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# Relationship between Condition of Deposition and Properties of W-Ti-N Thin Films Prepared by Reactive Magnetron Sputtering\*\*

By Andrian V. Kuchuk, Vasyl P. Kladko,\*  
Oksana S. Lytvyn, Anna Piotrowska,  
Roman A. Minikayev, and Renata Ratajczak

Investigations of transition metal nitrides have a scientific and practical interest. The unique combination of properties, like a high melting point, good chemical stability, high electric conductivity, excellent diffusion barrier performance and hardness, makes them a widely used. A special interest has an application in the areas of high temperature electronics, microelectromechanics, and aeronautics. Various binary metal-nitride alloys, especially  $W_{1-x}N_x$  and  $Ti_{1-x}N_x$ , have been mostly investigated. But a lot efforts are exerted to the preparation and characterization of ternary metal-metal-nitride films now. It was shown that addition of a small amount of Ti (10–30 at.%) in W-N films improves the adhesion and corrosion resistance.<sup>[1,2]</sup>

Currently, reactive magnetron sputtering of thin films is the most popular technique for synthesizing of W-Ti-N alloys. Films should be easily and reproducibly formed by reactive sputtering of  $W_{1-x}Ti_x$  target in Ar/ $N_2$  plasma.<sup>[2–6]</sup> Of course, the properties of W-Ti-N films are in strong dependence on deposition conditions.

Accordingly to Musil et al.,<sup>[7]</sup> the reactive sputtering process, in dependences of sputtering conditions, should be real-

ized as following modes: (i) metallic, (ii) transition and (iii) reactive. Films of various crystalline structures and, consequently, of various electro-physical properties should be obtained at different sputtering modes.

In our previous study,<sup>[8]</sup> we investigate the influence of sputtering-deposition parameters on efficiency of diffusion barriers based on W-Ti-N films in the Au-GaAs system. It was shown, that  $W_{64}Ti_{16}N_{20}$  film of 100 nm suppresses inter-diffusion between Au-overlayer and GaAs under thermal annealing at 750 °C. Now, we present the results illustrating dependence of sputtered W-Ti-N films properties (chemical composition, phase composition, surface morphology and resistivity) on deposition parameters, especially the partial pressure of nitrogen  $pN_2$ . A correlation between sputtering parameters (modes), films structure and electrical properties is discussed.

**Results and discussion.** *The deposition rate and chemical composition:* The dependences of deposition rate and chemical composition of W-Ti-N thin films, as a function of partial pressure of nitrogen  $pN_2$  are shown in Figure 1. Deposition rate of films sputtered in the metallic mode (MM: 0 Pa <  $pN_2$  < 0.01 Pa) slightly increase (Fig. 1(a)). It should be explained by incorporation of reactive nitrogen atoms into a growing film. Strong decreasing of film deposition rate in the case of transition mode (TM: 0.01 Pa <  $pN_2$  < 0.05 Pa) is caused by target poisoning (formation of denser nitride layer on the target surface). The sputtering yield for nitride is much smaller in comparison with pure metal. In the nitride mode (NM: 0.05 Pa <  $pN_2$  < 0.35 Pa) the deposition rate continues to decrease due to the changing of sputtering agents from  $Ar^+$  to a mixture of  $Ar^+$ ,  $N_2^+$ , and  $N^+$ .<sup>[5]</sup> The nitrogen ions have weaker efficiency in sputtering process, in comparison with the argon ions.

The evolution of films chemical composition as a function of partial pressure of nitrogen  $pN_2$  (Fig. 1(b)) shows that increasing of the reactive gas partial pressure in the chamber during the sputtering leads to the increasing of the N content

[\*] A. V. Kuchuk, Prof. V. P. Kladko, Dr. O. S. Lytvyn  
V. Lashkaryov Institute of Semiconductor Physics  
National Academy of Sciences of Ukraine  
41 pr. Nauky, 03028 Kyiv, Ukraine  
E-mail: kuchuk@isp.kiev.ua (A. V. Kuchuk)

Prof. A. Piotrowska  
Institute of Electron Technology  
Al. Lotnikow 32/46, 02-668 Warsaw, Poland  
R. A. Minikayev  
Institute of Physics  
Polish Academy of Sciences  
Al. Lotnikow 32/46, 02-668 Warsaw, Poland

