Titanium Oxide Reactive Magnetron Deposition Process Using Pulsed DC Power Supply

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ABSTRACT

Titanium dioxide coatings are commonly used material in a wide range of applications in industrial production, for example, optical coatings. Titanium oxide coating can be obtained using ceramic or metallic titanium target. Using a ceramic target, it is not necessary and sometimes not even possible high-speed process control. Metallic titanium target advantages are cheap material and greater dynamic deposition rate. Compared with ceramic titanium dioxide target metallic titanium target has ~ 30 % below the target price. The oxide deposition is characterized by voltage hysteresis and it differs for different materials. We used constant current or constant power mode and voltage stability was provided by changing oxygen flow. By the help of developed process control system, it was provided coating parameter stability during deposition, regardless of the deposition process length. Necessary quantity of oxygen was automatically calculated, taking into account the release of oxygen from the vacuum chamber walls and from substrate. Voltage hysteresis loop characteristic is different at different power supply frequencies, pumping speed and argon (inert gas) flow. From hysteresis loops we can determine necessary voltage and oxygen flow for transition mode. It was found optimum range of parameters for transition mode, which are maintained through a process by developed control system.

INTRODUCTION

TiO_2 coatings draw attention of researchers and technologists due to their unique physical properties: chemical stability, mechanical hardness, big index of refraction, high transparency, big dielectric constant, as well as photo catalytic properties with excellent self-cleaning, anti-misting, antibacterial and self-sterilizing abilities, etc.

Titanium has several oxides: TiO, Ti_2O_3, TiO_2 with different amount of oxygen. The most widespread is titanium dioxide TiO_2. It is known in the form of several modifications: rutile, anatase, brookite, etc. that differ by their crystal structure. Rutile modification is the steadiest; it is most often used in the magnetron sputtering processes. It is characteristic for titanium dioxide that the coefficient of ion induced secondary electronic emission (ISEE) yield from the titan is higher, than from oxide, and it is different, for example, from silicon oxide which ISEE from oxide is higher, than from silicon.

In respect of the ISEE metals and semiconductors are divided into two classes [1]. Wide variety of titanium oxides and crystal structures of the titanium dioxide complicates the analysis of deposition processes comparing to oxides of other metals and semiconductors like silicon.

EXPERIMENTAL

For deposition of TiO_2 the Pulse DC power supply was used. Power of the source was 10 kW, the frequency 0 - 350 kHz. According to the goals of the work, the research was conducted at initially lowered flow of argon and lowered speed of pumping.

Initial conditions for carrying out the experiments of TiO_2 deposition were set by initial flow and partial pressure of argon. The argon flow in to the chamber during the process was maintained as constant.

FEATURES OF VOLTAGE HYSTERESIS DURING REACTIVE SPUTTERING OF TI

Voltage hysteresis during reactive sputtering of Ti metal target together with a hysteresis of partial pressure of oxygen is presented in Figure 1. Voltage hysteresis during reactive sputtering of Ti metal target has number of differences comparing to sputtering of silicon, Figure 2 [2]. Joint consideration of voltage hysteresis and partial pressure allows to reveal and explain certain amount of regularities.

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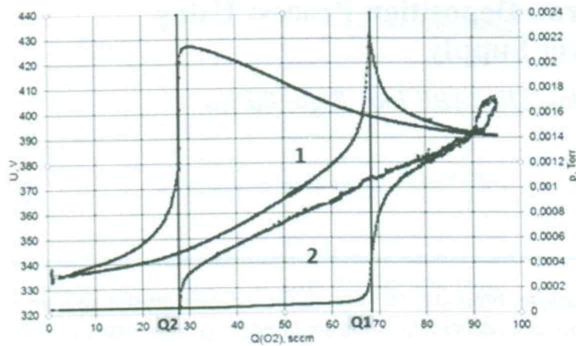

Figure 1: Voltage hysteresis (1) and hysteresis of partial pressure of oxygen (2) during reactive sputtering of Ti at I = const.

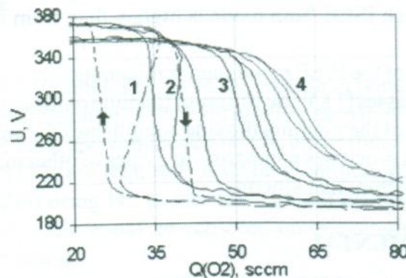

Figure 2: Voltage hysteresis loop dependence on the pumping speed, SiO_2, Puls DC. 1 – 0.4 m³/s, 2 – 0.8 m³/s, 3 – 1.7 m³/s, 4 – 3.4 m³/s [2].

For voltage hysteresis loop during reactive sputtering of Ti it is characteristic that voltage in the metal mode for titanium is less than voltage in the oxide mode (it is opposite, for example, to silicon oxide, Figure 2). At first approximation, it could be explained by secondary ion-electronic emission from titanium and titanium dioxide. The ISEE coefficient for titanium is higher, than for oxide. Really, for titanium dioxide in [1] received γ_{TiO2} value is 0,078. Using data [1] it is possible to calculate the ISEE coefficient for titanium, $\gamma_{Ti} = 0{,}111$. Assessment of the ISEE coefficient during reactive sputtering of Ti is made in [3]. At pressure of 1Pa in pure Ar, i.e. during sputtering of metallic Ti the ISEE coefficient is equal to 0,075. After oxygen addition the coefficient sudden falls to 0,05 for poisoned target and further slowly decreases to 0,035. The received values of the ISEE differ from results of work [1]; though, the order of values coincides. Change of the ISEE coefficient for titanium and titanium dioxide qualitatively explains increase of discharge voltage upon transition from metal to oxide mode.

