Katarzyna TADASZAK

REACTIVE PULSED MAGNETRON SPUTTERING OF TITANIUM – INFLUENCE OF PROCESS PARAMETERS ON RESISTIVITY AND OPTICAL PROPERTIES

ABSTRACT *Titanium nitride and titanium oxide thin films were deposited by pulsed DC reactive magnetron sputtering. In this paper the influence of reactive gas partial pressure on the properties has been studied. The process control was realized by tracking the changes in the power supply parameter – circulating power. Presented technology enables free modification in the chemical composition, from titanium–rich to stoichiometric and overstoichiometric materials. The electrical and optical properties of titanium compounds were measured and then evaluated for possible electrode applications. Thanks to the special power supply and process control, it was possible to deposit low resistivity thin films without additional substrate heating and with high deposition rate. Presented technology is suitable for substrates with low temperature resistance.*

Keywords: *reactive magnetron sputtering, titanium nitride, titanium oxide*

1. INTRODUCTION

Both titanium oxides and nitrides have many appreciated physical, and chemical properties, which makes them a promising materials for number of

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applications. TiN, thanks to high hardness, melting temperature and thermal conductivity, could be used as a protective coating on cutting tools for improved hardness and wear resistance [1]. It is well known for lustrous golden colour [2] which is useful for decorative applications. Golden colour is a result of the high reflectance of TiN at the red end of the visible part of spectrum with low reflectance near the ultraviolet region. This makes it a potential coating for IR-reflective back contacts material and a solar energy absorber suitable for solar cells [3]. In addition, titanium nitride could replace the poly crystalline silicon and be used as gate electrode in MOS devices [4]. It may be also used in biomedical materials because of its noncytotoxical nature [5].

The second investigated material, titanium oxide (TiO_2), has high refractive index (2.75 at 550 nm), dielectric constant and a good thermal stability. This material is widely used as antireflective and protective layers for optical coatings [6]. Recently it attracts attention as a material for transparent conductive electrode [7], especially for solar applications.

Both the TiN and TiO_2 films can be deposited by RF (Radio Frequency) magnetron sputtering, DC (Direct Current) magnetron sputtering [8] [9], but also by sol-gel method, laser ablation, pulsed laser deposition, hollow cathode ion plating or vacuum arc. All those technologies are popular and improving. However, there is still a high demand for developing low-temperature deposition processes for hard and optical coatings, suitable for substrates with low temperature resistance and large coating applications (e.g. architecture glass, solar cells).

The deposition by magnetron sputtering has important advantage – lower temperatures of processes than in CVD (Chemical Vapour Deposition) technology. This method also enables the production of thin films of various morphology and crystallographic structure. Magnetron sputtering is a widely used PVD (Physical Vapour Deposition) technique for deposition of thin films and it is based on the generation of a magnetically enhanced glow discharge, the so-called magnetron discharge. It is a special diode system, in which over the cathode (target) surface properly directed magnetic field is produced.

In this paper the method of effective magnetron sputtering of thin film titanium compound coatings was described as well as the way of process control. This technology allowed deposition of conductive nitrides and oxides with different compositions and properties suitable for electrode applications.

2. INSTRUMENTATION AND SETUP

The sputtering processes were performed in a vacuum system equipped with a rotary and diffusion pump with a pumping speed of 2000 l/s (the final

pressure was about 2.6 mPa). In the presented research the unbalanced WMK-50 magnetron with the titanium target (50 mm in diameter) was used. The total pressure of gas mixture (argon and reactive gas – oxygen or nitrogen) was stable and equal to 0.53 Pa. Thin films were deposited at a glass and silicon substrates placed in 80 mm or 130 mm distance from target. There was no additional heating of the substrate. The medium frequency sputtering processes were carried out using the 5kW Dora Power Supply (DPS) operating at the frequency of 100 kHz with 4 kHz Pulse Quantity Modulation (PQM) for the output power control [10] [11]. Using this DPS unit, the power supply work can be described by so called effective P_E and circulating P_C power [13]. With the decrease of load impedance the DPS power supply output changes from voltage type (1.2 kV) to current type (max. 8A) and a part of stored energy in the oscillator resonance circuit is moved back to the supply block. The measure of this energy is circulating power P_C. This parameter is very sensitive to the changes in plasma impedance, process atmosphere or target condition and therefore could be used to control reactive sputtering [11].

3. RESULTS AND DISCUSSION

One of the important features of magnetron sputtering is a great role of secondary electrons in maintaining the discharge. The addition of the reactive gas to process atmosphere results, not only in the formation of a compound on the substrate, but also on the target. Both titanium oxides and nitrides decrease sputtering yield and emission of secondary electrons [12] and their formation on the target strongly affects the power characteristics of magnetron sputtering.