R. Ratajczak  
The Andrzej Soltan Institute for Nuclear Studies  
69 Hoza str., 00-681 Warsaw, Poland

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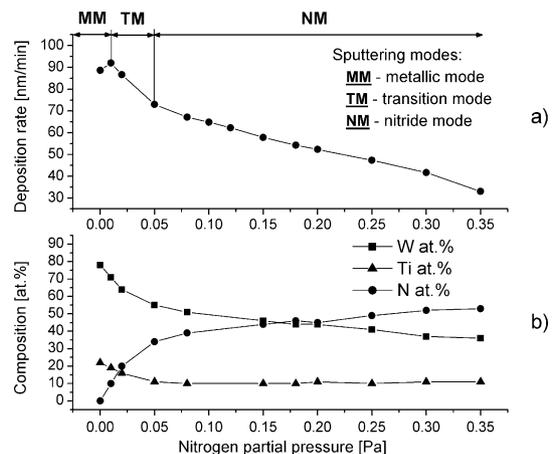


Fig. 1. Deposition rate (a) and chemical composition (b) of reactively sputtered W-Ti-N thin films as a function of partial pressure of nitrogen  $pN_2$ . The films growth rate in dependences of partial pressure of reactive nitrogen gas is deviated into three regions of sputtering: (i) MM – metallic mode; (ii) TM – transition mode; (iii) NM – nitride mode.

into the films. The  $N_2$  concentration increases because a greater number of reactive nitrogen incorporates into the film during the sputtering process, as well as due to sputtering rate decreasing at increasing of the  $pN_2$ . The nitrogen content tends to saturation at the higher N partial pressure ( $pN_2 > 0.2$  Pa). Analysis of the W/Ti atomic ratios indicates that films have lower titanium content as it should be expected from the target composition. This can be explained by preferential re-sputtering of Ti atoms from the films by plasma ions and by the fast neutrals atoms reflecting from the target, as previously reported by Shaginyan et al.<sup>[5,6]</sup> and Bergstrom et al.<sup>[9]</sup>

*The phase composition and surface morphology:* The crystalline structure and surface morphology of the W-Ti-N films depends on amount of N in the films (which strongly depend on partial pressure of nitrogen  $N_2$ ), and sputtering mode. X-ray diffraction patterns obtained on the W-Ti-N films sputtered with increasing  $pN_2$  are shown in Figure 2. There are three different structural changes representing each of the three different sputtering modes. It seen that films contain mainly b.c.c. W phase with the (110) crystallite preferred orientation in the case of metallic mode deposition (low N concentration). The lattice parameters of the pure W-Ti and film containing 10 at.% of N are  $\sim 0.3204$  and  $\sim 0.3241$  nm, respectively. The data are close enough, but are higher of the bulk b.c.c. W lattice parameter (0.3165 nm). An interpretation of the difference between lattice parameters of bulk material and experimentally obtained films should be the following: (i) an increasing of the lattice parameter for tungsten-rich film sputtered in pure Ar is induced by presence of the larger Ti atoms; (ii) the lattice parameter changing after small amount of nitrogen incorporation into the films can be explained by expansion of lattice constant by N atoms. The last results indicate an increasing of lattice strain (microstrain) due to the interstitial incorporation

of N atoms, which with decreasing of crystallite sizes (from 15 to 7 nm by XRD), commonly explanations: (i) diffraction line broadening; (ii) decreases of XRD intensity; (iii) shift to lower diffraction angles of the strong 110 diffraction peak. Above-mentioned results testify that films sputter-deposited in the metallic mode can be regarded as a metastable interstitial solid solution of b.c.c.  $\alpha$ -W( $Ti_x, N_y$ ).

The broad peak in the range of 35 and 45° was observed on XRD pattern from the film with 20 at.% of N obtained in transition mode. This structure can be characterized as a quasi-amorphous. The broad peak from the ternary  $W_{64}Ti_{16}N_{20}$  film indicates a complex character of microstructure, which consist, probably, from small crystallites of pure b.c.c. W and nitrides of metals  $Me_{1-x}N_x$  (Me: W, Ti) embedded into amorphous matrix. Dirks et al.<sup>[3]</sup> using TEM results, described W-Ti-N film with 25 at.% of N as a dense mixture of ultrafine crystallites of TiN, tungsten,  $W_2N$ , and/or  $Ti_2N$ , as well as WN. A possibility to form nanocomposite and/or amorphous film, are typical for transition mode of sputtering.<sup>[7]</sup>

