THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
Nº. 1 - 2017, ISSN 1453-083X

STUDIES AND RESEARCH ON THE PRODUCTION OF TiO_2 AND TiN THIN FILMS BY ASSISTED PHYSICAL VAPOR DEPOSITION MAGNETRON PROCESS

Simona BOICIUC, Petrică ALEXANDRU
"Dunarea de Jos" University of Galati
e-mail: simonaboiciuc@yahoo.com

ABSTRACT

The experimental research carried out in this paper aims at obtaining thin films of TiO_2 and TiN and at characterizing them in terms of morphology, structure, transparency and electrical properties. The films were obtained using a PVD device of sputtering coating, consisting of a vacuum chamber with a capacity of 2 liters, a planar magnetron with ferrite magnets (ϕ40 x 22 x 9), neodymium (ϕ15 x 8), a vacuum pump with sliding blades, a variable DC source voltage of 100-600 volts. The atmosphere used to maintain the plasma during deposition was oxygen and then N_2 rarefied within a pressure range between $3 \cdot 10^{-2}$-$8 \cdot 10^{-3}$ mbar at a flow rate of 1.4 cm^3/min. It was found that the structures and properties of the films are influenced by the parameters used and their color depends on the working atmosphere, the deposition parameters and the layer stoichiometry.

KEYWORDS: TiN, TiO_2, d.c. magnetron, electrical and optical properties

1. Introduction

Thin films are widely applied in many fields of science and technology. The most important applications are registered in microelectronics, optoelectronics and cutting tools industry.

The films of Ti, TiN, TiO_2 can be achieved by physical methods such as PVD (sputtering under DC or RF modes, evaporation with electron beam, thermal evaporation) or by chemical methods such as sol - gel, anodic oxidation, spray pyrolysis, CVD.

There are several PVD deposit methods and choosing one of them depends on: the requirements for the thin layer properties, the maximum temperature the substrate can withstand, procedure compatibility with the processes applied to the substrate before and after deposition and last but not least the production costs, efficiency and large-scale manufacture of the products.

Titanium has superior characteristics compared to other metals, such as low density (4.5 g/cm^3), high melting temperature (Tt = 1660 °C), low coefficient of thermal expansion, high electrical resistivity, elasticity modulus twice lower than that of iron and steel, very low thermal conductivity and excellent paramagnetism.

The hardness of titanium is relatively low (100-225 HB) and is directly proportional to the increase of the impurity concentration. Soluble impurities (interstitial H, C, N and O_2 by substitution) contribute to the increase of titanium hardness, increasing the mechanical strength as well, while plasticity and corrosion resistance decrease [1-4].

Titan has two stable allotropes: Ti α (stable up to 882 °C) with compact hexagonal network/lattice and Ti β (stable between 885-1672 °C) with body-centered cubic network; passing from one phase to another Ti α → Ti β occurs when temperature increases over 882 °C [1-4].

Titanium dioxide (TiO_2) has attracted the interest of many researchers in materials science due to its unique combination of properties: chemical stability, corrosion/photo-corrosion resistance, photocatalytic potential, high dielectric constant (εr ≈ 60-100), high electrical conductivity, sensitivity to UV, favorable energy band, very high refractive index (2.6-2.9), non-toxicity, biocompatibility. These properties make it useful in purifying water and air, in achieving solar cells, photochemical devices, gas sensors (H_2, CO, CO_2, CH_3), capacitors, microelectronic devices, components requiring biocompatible (antibacterial, self - cleaning) properties [1-4].

Thin layers of titanium nitride (TiN) were the first coatings industrially used to increase wear resistance of tools. In the beginning, these layers were

deposited by chemical vapor-phase deposition (CVD). In the 80s industrial-scale deposits began by plasma - assisted physical vapor-phase (PVD). These coatings have been used mainly as a tribological layer for cutting and plastic deformation tools, bearings, seals and as corrosion and erosion resistant layers. TiN is also used as a decorative coating as it possesses excellent infrared reflectance (IR), the reflection spectrum being similar to that of gold, which gives it a golden color [1-4].

TiN crystallizes in the NaCl-type CFC network (a = 4.256 Ä) has a golden color, the density of 5.40 g/cm^3, melting point of 2930 °C, Vickers hardness of 18-21 GPa, the elasticity modulus of 251 GPa, the thermal conductivity 19.2 W/m·°C, thermal expansion of $9.35*10^{-6}$ K^{-1} [2].

