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STRUCTURAL, OPTICAL AND DECORATIVE PROPERTIES OF TaN_x THIN FILMS PREPARED BY REACTIVE MAGNETRON SPUTTERING

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Abstract: *Within the frame of this work the tantalum nitride - TaN_x thin films were deposited by d.c. reactive magnetron sputtering. These films have been characterized in terms of optical, decorative and structural properties taking into account the influence of reactive gas flow variation (N_2) during the deposition procedures. Different colours were obtained, from metallic-like to silver-like tones and they are directly correlated with the deposition conditions, respectively, with the structure. The structure was assessed using X-ray diffraction. The results showed clear changes of phases in the films from typical fcc TaN structure to stoichiometric fcc (face-centered cubic) TaN and amorphous TaN.*

Key words: *tantalum nitride, reactive sputtering, structure, optical properties, decorative aspect.*

1. Introduction

Metal nitrides have various unique properties such as high hardness, high melting point, high chemical and temperature stability, high thermal conductivity, low electrical resistivity, good oxidation resistance [9], which have gained considerable interests [14]. Due to these attractive properties, metal nitrides have extensive applications in many areas such as the industry of different categories of cutting tools, the electronics field, the biomedical domain, decorations [10], [7], [22].

In the family of metal nitrides, tantalum nitride (TaN) has become a promising material to be used as diffusion barrier in Cu-based metallization, wear and corrosion-resistance material in mechanical industries, high-speed thermal printing head for facsimile machinery as well as thin film resistors [2], [12], [13].

This wide range of interesting applications has led to numerous efforts to synthesize tantalum nitride layers, using a number of different techniques, including chemical vapour deposition (CVD), atomic layer deposition (ALD), ion beam assisted deposition (IBAD) [8], [2].

The reactive d.c. magnetron sputtering, - PVD technique, which is studied here, has the advantage over several other techniques listed above that it can be easily scaled from small sized laboratory targets to industrial applications on large area substrates such as the coating of architectural glass.

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To obtain TaN_x films with tailored properties, however, one of the most challenges is to control the implementation of nitrogen into the growing film. Besides the fact that sputter deposition technique in general leads to either a pure amorphous microstructure or a mixture of crystalline phases with amorphous fractions, film synthetization is further complicated as many different equilibrium and non-equilibrium phases exist for TaN_x. According to Ta-N equilibrium phase diagram [4] a lot of phases could be developed, depending on the nitrogen content. Relating to this, it can be explained the large number of reference diffraction patterns for TaN_x and their complicated identification, as little changes in the nitrogen content in the film. Despite all these studies reported in literature, detailed investigations are needed combining a large variety of different analysing techniques to determine important features of TaN_x films deposited under comparable conditions [6].

In the present work, we investigate the influence of deposition parameters on the TaN_x film structural, optical and decorative properties. The films have been prepared using different nitrogen flow rates by d.c. reactive magnetron sputtering technique.

2. Experimental Details

The TaN_x films were deposited by d.c. reactive magnetron sputtering system from high purity Ta (99.6 at. %) target onto polished stainless steel substrates - samples (AISI 316) for residual stresses analysis, silicon with a (100) crystalline orientation (for structural analysis) and onto microscopic glass with thickness of 0.95/1.05 mm (for optical characterization).

The films were prepared with the substrate holder positioned at 65 mm from the target in all runs, using a gaseous atmosphere containing argon and nitrogen with a base pressure in the deposition chamber of $5x10^{-3}$ mbar. The deposition temperature was kept constant at 100 °C. Before each deposition the substrates were subjected to an etching process, using pure argon (8 sccm) and a pulsed current of 0.5 A (T_{on} = 1536 ns and f = 200 kHz) for 600 s.

The deposition processes supposed 4 variants of experimental conditions in terms of the variation of the reactive gas flow (N_2). It has been varied from 4.5 to 17.5 sccm (4.5, 9, 12.5, 17.5 sccm); the substrate bias voltage was maintained constant at −50 V and the deposition time was kept constant at 3600 s for all the samples.

During the deposition processes, the substrates were heated at T_s = 100 ^{0}C using d.c. bias grounded, with a current of 1 A. Argon flow was kept constant at 7 sccm.

Constant temperature was monitored with a thermocouple placed close to the surface of the substrate holder. The experimental parameters are presented in Table 1.

Table 1

Experimental parameters used for TaN_x films

Samples	N_2 flow [sccm]	Deposition time [s]	Thickness [nm]
R2	4.5	3600	1025.5
R4	9	3600	947
R5	12.5	3600	947.5
R8	17.5	3600	899.5

The characterization of film's colour was obtained with a commercial MINOLTA CM-2600d portable spectrophotometer (wavelength range 400-700 nm). Colour specification was computed under the standard CIE illuminate D65 and represented in the CIE LAB 1976 colour space. This equipment is equipped with a 52 mm diameter integrating sphere and 3 pulsed xenon lamps. The observer was placed at a 10º angle. The reflectivity was measured using a Shimadzu UV-2501 spectrophotometer.

