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HIGH RATE DEPOSITION OF THIN FILM COMPOUNDS – MODELING OF REACTIVE MAGNETRON SPUTTERING PROCESS

ABSTRACT *Deposition of compound thin films with reactive magnetron sputtering method causes a lot of difficulties, of which the main ones are the instability of the process and decrease of the deposition rate. Computer simulations were performed using Berg's model assumptions. Firstly, effect of basic process parameters on aluminum oxide deposition was examined, also theoretical characteristics of the deposition of Al_2O_3, AlN, TiO_2, TiN were compared. Next, the parameters for efficient deposition of titanium oxide were determined. Simulations were confirmed by the results of experimental work. The purpose of presented work was to define, with Berg's model, mechanisms which enable deposition, in metallic mode of magnetron work, of oxides with properties near to stochiometric. Presented analysis results were compared to real process parameters observed during reactive sputtering .*

Keywords: *Reactive magnetron sputtering, thin films, modeling of magnetron sputering*

1. INTRODUCTION

Magnetron sputtering is a method of physical vapor deposition of thin films (PVD). It is used for deposition of different kinds of materials – metal, compounds, composites or alloys, which could be applied in many brunches of industry, from

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electronics, medicine, mechanics, architecture to solar industry. It is widely used technique for deposition of metallic films, as well as antireflective, protective or self-cleaning coatings [1].

Magnetron source is a special case of diode sputtering system, with crossed electric and magnetic fields. Positive ions of working gas are bombarding negatively charged target causing kinetic emission of atoms from its surface and their deposition on the substrate. Addition of reactive gas leads to formation of compound both on target and substrate surface. Reaction mechanisms between the sputtered material and the reactive gas may cause some processing stability problems. In most cases, the sputtering yield of the compound material is lower than the sputtering yield of the elemental target material [2]. This causes the drop of deposition rate as the supply of the reactive gas increases. Therefore condition of sputtered material surface is an important technological parameter of the sputtering process. The target surface coverage describes the mode of magnetron work [3]: metallic – for clean target surface, transient – partially covered with compound and reactive – fully covered.

1.1. Berg's model of reactive sputtering

Several models have been developed to describe reactive magnetron sputtering process. Most of them are based on the classical model derived by Berg et al. [4, 5]. With reference to this model, high rate reactive pulsed magnetron sputtering of the aluminum and titanium targets in argon and reactive gas mixtures has been studied.

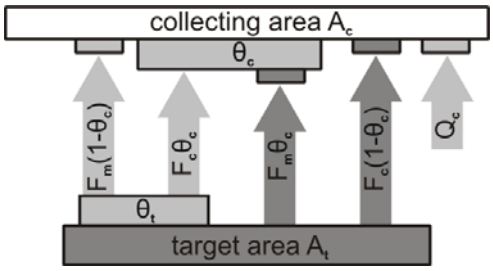

Fig. 1. Illustration of flux of sputtered material to the substrate area A_c

During sputtering process in present of reactive gas, the reactions between elemental target atoms take place and the compound is formed, which create θ_t fraction of the target (Fig. 1). This compound is uniformly distributed over the whole target surface. To clearly illustrate that a fraction θ_t has a different composition (only compound) it is treated as a continuous area, separate from $(1 - \theta_t)$ fraction, consisting elemental non-reacted target atoms. The state of surface of the collecting area A_c could be described in a similar way – all sputtered material is assumed to be uniformly collected and the compound fraction θ_c consist compound molecules. In metallic mode the compound fraction θ_t on the target surface should be very close to 0, while for reactive mode $\theta_t \rightarrow 1$. Stoichiometry indicator of deposited film could be defined as the rate between reacted to non-reacted fraction $\theta_c/(1 - \theta_c)$, thus layers with non-reacted atoms domination fulfill condition – $\theta_c/(1 - \theta_c) < 1$ and those with compound domination follow $\theta_c/(1 - \theta_c) > 1$. Whereas, stoichiometric layers should consist only compound $\theta_c = 1$, hence the $\theta_c/(1 - \theta_c)$ factor tends to infinity.

The previous analysis [6] of edge effects gave the following equation for deposition of compound in metallic mode of magnetron work:

$$\frac{\theta_C}{1-\theta_C} = \frac{2\alpha p A_C}{\frac{J}{q} Y_m A_t \sqrt{2\pi k T m}}$$

where:

α – sticking coefficient,
p – reactive gas partial pressure,
A_c – collecting area,
J – ion current density over target surface,
q – elementary charge,
Y_m – metal sputtering yield,
A_t – target area,
k – Boltzmann constant,
T – temperature,
m – mass.