TiN oxidizes at 800 °C in atmospheric pressure. The compound is stable at ambient temperature and concentrated at hot acids attack. Depending on the material of the substrate and its roughness, TiN has a coefficient of friction between 0.4-0.9. At low temperatures ~4 K titanium nitride becomes super isolator having resistance to 5 orders of magnitude greater than at ambient temperature [1-4].

Due to the higher biostability of TiN layers, they are used as electrodes in bioelectronic applications in intelligent implants, prosthetic or sensors which must resist to corrosion caused by body fluids, to make medical instruments such as bistoury blades and bone saw. These electrodes have already been applied to sub-retinal prosthesis as well as in biomedical microelectromechanical systems (BioMEMS). TiN thin films are also used in microelectronics as buffer layers (diffusion barrier) to manufacture transistors etc. [1-4].

Film forming can be described through several stages. In the first stage, the atoms sprayed from the target are adsorbed on the substrate surface. Then they diffuse (moving along the surface of the substrate until reaching a stationary position). When adsorbed atoms are grouped, they form nuclei and this stage is called nucleation. Subsequently, these nuclei continue to grow and lead to the formation of a continuous thin film (stage called coalescence).

There are three ways to increase the films based on the interactions between the atoms of the substrate and the deposited atoms: a - 3D island growth (Volmer - Weber); b - 2D layer growth (Frank van de Merwe,) (seen in homoepitaxial growth); c - 3D cluster growth (island) and stratified growth (Stranski - Krastanov) [1-4].

Nucleation and growth mechanisms are even more intense as the power and duration of sputtering deposition are higher.

By increasing deposition temperature, an increase in the roughness and crystallite size occurs.

The most important parameters which may influence the properties of the films are: nitrogen partial pressure, deposition temperature and substrate polarization [4].

The research in this paper is focused on the development of a technology for producing TiO_2, TiN thin films by DC magnetron sputtering process, using oxygen atmosphere and rarified N_2 in a pressure range between $3\cdot10^{-2}$-$8\cdot10^{-3}$ mbar, and on their characterization in terms of morphology, transparency and electrical properties.

2. Experimental conditions

Films were obtained with a PVD installation of sputtering coating, consisting of a vacuum chamber with a capacity of 2 liters, a ferrite magnets planar magnetron (ϕ40 x 22 x 9) neodymium (ϕ15 x 8), a vacuum pump with sliding blade, a variable DC source of 100-600 volts.

As target, use was made of a plate of 99.9% purity titanium, circular diameter of 46.5 mm and thickness of 1 mm.

a. b.

Fig. 1. *Magnetron image: a - without anode; b - with anode glass substrate prepared for deposition*

The support material consisted of glass plates with dimensions of 76 x 25 x 1 mm.

Fig. 1.a illustrates the magnetron with anode and Figure 1.b. the complete picture of the magnetron with anode and glass substrate prepared for deposition.

The installation allows varying the distance magnetron - deposition substrate between 25 and 90 mm and the substrate temperature can be monitored with a chromel-alumel thermocouple.

The atmosphere used to maintain the plasma during deposition was rarefied oxygen in a pressure range between $3 \cdot 10^{-2}$-$8 \cdot 10^{-3}$ mbar and then rarefied N_2 in a pressure range between $3 \cdot 10^{-2}$-$8 \cdot 10^{-3}$ mbar with flow rates of 1.4 cm^3/min.

The microscopic analysis of the obtained films was conducted using an optical microscope Neophot 2 with computerized data acquisition. The transparency of the films was determined with an electronic device that uses a light source and a photoreceptor. Light, after passing through the deposited film, is measured by the photoreceptor and an amplifier and the result is displayed by an analog device.

The electrical properties (resistivity) of the films were measured using the collinear four-point method (probes) using a laboratory facility. In principle, it consists in injecting current through two external points and measuring voltage in two internal points.

The device scheme is illustrated in Fig. 2.