The thickness of the deposited samples was obtained by "Ball Cratering" technique using a Calotest System - CSM Instruments.

The crystallographic structure was investigated by X-ray diffraction (XRD), using a Philips PW 1710 diffractometer in a Bragg-Brentano θ-2θ configuration.

3. Results and Discussion

3.1. Deposition rate and thickness

In function as the variation of reactive gas flow, the thickness values of the produced coatings have been increased or decreased. It was observed that for increasing nitrogen gas flow from 4.5 sccm to 17.5 sccm, the thickness of the deposited layer decreased from 1025.5 nm to 899.5 nm.

The average deposition rates of deposited films were obtained from the ratio between the thickness of the films and the deposition time. According to this aspect, Figure 1 shows the dependence between the variation of reactive gas flow, and the deposition rate of TaN_x films. From this dependence it can be observed that the evolution of the deposition rate as a function of reactive gas flow can be divided in three different regimes.

In the first regime (I), corresponding to the samples deposited with the reactive gas flow below 4.5 sccm, the deposition rate show a linear decrease, which varied from $2.85x10^{-2}$ nm/s to $2.64x10^{-2}$ nm/s.

In the second regime (II), there is a stabilization of the deposition rate roughly $2.64x10^{-2}$ nm/s with the increase of the reactive gas flow (from 9 sccm to 12.5 sccm).

Coating from 3rd regime (III), deposited with the highest reactive gas flow (17.5 sccm), present the lowest value of the deposition rate (~$2.5x10^{-2}$ nm/s) corresponding to the R8 sample with the smallest value of the thickness (~899.5 nm).

Regarding the available literature about this deposition rate variation issue, and based on Safi's hysteresis behaviour of reactive magnetron sputtering [17], Spencer et al. [18] proposed a conceptual model of the reactive sputtering process, in which the deposition rate variations were the motive of extensive analysis. This model describes the effects of raising the reactive gas partial pressure at the target and the substrate.

At the target, the low reactive gas flow allows the cleaning sputtering rate overcomes the poisoning rate, and hence a metal flux arrives to the substrate, inducing higher deposition rates. A partially poisoned surface of the target results when the poisoning rate is higher than the cleaning rate. Since the sputtering yield of metal atoms from a poisoned surface is less than that from a pure metallic target, the metal flux from the target decreases with increasing reactive gas partial pressure, decreasing the deposition rate until the entire target is poisoned. At the substrate, for low gas partial pressures, the formation rate of the film is limited by the impact rate and utilization of the reactive gas atoms and hence the films are metal-rich, or sub-stoichiometric.

The increase of the partial pressure of the reactive gas induces an increase of the impact rate of the reactive gas atoms and hence, the reactive gas content of the film increases with the reactive gas partial pressure until a "gas-rich", or over-stoichiometric, film is deposited [3].

Taking this into account, at the low values of the reactive gas flow, almost all the available reactive gas is bettered at the condensation sites and as a result, the deposition rate is relatively high, and the deposited films presented surface appearances typical of metal-rich type films (from metallic to silver colours).

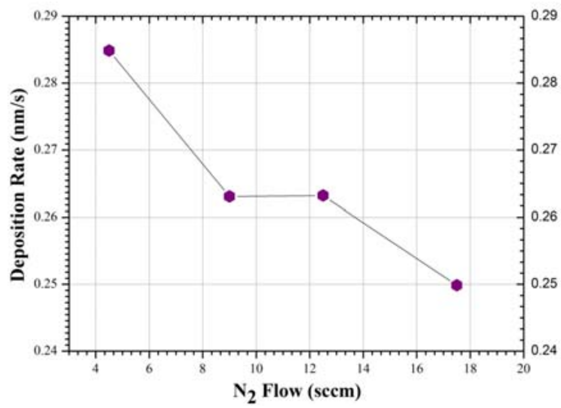

Fig. 1. *Deposition rate of the produced TaN_x coatings as function of the gas flow rate*

3.2. Structural Properties

Compared to well-known titanium nitride (Ti-N), in which the only two compound phases are Ti_2N and TiN [19], Ta-N thin films have various phases, which are relatively unexplored. In addition, to the equilibrium phases of Ta-N system are reported to be bcc α-Ta, solid-solution α-Ta(N), hexagonal γ-Ta_2N, and hexagonal ε-TaN while the metastable phases are tetragonal β-Ta, bcc β-TaN, hexagonal Ta_2N, hexagonal WC structure θ-TaN, cubic B1 NaCl-structure δ-TaN, hexagonal Ta_5N_6, tetragonal Ta_4N_5, and orthorhombic Ta_3N_5 [15]. The chemical and the phase compositions of such a TaN_x system critically depend on the technique and deposition parameters [5].