The films produced in nitride mode are composed from a single-crystalline f.c.c. phase structure. From Figure 2 it is seen that for films deposited at higher nitrogen partial pressure  $pN_2$  (N concentration  $> 20$  at.%), only 111 and 200 peaks are observed. The lattice parameter of crystal structure calculated using 111 and 200 diffraction peaks equal to  $\sim 0.4235$  nm for  $W_{55}Ti_{11}N_{34}$  and increase with increasing of N contents. In addition, a good linear relationship between lattice parameters of f.c.c. phase and content of the interstitial N in the films is observed. This fact and similar lattice parameters of  $W_2N$  and TiN nitrides (0.4126 nm and 0.4241 nm, respectively), which mean that they are miscible, indicates to characterize observed f.c.c. structure as mixed phase  $W_2N/TiN$  ( $W_xTi_yN_z$  homogenous solid solution). In the range of N concentrations from 34 to 44 at.%, the f.c.c.  $W_xTi_yN_z$  phase has strong (100) preferred crystallite orientation. However, at higher N concentration (46–53 at.%) the (100) preferred orientation changes drastically up to disappearance. It is connected, probably, with distortion of the f.c.c. lattice structure by extra N atoms. In addition, the increasing number of incorporated N atoms causes a progressive shift of the diffraction peaks from the f.c.c. phase towards lower angles. This indicates the expansion of lattice constant due to microstrains caused by excess of N atoms and decrease of crystallite sizes (from 12 to 8 nm by XRD).

Influences of partial pressure of nitrogen on grain size distribution, surface morphology and roughness of W-Ti-N films are shown in Figure 3. The grain sizes vary lateral dimensions in the range of 5 up to about 90 nm and surface RMS roughness is in the range of 1–2.5 nm. It must be note, that AFM is a pure surface technique, and images give us a hint towards the lateral surface dimension of the grains that is not the true lateral dimension of the crystallites. Thus, the surface grains with various lateral sizes consist of crystallites.

*The electrical resistivity of W-Ti-N films:* The dependences of reactively sputtered W-Ti-N films resistivity on partial pres-

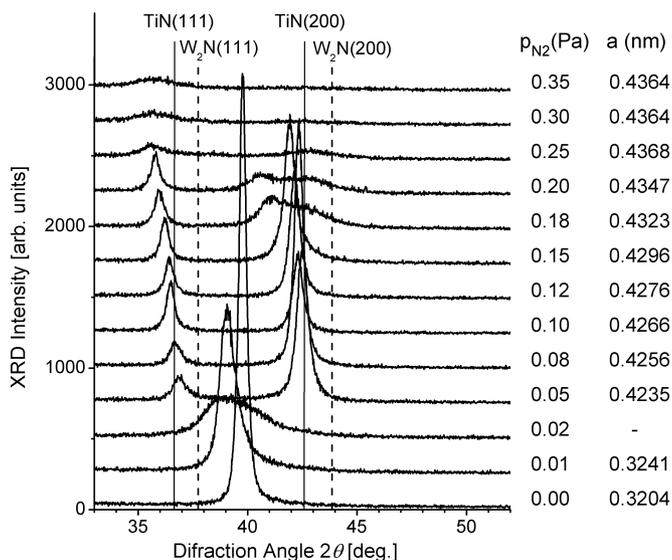


Fig. 2. Evolution of the  $\theta$ - $2\theta$  X-ray diffraction diagrams measured on the W-Ti-N sputtered films with increasing nitrogen partial pressure  $pN_2$ .