This led to the conclusion, that the possibility of stoichiometric compound deposition in metallic mode is related to many different parameters, like relatively low target area $A_c/A_t >> 1$, suitable high reactive gas partial pressure or ion current density. Too high current density cause more effective etching of target race track and the presence of extra metal particles, what leads to nonstoichiometric compound deposition. On the other hand too low current density could cause ineffective sputtering of compound from the target and poisoning of its surface and sudden drop of deposition rate.

The effective deposition of stoichiometric compound is possible thanks to keeping balance between high sputtering rate of metallic target (current density) and reactive gas partial pressure. The characteristics of process could change also due to other parameters, like target size, magnets configuration, target to surface distance or material parameters. The aim of presented paper is to find the link between process parameters and the possibility of high rate deposition of stoichiometric compound in metallic mode of magnetron work. The Bergs model was used in computer simulation of process characteristics to define conditions of sputtering. The theoretical results were compared to real characteristics of deposition process.

2. EXPERIMENTAL DETAILS

The first part of the research consisted of computer calculations of reactive magnetron sputtering process characteristics. Reactive sputtering process parameters were chosen in order to best suit the actual conditions (Tab. 1). For this reason, instead of single α coefficient [4], two sticking coefficients α_t and α_c were used, separate for

target and collecting area, cause on those surfaces reactions take place in different conditions (temperature, ion bombardment etc.) [7, 8].

TABLE 1
Basic parameters used in calculation of aluminum oxide deposition

Parameter	Aluminum oxide deposition
α_t – sticking coefficient to target area	0.7
α_c – sticking coefficient to collecting area	0.5
A_c – collecting area	450 cm^2
A_t – target area	10 cm^2
J – target ion current density	0.08 A/cm^2
S – pumping speed	300 l/s
Y_c – sputtering yield of compound	0.25
Y_m – sputtering yield of metal	0.9

After analysis of theoretical characteristics, measurements of deposition rate changes in real systems were done. The sputtering processes were performed in a vacuum system equipped with a rotary and diffusion pump with a real pumping speed of 300 l/s. The final pressure of the deposition chamber was about 0.02 mTorr. In the presented research the unbalanced WMK-50 magnetron was used. The titanium and aluminum target with 50 mm in diameter was sputtered in a mixture of working gas – argon and reactive gas – oxygen with total gas pressure 4 mTorr. The medium frequency sputtering processes were carried out using the Dora Power Supply (DPS—5 kW) operating at a frequency of 100 kHz with a 4 kHz pulse quantity modulation (PQM).

3. RESULTS AND DISCUSSION

To determine conditions of high rate reactive magnetron sputtering two kinds of theoretical process characteristics were analyzed – target θ_t and collecting (substrate) θ_c area covering with the compound, normalized deposition rate (S/S_{max}). Both were calculated due to equations taken from Bergs model [4, 5]. As the example the aluminum oxide deposition was used. Firstly, influence of three main parameters was described – target size, distance from the substrate to target and energy involved in sputtering – ion current density on the target. Then deposition characteristics of different materials were compared. Finally parameters of high rate titanium oxide deposition were determined and results were compared with experimental results.

The analysis included two sizes of targets corresponding to the magnetron sources WMK-50 and WMK-100 [3]. For bigger source the higher rate of deposition could be observed (Fig. 2b). However, in this case it seemed to be difficult to achieve stoichiometric compound deposition in metallic mode. The collecting area could be covered with Al_2O_3 ($\theta_c \approx 1$) only for high oxygen content in process atmosphere – for $\theta_t > 0.8$.

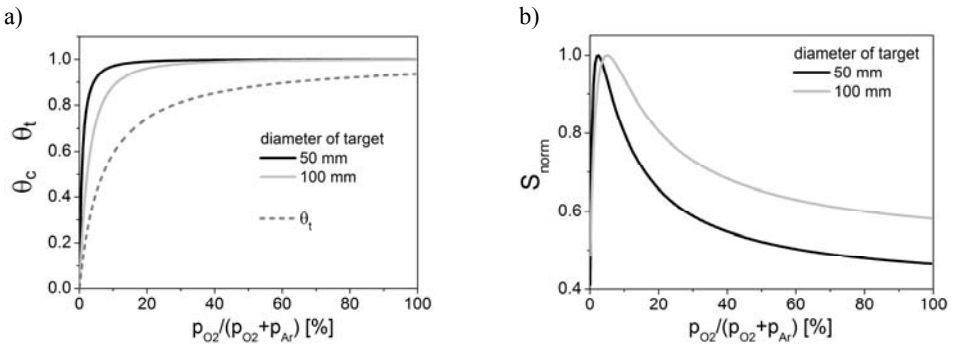

Fig. 2. Influence of target size on the deposition of aluminum oxide:
a) coverage of the target θ_t and collecting area θ_c with compound; b) normalized deposition rate

