_{N2}=0.07 Pa at which we observed the highest hardness for the negative substrate bias U_s=-100 V and the substrate ion current

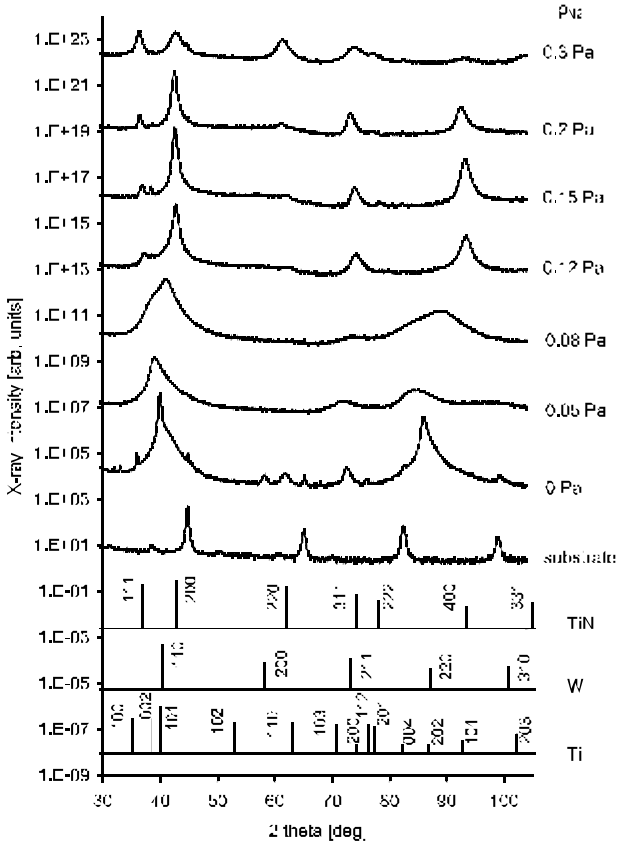

Figure 2: XRD patterns of the Ti-W-N films deposited under various partial pressures of nitrogen

Slika 2: XRD odsevi TiWN plasti deponiranih pri razli~nih parcialnih pritiskih du{ika

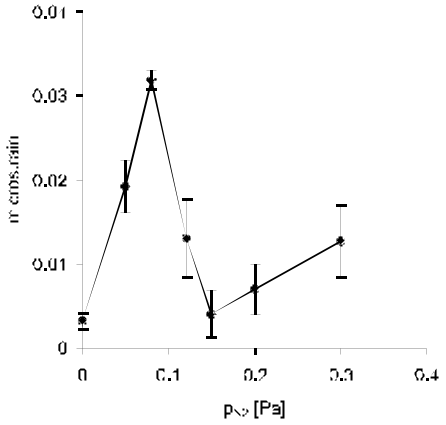

Figure 3: Microstrain as a function of the partial pressure of nitrogen
Slika 3: Mikrodeformacije v odvisnosti od parcialnega pritiska du{ika

i_s=1.2 mA/cm^2 was taken as the basis for further investigations during which the U_s and i_s were varied from a floating potential of about –22 to –400 V and from 0.25 to 2.15 mA/cm^2, respectively. The results are summarized in **Tables 1 and 2**. The XRD pattern of these films varied only slightly, i.e., the crystal structure remained the same: bcc W. The Ti/W ratio was in the range of 0.2-0.4 with the lower concentration of Ti found in the films deposited under higher re-sputtering, i.e., at higher i_s or more negative U_s. The microhardness in these films ranged from 46 GPa to 66 GPa.