With thin stratures, resistivity is calculated by relation:

$$\rho = \frac{\pi \cdot t}{\ln 2}\left(\frac{U}{I}\right)$$

where: t - film thickness, U - measured voltage, I - current applied.

$$\frac{\rho}{t} = \frac{\pi}{\ln 2}\left(\frac{U}{I}\right)$$ - film surface resistance

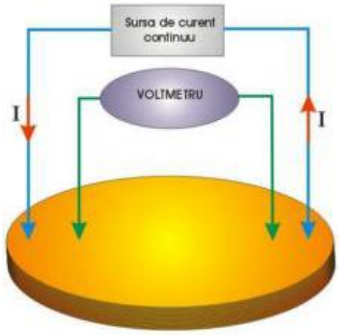


Fig. 2. *Collinear measuring configuration by four - probe method*

The stages of obtaining deposits were:

a. Preparation of the substrate surface.

b. Film deposition by DC magnetron sputtering process.

a. Preparation of the substrate surface

This step consisted in: washing the glass plates (size 76 x 25 x 1 mm) with a special detergent, washing them with water, then with distilled water, ultrasonic cleaning with ethanol followed by drying with compressed air.

b. Film deposition by DC magnetron sputtering process

To obtain the films, a number of regimes were used as presented in Table 1.

Table 1. *Working regimes used in film deposition*

Sample code	Voltage [V]	Current [mA]	Pressure [mbar]	Substrate temperature [°C]	Target-substrate distance [mm]	Deposition time [min]
P1 (Ti) O_2	420	55	5 x 10^{-3}	45	60	60
P2 (Ti) O_2	440	45	1 x 10^{-3}	30	60	120
P3 (Ti) O_2	550	150	5 x 10^{-3}	100	60	30
P4 (Ti) N_2	440	49	1 x 10^{-3}	46	60	180 N_2 ½ of time
P5 (Ti) N_2	450	50	2.5 x 10^{-3}	50	60	60
P6 (Ti) N_2	450	50	2.5 x 10^{-3}	50	60	240
P7 (Ti) N_2	450	50	2 x 10^{-3}	50	60	180

3. Experimental Results

3.1. Microstructural characterization of the deposited films

The macroscopic analysis reveals that the films do not show cracks, are homogenous and adherent as shown in Fig. 3 and 4.

Because of the working atmosphere used (rarefied oxygen in a pressure range between $3 \cdot 10^{-2}$-$8 \cdot 10^{-3}$ mbar, flow rate 1.4 cm^3/min), it is estimated that the film structure corresponding to samples P1, P2, P3 would consist of Ti and TiO_2.

For samples P4, P5, P6, P7 achieved with the addition of N_2, the obtained films have different colors being darker as the duration of maintenance is higher. Because of the working atmosphere used (rarefied N_2 in a pressure range between $3 \cdot 10^{-2}$-$8 \cdot 10^{-3}$ mbar, flow rate 1.4 cm^3/min), samples structure is estimated to consist of Ti and TiN.

The film color depends on the layer stoichiometry, the working atmosphere and the parameters used. It ranged from gray to golden brown (Figure 4).