Thus, reactive sputtering is a very common way to deposit TaN_x. Depending on the ratio of Ar and N_2 flow rates, chamber pressure and power density, the atomic ratio of Ta versus N in TaN films can be very different. This will result in different microstructures, thermal stability and other material properties. Kang et al. [11] have studied the effects of varying N_2 flow rates (0 to 20 sccm) on the structural properties of sputtered TaN films. They found that for a fixed Ar flow rate, the TaN films exhibit a single fcc structure (ratio of Ta: N ≈ 1: 1, for a N_2 flow rate between 8 and 10 sccm). Valleti et al. [21] also investigated the structural properties of TaN_x films obtained by reactive sputtering. The different phases have been prepared by varying the nitrogen (N_2) to argon (Ar) gas ratio in the range 0.04-0.30. The grown TaN thin films are found to contain mainly cubic-$TaN_{0.1}$, orthorhombic-Ta_4N, orthorhombic-$Ta_6N_{2.5}$, hexagonal-$TaN_{0.8}$ and cubic-TaN. The high hardness of ~61.9 GPa corresponding to orthorhombic Ta_4N phase. Thus, we can say that a several different phases may exist in the as-deposited TaN_x films and depending on the nitrogen content. It indicates that the structural properties of TaN_x depend critically on the specific chamber structure of a sputter machine and sputter conditions such as the N_2/Ar ratio.

The experimental results in terms of structural features of as-deposited TaN_x (on silicon substrates) thin films are presented in Figure 2. In comparison with the equilibrium situation presented in [11], the obtained results revealed that the diffraction pattern exhibits a slight decrease of scattered intensities of <110> and <200> lines, when the reactive gas flow was increased. For value of N_2 flow (4.5 sccm) we can see a changes of the <011> to <220> diffraction peaks of the typical fcc TaN structure.

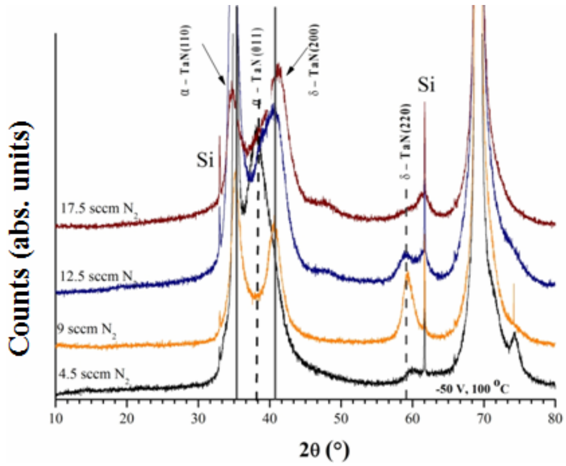

Fig. 2. *XRD patterns for TaN_x films for different values of nitrogen flow*

Continue to increase the flow of N_2 (at 9 sccm) leading to formation of stoichiometric TaN of *fcc*-type NaCl with <200> and <220> orientations. Increasing continued concentration of N_2 (from 12.5 to 17.5 sccm) leads to the decrease height of the peak of TaN with <220> orientation, indicating a tendency to amorphous, probably due to higher nitrogen content.

Generally, all the d.c. sputtered TaN thin films deposited under these conditions show strong <110> preferred orientations compared to TaN_x thin films, where the <200> intensity is the highest as the N/Ta ratio approaches to stoichiometry. In the literature, the <200> preferential orientation is also associated to high nitrogen partial pressures [1].

Although <200> planes represent the most stable planes resulting from the minimum surface energy, the film growth by DC sputtering is highly dynamically controlled, so that <110> planes, with faster growth rate, dominate. This is the case of this work for the films prepared with low gas flows [20]. One possible explanation of the orientation change from <110> to <200> orientation within first regime is that the continuous approach of composition towards stoichiometric condition brings the system closer to its thermodynamically stable condition, and thus favouring the <200> growth.

M. Ohring [16] stated that the change from <110> to <200> orientation can also be the result of distinct growth modes, such as the microstructure changes according to Thornton's zone model. In fact, the increases in flow rate, and the consequent changes in the deposition rate, are inducing these different morphological growth features and textures.

These <110> and <200> orientations revealed a significant decrease for the sample prepared with the highest gas flow (17.5 sccm).

The growth rate of grains with <200> orientation is then inhibited further due to the lattice distortion or interstitial site occupancy by the excess nitrogen atoms. In fact, for an *fcc* NaCl structure, growth of <200> orientation needs more coalescent energy than <110> orientation and therefore, for films prepared with the highest flows and developing this *fcc*-type structure (first regime), crystallization becomes difficult and the <200> orientation tends to decreased from the X-ray pattern.

