Characterization and properties of highly adhesive titanium nitride and tungsten nitride thin films

I N Martev 1,4, D A Dechev 1,2, N P Ivanov 1,2, T D Uzunov 2 and E P Kashchieva 3

1 Institute of Electronics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
2 Faculty of Engineering and Education, Technical University of Sofia, 59 Bourgasko Chaussee, 8800 Sliven, Bulgaria
3 Department of Physics, University of Chemical Technology and Metallurgy, 8 Kl. Ohridski Blvd., 1756 Sofia, Bulgaria

E-mail: inmartev@ie.bas.bg

Abstract. The paper presents results on the physical characteristics and mechanical properties of titanium nitride (TiN) and tungsten nitride (W2N) thin films grown by reactive DC magnetron sputtering. The films were deposited in a system with several magnetron modules of different sputtering materials suitable for deposition of single-layer metal nitride films and multilayer nitride coatings. The deposition conditions were optimized to obtain films with the highest adhesion to substrates of machine steel and sintered hard alloy. The adhesion of the films was measured in dependence on two principal process parameters: the nitrogen partial pressure in the magnetron discharge gas mixture of nitrogen and argon and the substrate temperature. The composition of the TiN films was determined by Auger electron spectroscopy. The microstructure and the crystallization trend of the films were studied by transmission electron microscopy and selected area electron diffraction. The hardness of the films was examined using standard measuring methods.

1. Introduction
Films of transition metal nitrides are widely used as hard, wear resistant coatings on cutting tools. Titanium forms stable compounds with nitrogen, namely, ε-Ti2N phase (tetragonal crystal lattice), as well as δ-TiN phase (fcc crystal lattice), the latter being one of the most popular materials in this area of application. Tungsten and nitrogen form hexagonal and cubic crystal lattices of WN and W2N compounds. Films of these two materials have been most frequently produced by physical vapour deposition (PVD), and by magnetron sputtering.

In this work we present results on studies of the physical characteristics and mechanical properties of titanium nitride and tungsten nitride films deposited by reactive magnetron sputtering. The purpose of this study is to establish the deposition conditions that lead to in-situ synthesis of thin TiN and W2N films with desired characteristics: composition, phases, microstructure, adhesion, etc. The substrate temperature and the reactive gas (nitrogen) supply to the surface of the growing film are among the principal parameters governing the characteristics and properties of the films. We intend to continue this work in the direction of forming multilayer structures of these two materials. Multilayer coatings

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4 To whom any correspondence should be addressed.
of alternatively ordered thin films of transition metal nitrides with nanometric thickness possess hardness higher than that of single films. Different physical mechanisms were proposed to explain this effect, the most likely one being the dislocation blocking at interfaces of the individual layers. The term “composite hardness” has been introduced in the literature [1]. Multilayer structures with improved mechanical properties have been obtained by different PVD methods [2-5]. The best results have been achieved at thickness periods lower than 20 nm [6-8].

1. Experimental
The films were deposited in a specially designed high vacuum system supplied with four magnetron targets of pure metals suitable for deposition of complex metal nitrides. Targets of Ti (99,8% purity) and W (99,65% purity) with diameter of 100 mm and thickness of 5 mm and 1 mm, respectively, were clipped on water-cooled target holders. The magnetron discharge in Ar and mixed Ar/N₂ atmosphere were utilized for the two technological regimes: surface pre-treatment (cleaning of the substrates immediately prior to deposition) and films deposition. The substrate holder can be heated up to temperature of 500 °C. The films were deposited on substrates of tool steel R18 and sintered hard alloy KM1. Apart of these substrates, other substrates appropriate for analytical studies and thickness measurements were also used: cleaved NaCl for TEM and ED observations, Si wafers for AES analysis, glass for thickness measurements.

The process parameters for the two regimes are presented in tables 1 and 2.

| Discharge gas | Discharge pressure, Pa | Discharge voltage, V | Discharge current, A | Substrate temperature, °C | Treatment time, s |
|---------------|------------------------|----------------------|----------------------|----------------------------|-------------------|
| Argon         | 4.0                    | 1200                 | 0.1                  | 300 - 320                  | 600               |

Table 1. Substrates pre-treatment parameters.

| Film Material | Process pressure, (N₂/Ar), Pa | N₂ partial pressure, Pa | Discharge Voltage, V | Discharge current, A | Deposition temperature, °C |
|---------------|--------------------------------|-------------------------|----------------------|----------------------|--------------------------|
| TiN           | 1.2 10⁻¹                        | 4.5 10⁻¹                | 460                  | 1.0                  | 300                      |
| W₂N           | 1.2 10⁻¹                        | 8.0 10⁻²                | 580                  | 0.8                  | 308                      |

Table 2. Film deposition parameters.