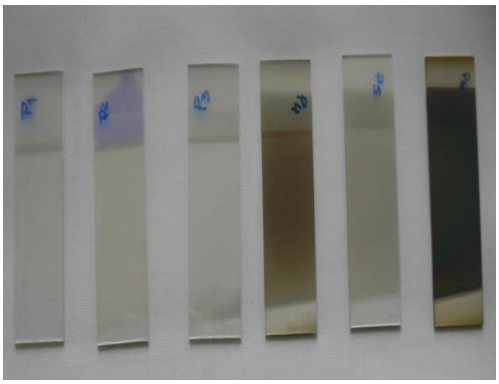
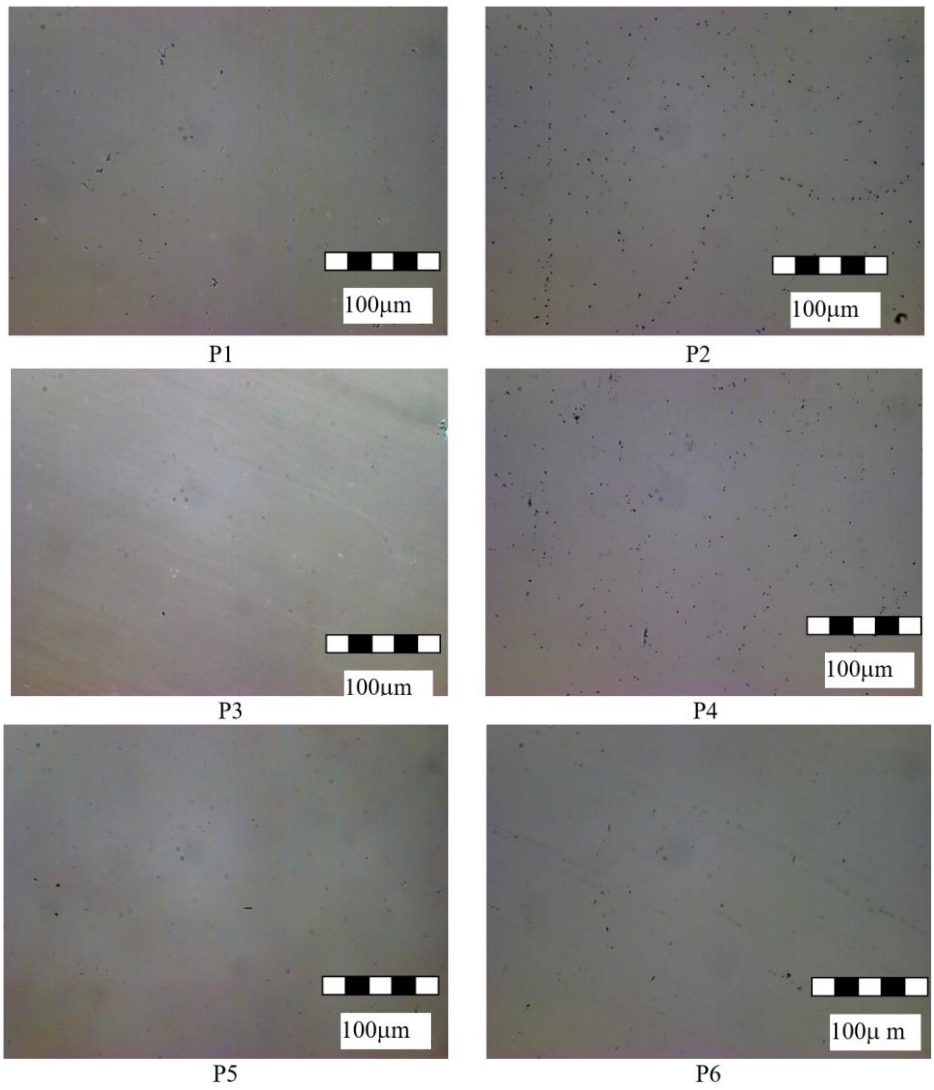
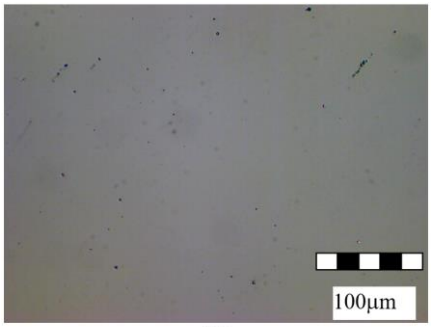


Fig. 3. *Image of films deposited under different regimes*





P7

Fig. 4. *Image of films deposited under different regimes*

3.2. Establishing the optical and electrical characteristics of the deposited films

The films corresponding to samples P1, P2, P3 obtained in vacuum have high transparency of about 97% and the surface resistance could not be determined.

The results of transparency and electrical resistance measurements for samples P4, P5, P6, P7 are shown in Table 2.

Table 2 shows that, with increased deposition time, the surface resistance and transparency decrease. This behavior is due on the one hand to increased deposited film thickness, and on the other hand to oxidation and formation of TiN.

This can be observed on the graphs in Fig. 5 and Fig. 6.