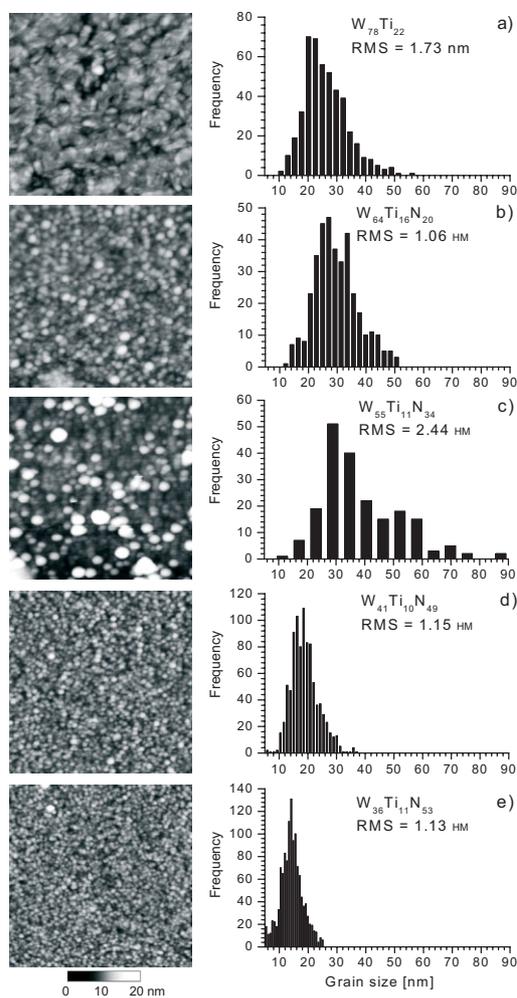


Fig. 3. AFM images of surface (left) and grain size distribution histograms (right) of: (a)  $W_{78}Ti_{22}$ ; (b)  $W_{64}Ti_{16}N_{20}$ ; (c)  $W_{55}Ti_{11}N_{34}$ ; (d)  $W_{41}Ti_{10}N_{49}$ ; (e)  $W_{36}Ti_{11}N_{53}$  films. Scan size  $1 \times 1 \mu m^2$ .

sure of nitrogen  $pN_2$ , is presented in Figure 4. It can be seen that electrical resistivity of as-deposited W-Ti-N thin films increases with increasing of  $pN_2$ . The increasing takes place due to a gradual incorporation of nitrogen atoms into the films. The resistivity of pure binary  $W_{78}Ti_{22}$  film (formed only with argon gas) is about  $106 \mu\Omega\text{-cm}$  and rises slowly up to  $365 \mu\Omega\text{-cm}$  for the ternary  $W_{44}Ti_{11}N_{45}$  film. The film resistivity increases steeply, if the nitrogen concentration exceeds 45 at.%. The increasing of film resistivity can be caused by following reasons: (i) electron scattering by incorporated Ti and N atoms in the W lattice which acts as impurities; (ii) the saturation of the matrix with nitrogen atoms (decreasing of metal atoms amount and increasing of correspondent inter-atomic distances); (iii) formation of nitride phases. The abrupt increasing of resistivity for films containing nearly the same number of nitrogen atoms (from 49 to 53 at.% N) can be attributed to the grain size decreasing (Fig. 3(d, e)). It is about 20 nm for  $W_{41}Ti_{10}N_{49}$  ( $464 \mu\Omega\text{-cm}$ ) and about 14 nm in the case of  $W_{36}Ti_{11}N_{53}$  ( $848 \mu\Omega\text{-cm}$ ).

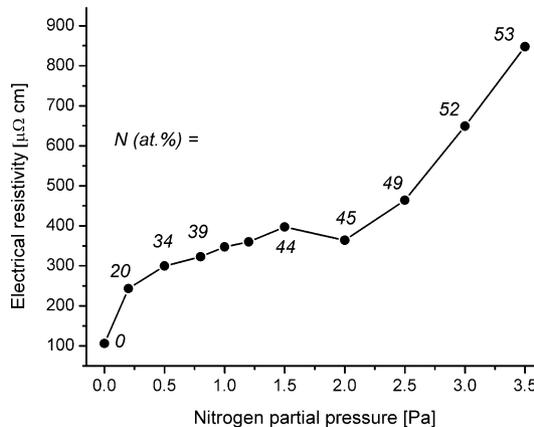


Fig. 4. Electrical resistivity of the W-Ti-N sputtered films as a function of nitrogen partial pressure  $pN_2$ . Labels indicate the nitrogen concentration in the films.

**Conclusions:** The relationship between magnetron deposition parameters (especially, nitrogen partial pressure) and properties (chemical and phase compositions, surface morphology, and resistivity) of W-Ti-N thin films has been studied.

Thin binary W-Ti and ternary W-Ti-N films were deposited by reactive magnetron sputtering from the W-Ti (30 at.%) target in Ar and Ar/ $N_2$  discharges. The d.c. power density of  $1.7 \text{ W/cm}^2$  was applied to the target and the partial pressure of nitrogen  $pN_2$  was varied from 0 to 0.35 Pa at a total gas pressure of 0.5 Pa. The deposition rate, composition and resistivity were measured and the structure of the films was characterized using XRD and AFM techniques. It was shown that increasing of the nitrogen partial pressure  $pN_2$  leads to decreasing of W-Ti-N deposition rate and to increasing of film resistivity and nitrogen content. Films with N concentration of 0 ÷ 10 at.% sputter-deposited in the metallic mode ( $0 \text{ Pa} < pN_2 < 0.01 \text{ Pa}$ ) are formed by a interstitial solid solution of Ti(N) in b.c.c.  $\alpha$ -W phase. In transition mode ( $0.01 \text{ Pa} < pN_2 < 0.05 \text{ Pa}$ ) amorphous-like structure of  $W_{64}Ti_{16}N_{20}$  film is observed. Nitrogen contents in the range 34–53 at.% leads to formation of the single f.c.c.  $W_xTi_yN_z$  phase in the W-Ti-N films produced in nitride mode ( $0.05 \text{ Pa} < pN_2 < 0.35 \text{ Pa}$ ). The electrical resistivity of as-deposited W-Ti-N thin films increase with  $pN_2$  increasing due to the gradual incorporation of nitrogen atoms into the films and as consequence changes of films structure. A correlation between increase of film resistivity and structural changes has been observed.