Increase of the substrate to target distance was introduced to simulation by the changes in collecting area size, based on the equation for deposited film thickness. The collecting area was assumed as the surface with less than 90% drop of thickness [9]:

$$d = \frac{mh^2}{\pi\rho} \frac{\left(d_{S-T}^2 + A^2 + R^2\right)}{\left(d_{S-T}^2 + A^2 + R^2 + 2AR\right)^{3/2}\left(d_{S-T}^2 + A^2 + R^2 - 2AR\right)^{3/2}}$$

where

A – distance from point of the substrate to the target center,
R – radius of the target erosion zone,
$d_{S\text{-}T}$ – substrate to target distance,
m – mass of deposited molecule,
ρ – density of deposited material.

It was found, that due to the chemical composition, it was better to deposit on the substrates placed at a greater distance (Fig. 3a). However, as the distance increased the deposition rate dropped, and thus the efficiency of the process (Fig. 3b).

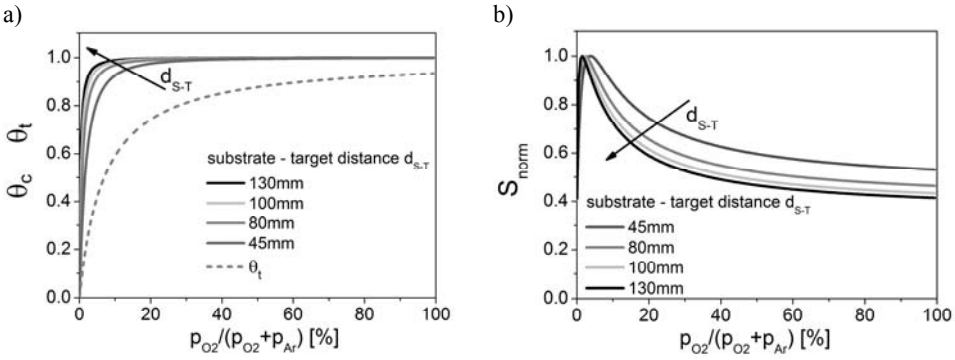

Fig. 3. Influence of substrate to target distance on the deposition of aluminum oxide:
a) coverage of the target θ_t and collecting area θ_c with compound; b) normalized deposition rate

It could be seen at figure 4a that with increasing target power (ion current density) the surface of the target θ_t would be covered with the compound only for high partial pressures of oxygen. Slowing down the target poisoning seemed to be good for efficiency (Fig. 4b). However, simultaneously increased the amount of unreacted aluminum in the atmosphere and, for large current density, composition of the compound formed on the substrate deviated significantly from the stoichiometric.

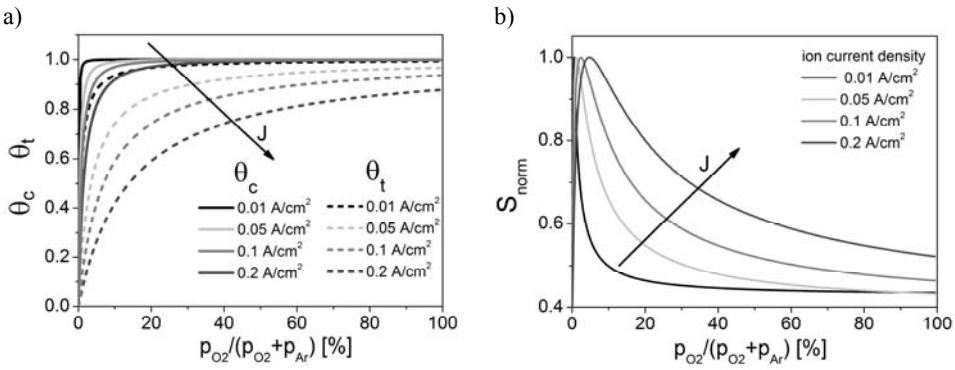

Fig. 4. Influence of target ion current density on the deposition of aluminum oxide: a) coverage of the target θ_t and collecting area θ_c with compound; b) normalized deposition rate