Table 2. *Determining transparency and electrical properties of films*

Sample code	Film transparency	Film surface resistance [Ω]	Deposition time [min]
P4 (Ti) N_2	0.3	2806.19	180
P5 (Ti) N_2	0.6	39534.54	60
P6(Ti) N_2	0.0125	693.36	240
P7 (Ti) N_2	0.08125	3939.13	180

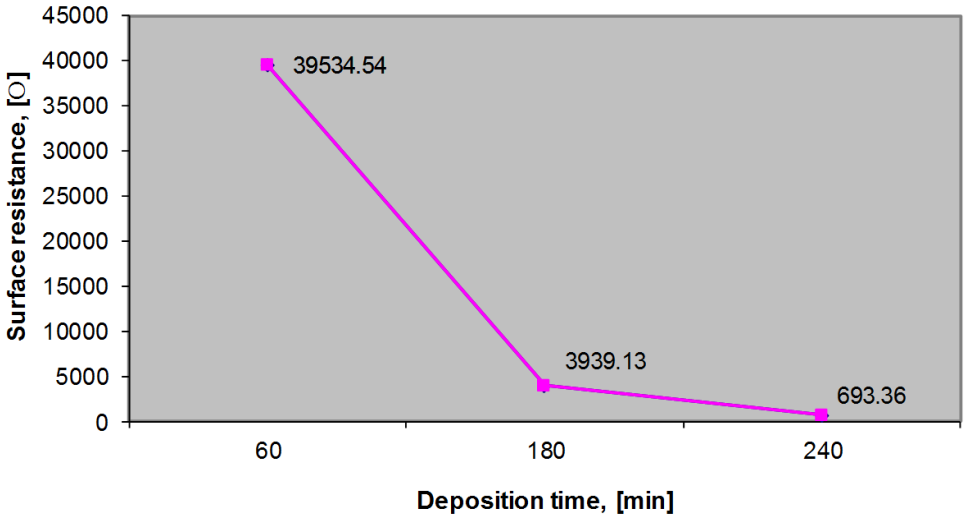


Fig. 5. *Influence of deposition time on the surface resistance of the deposited film*

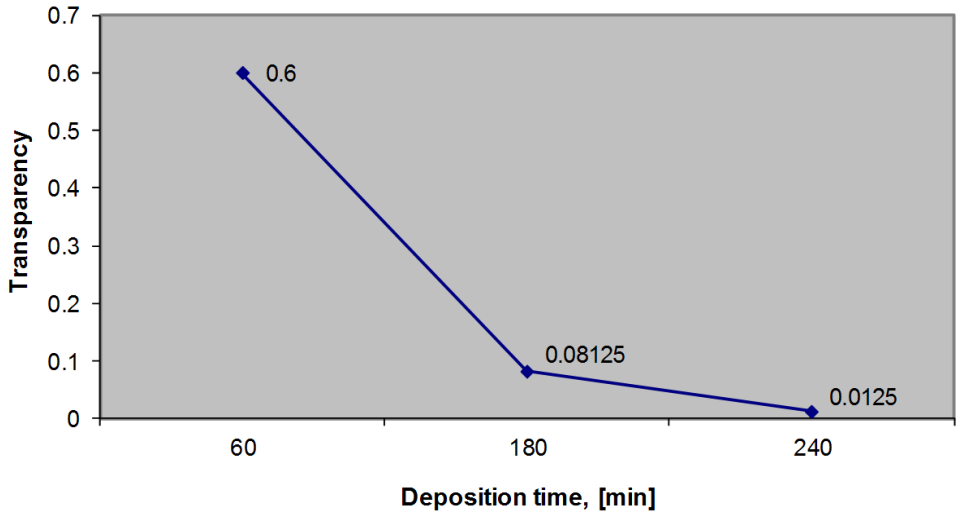


Fig. 6. *Influence of deposition time on the transparency of the deposited film*

3.3. EDX characterization of the deposited film

Figures 7, 8, 9 present the EDX analysis of the film corresponding to samples P2, P5 and P6. It may be noted that with sample P6 where the deposition time was longer, therefore the thickness is higher, the titanium content is higher.

