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Influence of technological parameters on the mechanical properties of titanium nitride films deposited by hot target reactive sputtering

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Abstract. The impact of the discharge current density and nitrogen flowrate on the mechanical properties of titanium nitride films deposited by reactive magnetron sputtering of a hot target was studied. It was found that the films deposited at the highest discharge current density have the highest hardness and modulus of elasticity. These films have a texture with a significant predominance of the peak corresponding to the [111] direction in a face-centered cubic lattice of TiN.

Titanium nitride (TiN) keeps leading positions among nitrides of transition metals synthesized as films or coatings [1–3]. Having high electrical conductivity TiN films possess high adhesion, hardness and chemical inertness, and they are used as decorative, wear-resistant and corrosion-resistant coatings to modify the metal surface against fretting corrosion. These films are also applied in the silicon technology as the diffusion barriers for aluminum and copper metallization in production of MOS transistors, ohmic and rectifying contacts. Recently, high-power reactive sputtering including hot target sputtering [4–7] has become the most popular method for the synthesis of TiN films and coatings.

This paper presents a study on the influence of the discharge current density and nitrogen flowrate on the mechanical properties of the titanium nitride films deposited by reactive magnetron sputtering of a hot target.

The films are made in a vacuum chamber with a volume of $7.8 \cdot 10^{-2}$ m^3 equipped with a flat dc magnetron with a titanium target of 130 mm in diameter. The hot target mode is provided by fixing a 1 mm thick titanium disk with a gap of 1 mm on a 4 mm thick copper plate cooled by running water. The residual pressure in the chamber did not exceed 10^{-2} mTorr. Sputtering was carried out in an argon and nitrogen environment at a pressure of p_{Ar} = 1 mTorr, a nitrogen flowrate of 2–6 cm^3/min and a discharge current density of 14 and 33 mA/cm^2. The measurement of the mechanical properties (nanohardness and modulus of elasticity) was performed by the nano-hardness tester “NanoScan-4D” using the nanoindentation method. X-ray phase studies of the films were carried out on the X-ray powder diffractometer D8-Advance “Bruker” (CuK$_\alpha$ radiation, 40 kV operating voltage at a current of 40 mA).

Analysis of the measurements of nanohardness and the Young’s modulus of films revealed that the nitrogen flowrate has an impact on the above properties, and this impact cannot be expressed functionally. The relationship is shown by scattering the dependences $H(d)$ and $E(d)$ using the highly simplified qualitative form of the dispersion analysis [8].

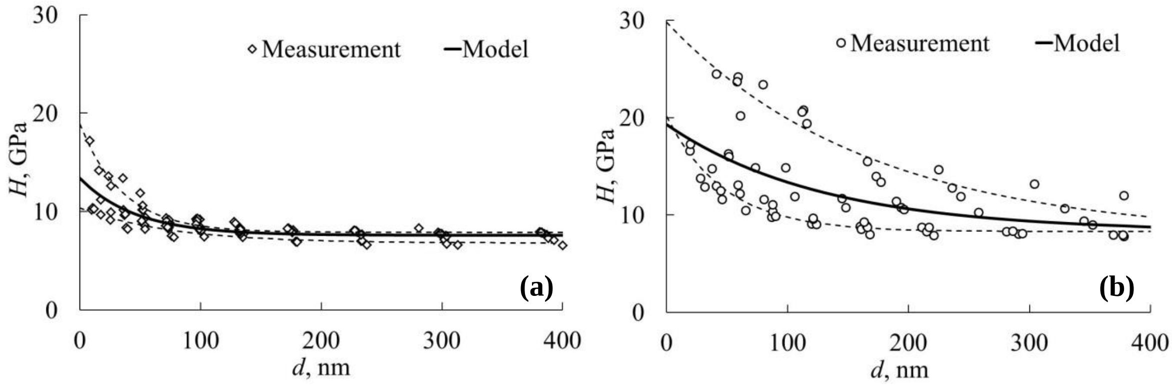

Figure 1. Nanohardness of TiN films deposited at a nitrogen flowrate in the range 2–6 cm^3/min and a current density (mA/cm^2): **(a)** – 14; **(b)** – 33. Points show the measurement results when the indenter is immersed in depth *d*, solid lines are approximated

The samples were combined into two groups deposited at different current densities. The results for each of them, shown in figure 1 by the points, were considered as measurements performed on one sample. The solid lines in figure 1 reflect the approximation of the experimental data using the formula

$$H(d) \approx a_H + b_H \exp\left(-d/c_H\right), \qquad (1)$$

with a_H, b_H and c_H model parameters calculated by the least square method.

The dashed lines in figure 1 outline the ranges of nanohardness variation in each group of samples. They are described by the expressions of the type (1) but with other sets of parameters. They were calculated based on the measurements of individual samples having the largest and smallest nanohardness in a given batch. The results for the modulus of elasticity, which were obtained similarly using expression (1) are shown in figure 2.