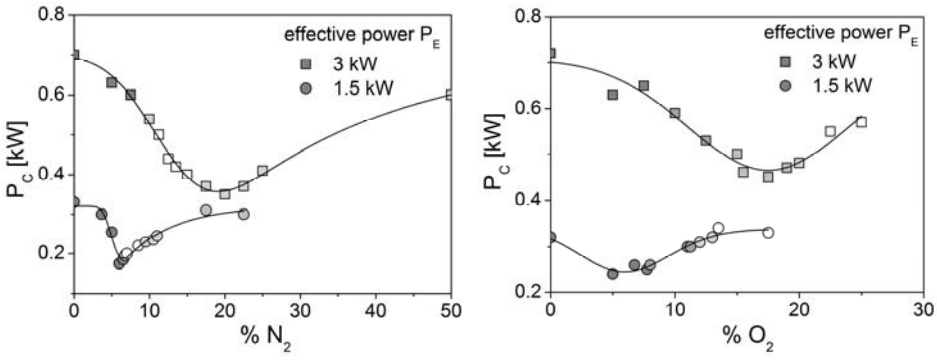

Fig. 1. Circulating power versus reactive gas partial pressure for magnetron sputtering of Ti target: a) sputtering in N_2+Ar gas mixture b) sputtering in O_2+Ar gas mixture

With DPS power supply it was possible to control magnetron sputtering process *in situ* and indicate the moment of target covering with TiN or TiO_2. The circulating power was changing with the composition of process atmosphere (Fig. 1). Stoichiometric and near-stoichiometric compound formation was marked by white points on characteristic, other grey-scale points corresponded to changes in colour and transparency of deposited films. For sputtering in presence of nitrogen the colour was changing form metallic grey through gold (TiN) to dark brown with rising N_2 content in gas mixture. The colour could be used as a sensitive probe to investigate the titanium nitride stoichiometry [13], because as titanium metallic bonds decrease in the film, the absorbed part of the spectra moves towards lower energies. For overstoichiometric materials a shift to red could be observed.

The controlling of titanium reactive sputtering caused same difficulties, which were already reported by other authors for process with cathode voltage control [12]. Reactive sputtering of titanium had the minima and maxima of the circulating power (or discharge voltage) as the target got more and more poisoned. Although, with proper calibration, repeatable deposition of TiN or TiO_2 could be achieved. The drop of the characteristic corresponded to the target covering with compound, while the rise referred to the changes in atmosphere composition (high reactive gas contribution). The lowest point of P_C curve indicated the moment of fully target covering with compound. However, the target condition was not the only factor which influenced on compound formation. It could be observed that for higher sputtering power the moment of stoichiometric film formation was shifted (Fig. 1). It could be explained with phase diagram analysis [14]. Titanium nitride needed a higher energy for formation, so the TiN might be deposited with lower N_2 contribution, if the power density is higher, while for oxide, the amount of oxygen in the layer is highly important. For higher effective power the sputtering yield of titanium increased (rise of Ti flux) and the moment of TiO_2 formation was shifted to higher oxygen partial pressures.

Changes in P_C parameter corresponded to differences in thin film composition and morphology. With rising partial pressure of nitrogen the sudden drop in layer adhesion was observed (Fig. 2c). The overstoichiometric (Tab. 1) film has a poor wear resistance, due to presence of extra nitrogen atoms.

Resistivity was measured for 18 mm long and 2 mm wide thin film stripe (resistor) structures deposited on glass substrates. The presence of additional N atoms influenced resistivity of the layer, which was observed to grow (Fig. 3). This effect was a result of the nitrogen-rich atmosphere during the process. For higher N_2 concentrations, the sputtering yield of Ti dropped and the deposition was limited by mass transfer. As a consequence Ti vacancies in TiN films (N-rich films) could be present, which caused the rise in resistivity. For metal gate application the most suitable are processes with nitrogen content in

atmosphere up to 25% (deposition rate 5 nm/min). Sputtering with high power density (P_E = 3 kW) and without fully poisoned target (lower nitrogen content in atmosphere - about 10%) gave high deposition rate, about 60 nm/min and near-stoichiometric golden film. Moreover, there was no need for additional heating of the substrate.