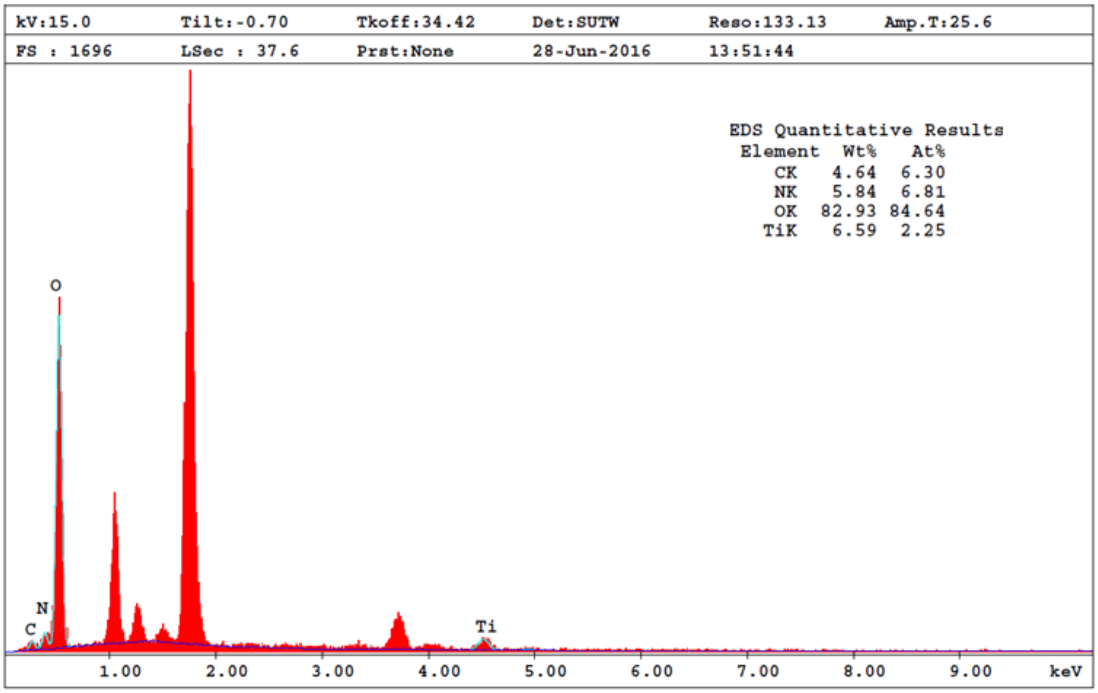


Fig. 7. *EDX analysis of the film corresponding to sample P2*

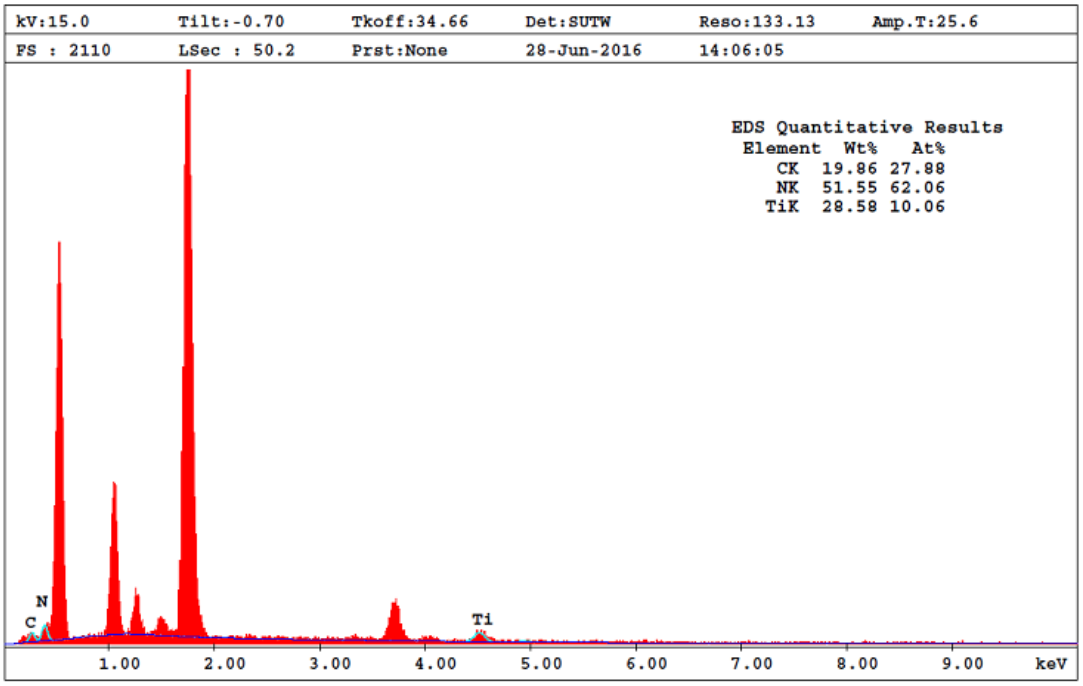


Fig. 8. *EDX analysis of the film corresponding to sample P5*

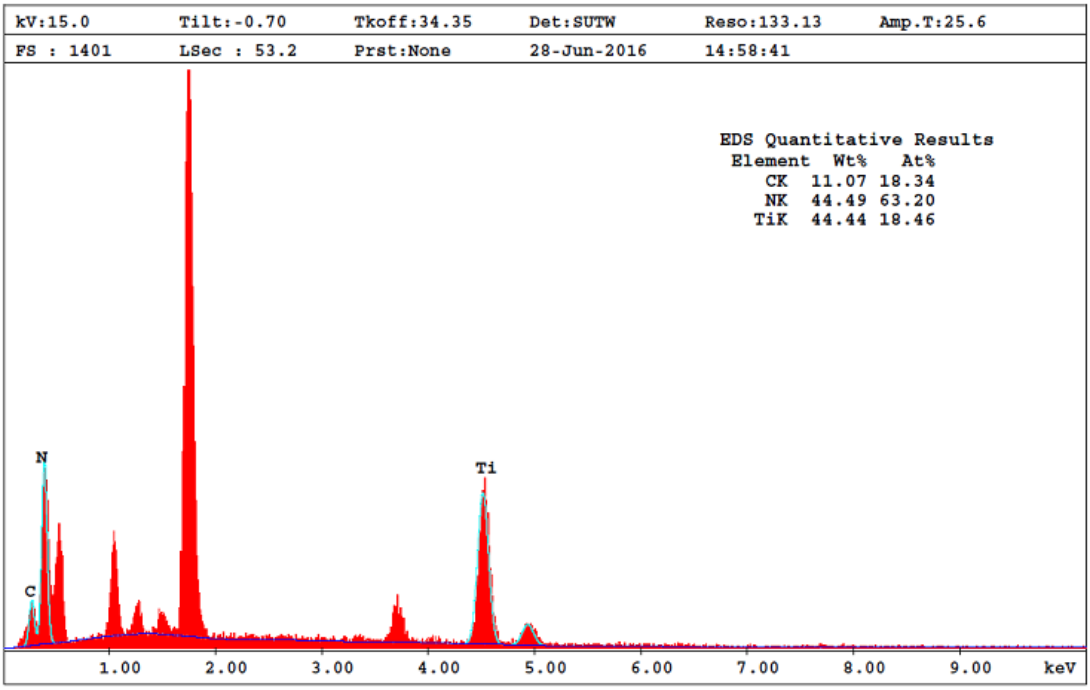


Fig. 9. *EDX analysis of the film corresponding to sample P6*

4. Conclusions

The films of titanium nitride (TiN) deposited by DC magnetron sputtering process, due to its outstanding properties (high hardness, low electrical resistivity, high wear resistance, excellent resistance to corrosion and high thermal stability) are increasingly used in various applications, such as: cutting tools, parts subject to wear and corrosion, microelectronics, decorative layers, diffusion barriers, electrodes in bio-electronics applications, medical devices.

The TiO_2 films are extensively studied as they have excellent photocatalytic, antibacterial (when

exposed to UVA - 320-400 nm) optical, antireflective characteristics.

The experimental research leads to the following conclusions:

- films deposited by DC magnetron sputtering process reveal an economical and simple way of producing coatings with multiple applications;
- it was found that the deposition modes are quite unstable in that there is a tendency to increase voltage and decrease current followed by plasma extinction;
- films were obtained using as atmosphere to maintain plasma, oxygen and then rarefied N_2 in a pressure range between $3 \cdot 10^{-2}$-$8 \cdot 10^{-3}$ mbar, with a flow rate of 1.4 cm^3/min;
- structures and properties of films obtained are influenced by the parameters used;
- the microscopic analysis reveals that the films obtained do not show cracks, are uniform and adherent to mirror surface;
- films color depends on the layer stoichiometry, working atmosphere and parameters used; it ranged from gray to golden brown;
- with increased time of deposition, the surface resistance and transparency decrease (this behavior is due to increasing deposited film thickness and to oxidation and formation of TiN;
- EDX analysis performed on films highlights their chemical composition, i.e. the presence of titanium, oxygen, and nitrogen, in line with the working environment used.

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