Table 1: Composition and microhardness of the films as a function of the substrate ion current density for p_{N2} = 0.07 Pa and U_s = -100 V

i_s (mA/cm^2)	Ti/W	$H_{0.002}$ (Gpa)
0.25	0.35	64
0.46	0.37	57
0.91	0.35	60
1.23	0.35	60
1.52	0.34	59
2.15	0.32	66

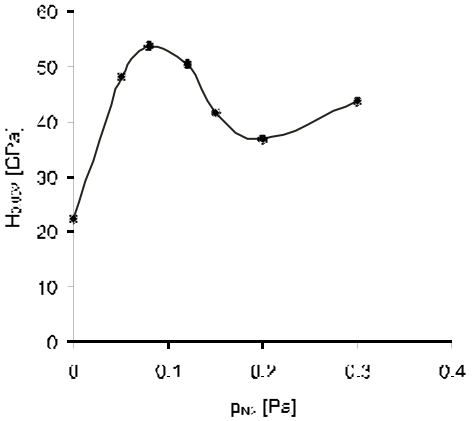

Figure 4: Microhardness of the Ti-W-N films as a function of the partial pressure of nitrogen
Slika 4: Mikrotrdota TiWN plasti v odvisnosti od parcialnega pritiska du{ika

Table 2: Composition and microhardness of the films as a function of the negative substrate bias for p_{N2} = 0.07 Pa and i_s = 1.2 mA/cm^2

U_s (V)	Ti/W	$H_{0.002}$ (Gpa)
-24	0.36	46
-75	0.36	57
-125	0.32	60
-175	0.30	57
-200	0.31	56
-300	0.18	55

4 DISCUSSION

The sputter deposition at low pressures is a non-equilibrium process where the incoming atoms possess kinetic energy of the order of 10 eV, i.e., well above the substrate temperature. Moreover, the bombardment of the growing film by plasma ions constitutes another source of non-equilibrium energy, causing so-called atomic scale heating during which a number of film atoms gain relatively high energy from the bombarding ion and subsequently are very rapidly cooled down. Under such conditions, high temperature phases are deposited at relatively low substrate temperatures[8]. In the Ti-W system there is an immiscibility gap below 740°C. However, a super-saturated solution of Ti in bcc W is possible in sputter deposited films. Nevertheless, the multiple peaks in XRD patterns show that Ti precipitates. The degree of segregated Ti and Ti solved in the bcc W phase is unclear. With increasing nitrogen content, the bcc W phase persists, however with more and more lattice defects as witnessed by the increasing microstrain.

The XRD results at high p_{N2} can be interpreted in two ways. The first hypothesis is that when the concentration of nitrogen in the film reaches approximately 30 at.%, tungsten becomes amorphous and distinct grains of TiN are formed. Affolter et al.[9] studied sputter-deposited tungsten films with various concentrations of nitrogen. They observed the formation of an fcc W_2N phase in the films with nitrogen, however amorphous films were also deposited at nitrogen partial pressures of 0.1 and 0.2 Pa. Lin et al.[10] found that as-deposited PECVD WN_x with various x were always amorphous. The formation of a-WN_x is therefore possible. Finally, the lattice parameter determined from the XRD spectra is closer to TiN, however we must bear in mind that this value can be influenced by stress as the Bragg-Brentano method does not allow us to obtain a relaxed stress-free lattice parameter.

The other possibility is that tungsten forms the fcc W_2N phase. Then titanium must be dissolved in this phase, otherwise the difference between the lattice parameters of TiN and W_2N would give rise to multiple peaks in the XRD patterns as it was observed for the bcc W and hcp Ti phases in the films without nitrogen.

Among the films investigated in the present work the microhardness reaches its maximum in the films with a highly strained lattice, i.e., where the film is crystalline but with a high degree of disorder. After the transition into films supposedly consisting of crystal grains surrounded by an amorphous matrix, the microhardness partially decreases. Supporting evidence suggests that the films with the maximum hardness also possessed a high degree of compressive residual stress. The relation between high stress and high hardness in the present system should be made clear.

5 CONCLUSIONS

The hardness, microstructure and phase composition of Ti-W-N films deposited by reactive magnetron sputtering were found to be strongly dependent on the nitrogen partial pressure in the working gas mixture. At low p_{N2}<0.1 Pa, the films are bcc W and the nitrogen concentration in the films and the microhardness strongly increase with increasing p_{N2}. Microhardness values up to 66 GPa were measured in these films. At p_{N2}>0.1 Pa, the films show a single fcc phase and their microhardness is about 40 GPa, which is somewhat lower than the maximum microhardness in the bcc W region, but it is still high.

The investigation of the film properties is still in progress of the microstructure is being assessed by TEM and SEM.

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