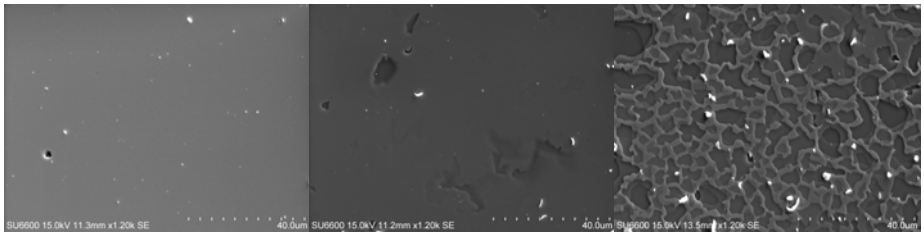

Fig. 2. SEM micrographs of TiN thin film deposited with effective power of 3 kW in atmosphere with nitrogen content of: a) 10% b) 11% c) 13,5%

TABLE 1
Titanium nitrite thin films stoichiometry (P_E = 3 kW)

Nitrogen content in gas mixture	Circulating power	Stoichiometry (x in TiN_X)	Deposition rate
9%	0.45 kW	0.67	61 nm/min
11%	0.43 kW	0.92	60 nm/min
13,5%	0.35 kW	1.14	46 nm/min

Films deposited with nitrogen content in atmosphere from 5% to 15% had golden colour with different shades. The small holes, present in the titanium nitride thin films (Fig. 2b), could reduce adherence and consequently cause loss of wear protection. There are the few solutions to this problem, like increase of the film thickness, use of substrate heating or deposition of multilayered structures. In the simplest case of a Ti/TiN multilayer system,

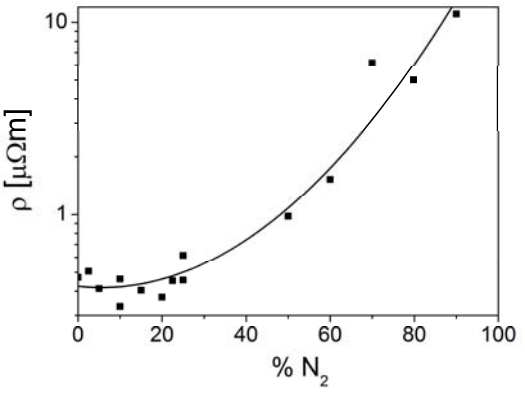

Fig. 3. Resistivity of titanium nitride film as a function of nitrogen content in sputtering gas atmosphere (P_E = 3 kW d_{S-T} = 130 mm)

TiN could be the outer layer, with an intermediate transition layer of Ti. The intermediate Ti layer will not only improve adhesion to the substrate, but also establish a gradient in the coefficient of thermal expansion from the substrate to the coating surface.

All deposited titanium oxide films had great adhesion to the silicon, glass or foil substrates also, no drastic changes were observed. Titanium-rich TiO_2 is promising material for transparent conductive coating, therefore optical properties of reactively sputtered titanium oxide films were investigated. The transmittance TiO_x film (x = 1.62 for p_{O2} = 63 mPa) was rather poor in all spectrum despite blue range - slightly blue colour (Fig. 4a).

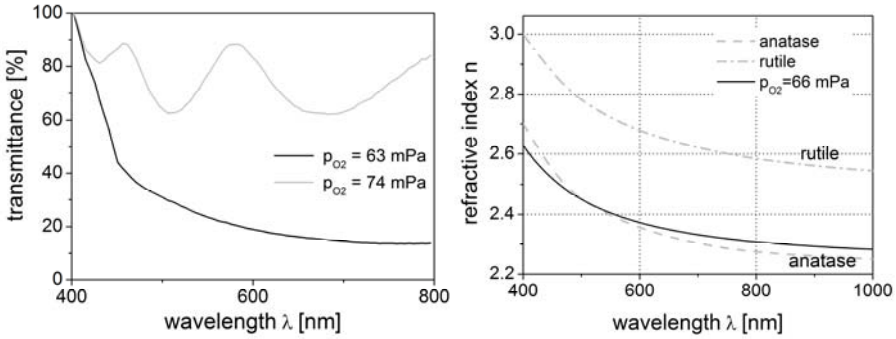

Fig. 4. Titanium oxide optical properties:
b) transmittance, a) refractive index compared with anatase and rutile [15]

The film transparency film increased for films with the composition close to stoichiometric. For TiO_x deposited with oxygen partial pressure of 74 mPa was much higher than with 63 Pa (16% O_2). Refractive index of TiO_2 layer was measured for a wide range of wavelength form 400 nm to 1000 nm, with the use of rotating analyser ellipsometer. The achieved values were comparable with anatase [15] phase and much lower than the rutile one (Fig. 4b). Rutile is reported to be more mechanical stable material, however it is easier to obtained in higher temperatures. Whereas, anatase phase TiO_x may be used as a transparent conductor. For electrode application thin film should have the resistivity lower than 10^{-5} Ωm and the transmittance in the visible range above 80%.