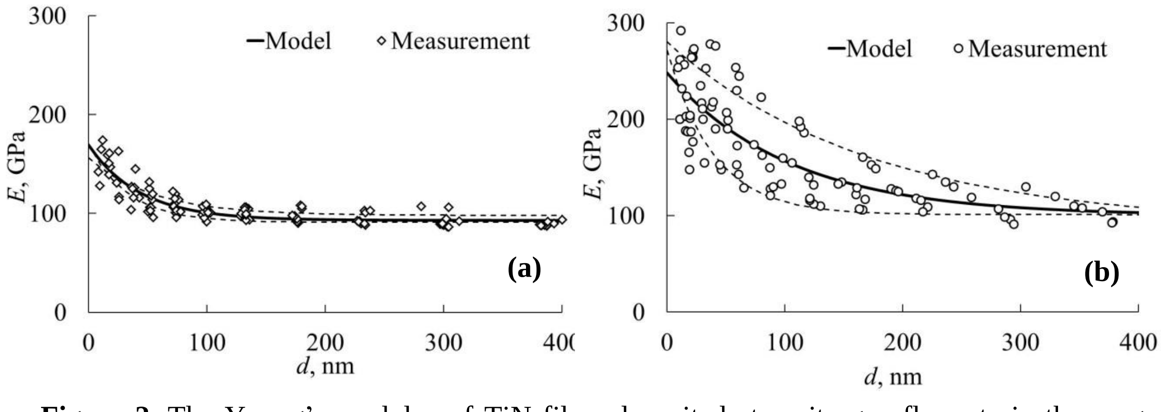

Figure 2. The Young's modulus of TiN films deposited at a nitrogen flowrate in the range 2–6 cm^3/min and a current density (mA/cm^2): **(a)** – 14; **(b)** – 33. Points show the measurement results when the indenter is immersed in depth *d*, solid lines are approximated

Thus, figure 1 and 2 reflect the effect of nitrogen flowrate on the mechanical properties of titanium nitride films. This influence appears in the scattering of experimental points. It is insignificant under the lowest current density (figure 1(a) and 2(a)) that indicates an insignificant impact of nitrogen flowrate on the properties of the films. The width of each scattering region increases under a larger current density (figure 1(b) and 2(b)) substantially. This effect is related to the increasing influence of the flow rate of the reactive gas on the parameters of the films.

The existence of the above influence is supported by the results of X-ray phase analysis. Two series of X-ray patterns corresponding to two groups of films deposited at different current densities are shown in figure 3.

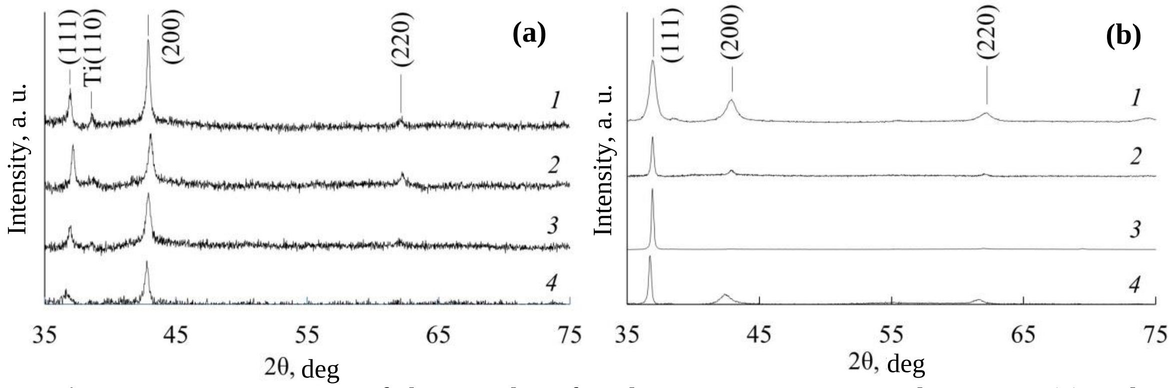

Figure 3. X-ray patterns of the samples after deposition at a current density 14 **(a)** and 33 **(b)** mA/cm^2. Nitrogen flowrate (cm^3/min): *1* – 2; *2* – 3; *3* – 4; *4* – 6.

All studied films had a crystalline phase. Strongly pronounced peaks were observed on the X-ray patterns at 2θ ~ 36.7°, ~ 42.6° and ~ 61.8°, corresponding to the face-centered cubic lattice TiN (space group of symmetry Fm-3m (225)), with the preferred orientation of the planes (111), (200) and (220). Moreover, the intensity ratio of the peaks on the X-ray patterns $I(111)/I(200) < 1$ at a current density of 14 mA/cm^2, which corresponds to the X-ray powder diffraction pattern (card 01-087-0630). In addition, they contain metallic titanium at a flowrate of nitrogen less than 4 cm^3/min. This is indicated by the peak at 2θ ~ 38.5° corresponding to the cubic lattice Ti with the predominant orientation of the plane (110), referring to the transformation group Im-3m (229) (card 00-044-1288). The films are textured (($I(111)/I(200) > 1$) in the [111] direction and there is no metal phase a current density of 33 mA/cm^2. At the same time, an increase in nitrogen flowrate leads to a decrease in the width of the main peak (111), which indicates an increase of the crystallite size.

Therefore, based on the analysis of X-ray patterns it can be concluded that the nitrogen flowrate has stronger impact on the film properties when the current density is higher.

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