3.3. Reflectivity and decorative aspects

The reflectivity spectrum of the produced films is shown in Figure 3 for all samples.

The coatings with highest values of the reflectivity correspond to coatings with stoichiometric fcc TaN structure and are the sample deposited with lower value of nitrogen flow (4.5 sccm), varying from around 48% in the violet limit of the visible region of the spectrum, to around 55% in the red limit of the spectrum.

It is a behaviour that is similar to the one obtained with metallic samples.

The samples produced with 9 sccm and 12.5 sccm of gas flow presented an increasing reflectivity, indicates also a metallic behaviour.

At the same time, the samples produced with the highest gas flows (17.5 sccm) presented amorphous structure and show lower reflectivity, because the visible region of the spectrum varying from around 34% to 45% indicating a silver behaviour.

Regarding the decorative aspects, we can say that the variation of the colour coordinates of the CIE Lab colour space as function of the nitrogen flow is represented

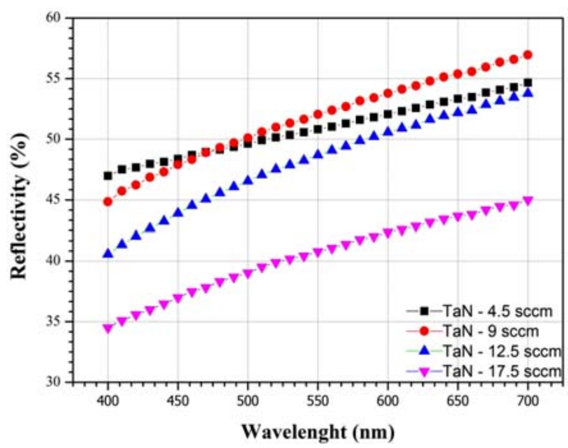

Fig. 3. *Reflectivity plot of the TaN_x coatings as function of the wavelength*

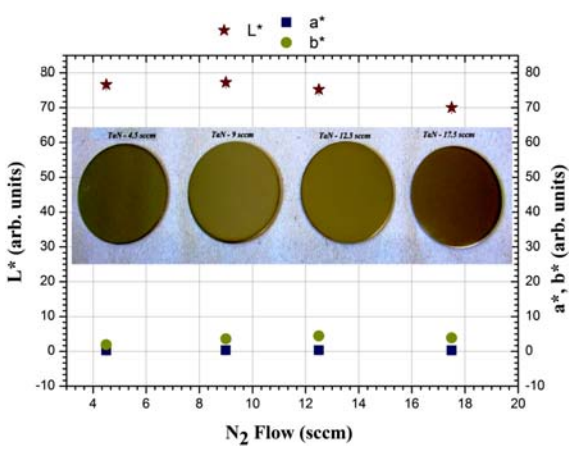

Fig. 4. *Variation of the colour coordinates, $L^*a^*b^*$, of TaN_x coatings as function of gas flow*

in Figure 4. All samples have a relatively high values of brightness (L^*), because are determined by interactions between incident photons and free electrons.

When the flow rate increases from 4.5 sccm to 17.5 sccm the values of a^* and b^* show no significant changes, but the colour were changes from metallic to silver and they are directly correlated with the deposition conditions and, as consequence, with the structure and composition.

4. Conclusions

TaN_x thin films were deposited by reactive d.c. magnetron sputtering, in a home made deposition system, from a pure tantalum target and nitrogen as reactive gas by varying the reactive gas. These films were deposited onto high - speed steel, stainless steel, glass, and crystal silicon <100> substrates.

The structural, decorative and optical properties of TaN_x films were investigated as function of deposition parameters (reactive gas flow - N_2). The nitrogen flow rate has varied from 4.5 sccm to 17.5 sccm, the substrate bias voltage was maintained constant at −50 V. Also, the N_2 flow rate is found to be an important parameter in controlling the film properties.

Structural aspects of all the produced TaN_x revealed a strong dependence by the variation of reactive gas flow (nitrogen content in the films). Thus, the TaN_x crystalline films were obtained when the nitrogen gas flow was smaller than 12.5 sccm and amorphous TaN_x films were obtained when the nitrogen gas flow was larger than 17.5 sccm.

In the film prepared by high nitrogen flow, the film thickness was controlled by the position of the substrate. On the hand, when the film had a relatively large thickness of 947.5 nm, the <110> and <200> preferred orientation was observed, including another two weak peaks namely <011> and <220>. On the other hand, when the film had a relatively small thickness of 899.5 nm, only the <110)> respectively <200> diffraction peaks was observed.

In terms of the optical analyses were obtained different colours, from metallic-like to silver-like tones and they are directly correlated with the deposition conditions, respectively, with the structure.

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