The magnetron sputtering enabled deposition of titanium oxide thin films with wide range of resistivity. However, only with certain amount of oxygen in atmosphere those layers could be transparent. In presented resistivity measurements, the stripe structures, such as for TiN, were used. Titanium oxide resistance changed from 10^{-6} Ωm to 1 Ωm with rise of oxygen content in atmosphere from 0% to 14% (Fig. 5). Measured resistivity of transparent

titanium oxide film was in the best case 10^{-4} Ωm, which was close to assumed value for conductor. With the right choice of process parameters it is possible to deposit a transparent conductive layer of oxide with acceptably high deposition rate. During research it occurred that transparent conductive TiO_x coating could be deposited only with high distance between target and substrate (it was changed from 80 mm to 130 mm). However, this caused the drop in deposition rate, which was almost four times lower. The solution was the increase of target power. It turned out, that it improved also the conductance of thin film.

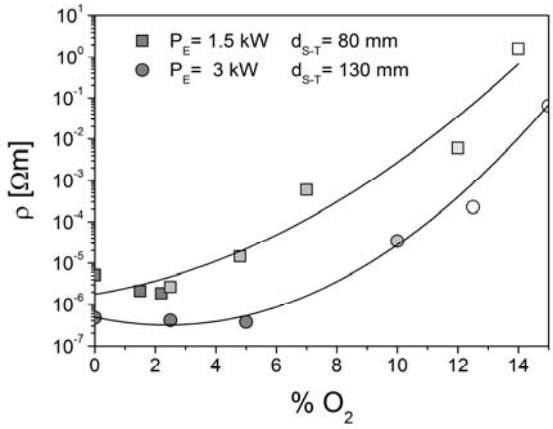

Fig. 5. Resistivity of titanium oxide film as a function of oxygen content in sputtering gas atmosphere

4. CONCLUSIONS

The reactive pulsed DC magnetron sputtering process of titanium compounds was studied. The process control mechanism with circulating power was demonstrated. It could be a great indicator of target condition and plasma impedance. The thin film characterization was done with the emphasis on colour, electrical and optical properties. For both titanium nitride and oxide, it was possible to deposit low resistivity thin films with acceptable high deposition rate (about 40-50 nm/min) without additional heating of the substrate. The achieved resistivity of the titanium oxide film and its transparency, is making the deposited material promising for transparent electrode. Presented technology could be applied in solar industry or in optoelectronic devices such as flat panel displays. It is also possible to use it for polymer coating because of low process temperature.

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REAKTYWNE IMPULSOWE ROZPYLANIE TYTANU – WPŁYW PARAMETRÓW PROCESU NA REZYSTYWNOŚĆ I WŁAŚCIWOŚCI OPTYCZNE

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STRESZCZENIE *Cienkie warstwy azotku i tlenku tytanu osadzane były z procesie impulsowego reaktywnego rozpylania magnetronowego. Przeanalizowano wpływ ciśnienia cząstkowego gazów reaktywnych na właściwości tych materiałów. Kontrola procesu oparta była na śledzeniu zmian parametru zasilacza – mocy krążącej. Zaprezentowana technologia umożliwia dowolne modyfikowanie składu chemicznego, od warstw z nadmiarową zawartością tytanu, przez składy stechiometryczne, po nad-stechiometryczne, co jest powodem obserwowanych zmian w mierzonych charakterystykach związków tytanu. Zbadano elektryczne i optyczne właściwości warstw, a następnie oceniono je pod względem możliwych zastosowań. Dzięki specjalnemu źródłu zasilania i kontroli procesu, możliwe było nanoszenie materiałów o niskiej rezystywności, bez dodatkowego podgrzewania podłoża i z wysoką szybkością osadzania. Zaprezentowana technologia może zostać wykorzystana do pokrywania podłoży nieodpornych na wysokie temperatury.*

Słowa kluczowe*: słowa kluczowe: reaktywne rozpylanie magnetronowe, azotek tytanu, tlenek tytanu*

Katarzyna TADASZAK, M.Sc. in 2003 began studies in Faculty of Microsystem Electronics and Photonics Wroclaw University of Technology. She was a member and president of Students Scientific Association "Optoelectronics and Microsystems". In 2008 she graduated with a work on "Conception and research of thin contact film with higher thermal resistivity". Currently, she is a PhD student in the same faculty and studies effective reactive magnetron sputtering with supervision of prof Witold Posadowski.