Summarizing, it was noted that only one from analyzed parameters – target current density, had influence on target poisoning θ_t. In order to minimize the impact of this phenomenon on the deposition process, it could be worth to use high power during reactive sputtering processes. On the other hand, an increase in current density led to more efficient sputtering and increased the amount of metal particles in the atmosphere, making it difficult to obtain stoichiometric compositions. The negative influence of this factor could be overcome by proper selection of other parameters, for example by increasing the distance between the target and the substrate, or the use of magnetron source with a different distribution of the magnetic field.

The choice of appropriate conditions for sputtering was crucial for the efficiency and had to be linked with the analysis of the properties of specific materials. The simulated deposition of oxides and nitrides of aluminum and titanium was compared (Fig. 6a and 6b). Those material systems were selected because of previously observed previously differences in sputtering process [3].

It was noticed that aluminum sputtering processes in the presence of oxygen and nitrogen were very similar (Fig. 6a). Although, for the sputtering in nitrogen, lower adhesion coefficient values were set due to the lower reactivity of the gas.

Reactive sputtering of titanium caused more difficulty. The figure 6b showed that the range of pressures corresponding to metallic mode was very narrow. For both titanium oxide and nitride efficient deposition of stoichiometric compounds was unlikely due to the low sputtering coefficient, which for the titanium oxide is only 0.015 [10]. It was therefore decided to check whether it was possible to select process parameters that allow to efficiently deposit TiO_2 in metallic mode of magnetron work or near border

of metallic and transient modes. In high rate deposition of chemical compounds it is very important to control the state of the target and the substrate using the process parameters described earlier. To deposit titanium oxide in metallic mode, the poisoning of the target should be slowed down and reaching the stoichiometric composition on the substrate should be speeded up. For this purpose, it was decided to increase the current density and the distance between the target and the substrate (Fig. 7).

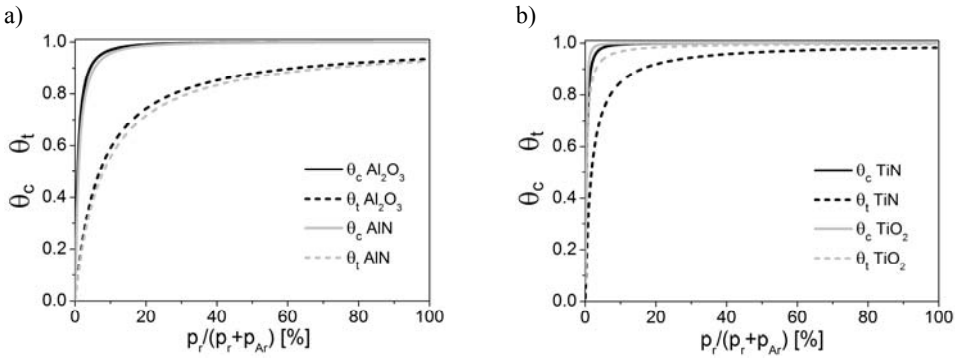

Fig. 6. Coverage of the target area θt and collecting area θc with compound: a) comparison of sputtering of aluminum in presence of O_2 and N_2; b) comparison of sputtering of titanium in presence of O_2 and N_2

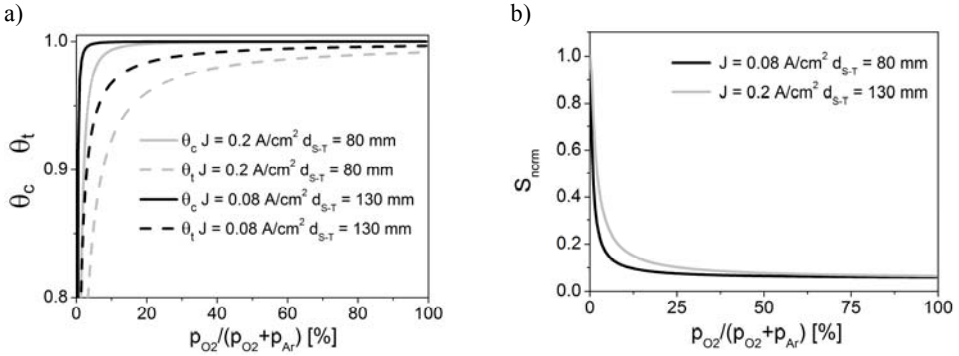

Fig. 7. Influence of process parameters (ion current density and substrate – target density) on the deposition of titanium oxide: a) coverage of the target θ_t and collecting area θ_c with compound; b) normalized deposition rate