### Experimental

**Film deposition:** Binary W-Ti and ternary W-Ti-N films were deposited on semiconducting GaAs (100) substrates ( $10 \times 10 \text{ mm}^2$ ) by d.c. magnetron sputtering of W-30 at.% Ti target ( $\varnothing 150 \text{ mm}$ ) in pure Ar and in Ar/ $N_2$  mixture, respectively. Substrates were conventionally cleaned<sup>[8]</sup> and mounted at 70 mm from the target centre. The vacuum was about of  $1 \cdot 10^{-4} \text{ Pa}$ . The power density of  $1.7 \text{ W/cm}^2$  was applied to the target under the  $N_2$  ( $pN_2$ ) partial pressure variations from 0 to 0.35 Pa at the total gas pressure of 0.5 Pa. The target was given a 1 min sputter clean against a shutter at  $2 \text{ W/cm}^2$  before each deposition.

**Film characterization:** The film thickness was measured by Tencor  $\alpha$ -step profilometer. Films of ~ 100 nm thickness were used in resistivity measurements by the four-point probe technique. Chemical composition of films was determined by Rutherford backscattering spectrometry (RBS) using the 2 MeV He<sup>+</sup> ions. Spectra were analyzed by RUMP simulation program.<sup>[10]</sup> Carbon substrates were used at RBS composition analysis in order to reduce the background in the nitrogen signal. In our case, the error of composition measurement was about 10 %.

Crystalline structure of films was investigated by X-ray diffraction (XRD) by means of the Philips X'Pert-MPD setup in the Bragg-Brentano geometry. The CuK<sub>α</sub> (wavelength  $\lambda = 0.15418$  nm) radiation was used. The lattice parameters and crystallite sizes were calculated from angular position and FWHM (full width at the half maximum) of diffraction peaks. Surface morphology, distribution of grains sizes and root-mean square (RMS) roughness were studied by NanoScope IIIa atomic-force microscope (AFM) operated in tapping mode. Both, X-ray and AFM measurements were performed *ex situ* under ambient conditions.

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## Mechanical Properties and Processing of Low-Temperature Diffusion-Welded Hybrid Joints

By Johannes Wilden,\* Jean Pierre Bergmann and Simon Jahn

The increasing interest in lightweight concepts for automobiles has led to the use of different material classes in the last decade, especially lightweight materials, with the aim to achieve superior mechanical properties at the sites where these are needed. For example, tailored blanking with different steel types and thicknesses was the first step towards this philosophy, which can be summarised as “high bearing capacity on demand”. Furthermore, tailored blanking with steel and aluminium and its forming behaviour are the focus of current research.<sup>[1]</sup>

Multi-material mix has therefore become over the last few years an established construction pattern. Beyond the automotive, also the aircraft, chemical and nuclear industries apply hybrid joints.<sup>[2,3]</sup>

Conventional fusion welding technologies such as laser, MSG or electron beam welding are now used in industrial production in order to enhance welding speed and productivity. Even if a wide range of alloys can be joined thanks to

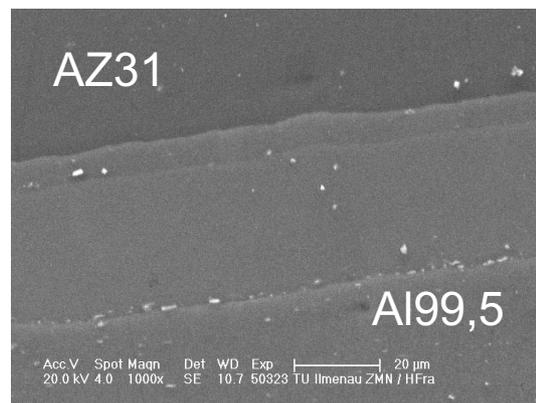


Fig. 1. Joint configuration after 180 mins at 420 °C.

[\*] Prof. J. Wilden, Dr. J. P. Bergmann, S. Jahn, S. Hägebarth, S. Herz  
Fachgebiet Fertigungstechnik  
Technische Universität Ilmenau,  
Neuhaus 1, 98698 Ilmenau, Germany  
E-mail: jeanpierre.bergmann@tu-ilmenau.de