The adhesion measurements were performed by a stretch machine working in a “normal stretch” mode. The stretch speed can be varied from 15 to 500 mm/min. The adhesion was calculated by the stretch force causing the unsticking (destruction) of a film with a certain area from the substrate. This method gives a quantitative estimate of the adhesion with accuracy within 10 %.

The composition of the TiN films was investigated by Auger electron spectroscopy (AES). The AES analysis was performed in a derivative mode by a cylindrical mirror analyzer. Argon ion beam was used for cleaning of the film surface.

The microstructure and the crystallization trend of the films were studied by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) using a Philips 400 electron microscope. The films were deposited on fresh fractured surfaces of NaCl crystals.

Vickers hardness was measured by a Fischerscope H100 nanotester loaded with 100 mN.

3. Results and discussion
The thickness of the TiN and W₂N films was measured by a TalysStep device. The respective deposition rates of these films were then calculated from the measured thickness and deposition time. The deposition rates of TiN and W₂N films were almost the same, 0.16 nm.s⁻¹. The adhesion measurements were carried out with TiN and W₂N films with thickness about 300 nm and 55 nm, respectively. The adhesion of TiN and W₂N films to substrates of tool steel R18 and sintered hard alloy KM1 was measured in dependence on two process parameters, nitrogen partial pressure and substrate temperature. The dependences are shown in figures 1 to 4.
The results show that at low partial pressures the adhesion is very weak. This is probably due to incomplete nitriding and formation of unstable solid solutions or compounds poorly bonded with substrate material at deposition temperature of 300 °C. This is more pronounced for tungsten nitride. The material synthesized was actually pure tungsten accumulated as powder on the surface so that it could be easily erased. Coatings of tungsten nitride with black color characteristic for W₂N and high adhesion started to form at nitrogen partial pressures above 7.10⁻² Pa. At higher values of the nitrogen pressure or in a discharge entirely sustained by nitrogen, brown coloured WN films were synthesized. These films possess worse mechanical properties and they do not present practical interest. Thus, it was experimentally established that the nitrogen partial pressure intervals for the formation of highly adhesive W₂N and TiN coatings are from 6 to 9.10⁻² Pa and from 4 to 7.10⁻³ Pa, respectively.

The adhesion increase as the substrate temperature is raised can be the result of two factors. The first one is that the higher temperature contributes to better surface cleaning prior to deposition, while the second one concerns the nucleation process: the higher temperature enhances the interaction of
incoming particles to the substrate surface in the initial stages of the film growth. The results show that temperatures below 200 °C are not sufficient for good adhesion of the films to substrates of steel R18 and hard alloy KM1. The favorable temperature region is from 300 to 350 °C, just below the annealing temperature of the materials.

The composition of the TiN films with the highest adhesion was evaluated by quantitative AES analysis. The AES spectra were recorded after ion cleaning of the film surface. The quantification of the TiN film composition was done by a comparative analytical approach [9] because the use of reference values of the relative sensitivity factors is not reliable due to peaks overlapping of the main Ti and N Auger transitions. Our evaluation gives nearly a stoichiometric composition of TiN films with an uncertainty of 15 %.

The TEM observations show that the TiN and W2N films are polycrystalline and homogeneous with uniformly distributed nano-crystals varying in size from 30 to 50 nm for TiN and 50 to 100 nm for W2N films. According to the SAED patterns, there exists some tendency towards texturing for the TiN films. The SAED patterns of W-N films confirm the presence of a W1N nano-sized polycrystalline phase.

The hardness of the two types of materials was measured at multiple points on the films thick enough to eliminate the influence of substrates on the accuracy of the results. The thickness of TiN films was 1000 nm and that of W2N was 400 nm. The averaged hardness values were 18400 MPa for TiN and 10900 MPa for W2N. For both thin film materials, the hardness is 10 % lower than that of the respective bulk materials, 20500 MPa for bulk TiN and 12200 MPa for bulk W2N, according to Samsonov’s data [10].

4. Conclusion
Optimization was successfully performed of the process parameters involved in reactive magnetron sputtering deposition of thin films of TiN and W2N with high adhesion to substrates of practical interest, tool steel and sintered hard alloy. Due to the two-step preparation process used, this was achieved at relatively low temperatures and films with desired compositions, phases and mono-dispersed polycrystalline microstructure possessing high hardness were synthesized. The results obtained in this study for single layer coatings of TiN and W2N are very promising for a further development of this work toward deposition of complex multilayer coatings of these two materials.

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