The figure 7 showed the state of the target surface and the substrate for the basic parameters (J = 0.08 A/cm^2 d_{S-T} = 80 mm) and the simultaneous change of power (J = 0.2 A/cm^2) and the distance from the target (d_{S-T} = 130 mm). Thanks to higher distance from the target surface the negative impact of power increase on composition of the thin film could be reduced.

Theoretical analysis and simulation were used to improve configuration of process parameters and magnetron source. Afterwards theory was experimentally confirmed both for aluminum oxide and titanium oxide deposition. For Al_2O_3 the characteristics presented at figure 2b was confirmed. However, theoretical characteristics, due to many simplification, could not be use for quantitative analysis. They gave only information about trends. Thanks to changes in process setup proposed as a result of presented research it was possible to deposit titanium oxide in metallic mode of magnetron work. The composition changes were marked at figure 8b with filling of the points, where empty are transparent TiO_2 and grey are non-stoichiometric films.

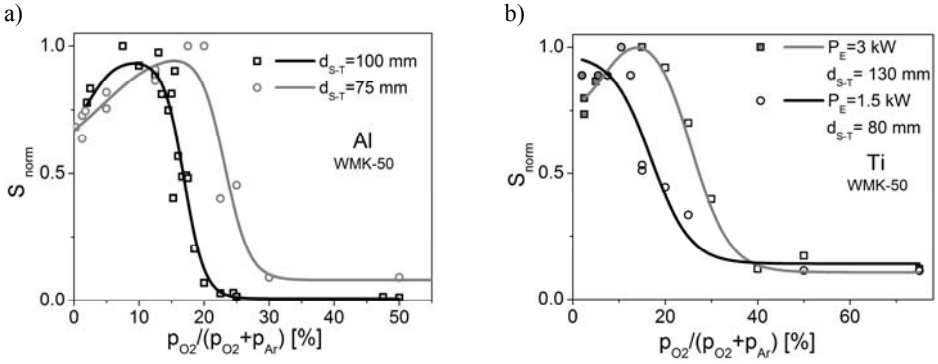

Fig. 8. Normalized deposition rate:
a) of aluminum oxide for two different target-substrate distances; b) of titanium oxide with different process conditions (P_E = 3 kW d_{S-T} = 130 mm and P_E = 1.5 kW d_{S-T} = 80 mm)

4. CONCLUSIONS

Presented analysis allowed to determine the configuration of the vacuum chamber and process parameters necessary for high rate reactive magnetron sputtering. Results confirmed that it is possible to deposit compound in metallic mode of magnetron work, without target poisoning with oxide. However, this requires a number of conditions and is difficult to use in large-sized systems. Thanks to calculation it was identified that with high enough power density and target to substrate distance it is possible to effectively deposit stoichiometric titanium oxide thin films. The analysis provided a starting point for following research in determining the parameters of the high rate reactive pulse magnetron sputtering.

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WYDAJNE OSADZANIE CIENKICH WARSTW ZWIĄZKÓW CHEMICZNYCH – MODELOWANIE PROCESU REAKTYWNEGO ROZPYLANIA MAGNETRONOWEGO

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Streszczenie *Osadzanie cienkich warstw związków metodą reaktywnego rozpylania magnetronowego sprawia wiele trudności, spośród których głównymi są niestabilność procesu i spadek szybkości osadzania. Komputerowe symulacje wykonano wykorzystując założenia modelu Berga. W pierwszej kolejności sprawdzono wpływ podstawowych parametrów procesu na osadzanie tlenku glinu. Porównano również teoretyczne charakterystyki osadzania Al_2O_3, AlN, TiO_2, TiN. Następnie określono parametry umożliwiające wydajne osadzanie tlenku tytanu. Symulacje potwierdzono wynikami prac eksperymentalnych. Głównym celem pracy była próba określenia mechanizmów umożliwiających osadzanie w modzie metalicznym tlenków o właściwościach zbliżonych do warstw o składzie stechiometrycznym.*

Słowa kluczowe: *reaktywne rozpylanie magnetronowe, cienkie warstwy, model procesu rozpylania*

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