At oxygen flow increase into the chamber the partial pressure of oxygen grows slightly, sputtering occurs in metal mode until transition from metal to oxide mode at Q1 oxygen flow. From the joint analysis of the hysteresis of oxygen partial pressure and voltage it follows that at the same value of oxygen flow Q1 the sharp maximum of voltage is observed. The sharp maximum of voltage is feature of reactive sputtering of Ti, Figure 1. Such maximum was also observed by other researchers [4]. For construction of the hysteresis by voltage points maximum upon transition from metal to of oxide mode can be omitted. We noticed that the sharp maximum is more clearly observed during work with pulse power supply, Figure 1.

The hysteresis is caused by different coefficients of secondary electronic emission of metal and products of reaction (the coefficient of secondary electronic emission depends on target surface's conditions) [5]. When composition of target's surface is changing due to oxidation, then quantity of secondary electrons emitted by ionic bombarding of the target also changes. This leads to change of ionic and electronic current ratio. It is impossible to divide ionic and electronic current in a circuit. Therefore, direct (invariable) discharge current does not mean constancy of the ionic current during bombarding of the target. Monotonous change of voltage speaks about the prevailing influence of the ISEE on discharge voltage and also about smooth change of the ISEE at oxidation of the target. The target covering by oxide influences an impedance of a target plasma system.

At oxygen flow reduction into the chamber the partial pressure of oxygen slowly decreases and discharge voltage increases. At oxygen flow Q2 there is a transition to the metal mode, the partial pressure of oxygen promptly falls. Increase of voltage is connected with reduction of secondary ion-electronic emission coefficient under the influence of the ionic bombarding of the target that loses oxygen. After cleaning of the target voltage falls and process passes into metal mode.

From the hysteresis of voltage it is seen that at direct current sputtering power in metal mode is lower than in oxide mode. In a maximum point power reaches a sharp maximum.

In the metal mode sputtered layer is not transparent and transmission is low. In the oxide mode sputtered layer is transparent and at change of layer's thickness the transmission aspires to a film transmission, $T \Rightarrow T_{film}$. At reduction of oxygen flow transmission decreases. The reason is that power grows, and oxygen flow (and the partial pressure of oxygen) falls, and the sputtered layer gets enriched with metal.

Thus, the transitional mode is observed in a range of oxygen flows (Q2, Q1). Work in the transitional mode requires control of the sputtering process.

Comparing voltage hysteresis and hysteresis of the partial pressure it is visible that only in the transitional mode it is possible to get a qualitative coating with at acceptable speed.

In [6] influence of Ti target oxidation level on discharge voltage at magnetron sputtering was studied. Titanium dioxide samples with different titanium content TiO_{2-x}, x = 0,25 - 2 were prepared for this purpose. Change of sputtering voltage of various structures of TiO_{2-x} testifies change of the ISEE at target's composition change and explains behavior of the voltage during the process. It must be kept in mind that under influence of ionic bombarding on target's surface suboxide instead of oxide is formed. Therefore, electronic properties of the target also change. On this basis it is possible to predict discharge voltage behavior during the reactive sputtering which is technologically interesting for control of the sputtering process.

VOLTAGE HYSTERESIS AT CHANGE OF DISCHARGE FREQUENCY

Features of pulse power supplies have impact on reactive sputtering process. Our research of the voltage hysteresis confirm complexity of the problems arising during reactive sputtering of Ti. During the reactive sputtering of Ti depending on discharge we observed number of features that were not noticed during Si sputtering.

At increase in frequency from 25 kHz to 100 kHz there is a change of a form of the hysteresis loop. On Figure 3. arrows show the direction of oxygen flow change into the chamber. The loop of the hysteresis of reactive Ti sputtering, that is characteristic for direct current and frequency of 25 kHz, after increase of frequency degenerates and at 100 kHz takes a form characteristic for silicon, Figure 4. The hysteresis loop form for titanium dioxide and silicon oxide at direct current is explained by change of the ISEE coefficient. Evidently, at increase of discharge frequency during reactive sputtering of Ti there is a ratio change of titanium and titanium dioxide ISEE coefficients: $\gamma_{Ti} < \gamma_{TiO2}$.

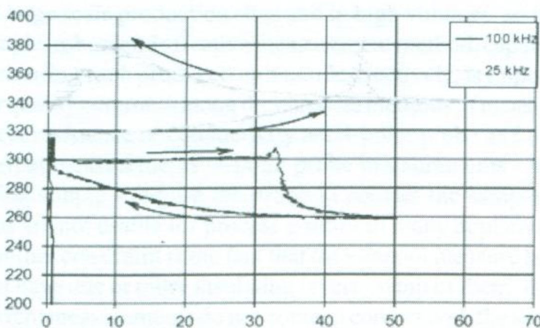

Figure 3: Change of the hysteresis loop during reactive sputtering of Ti. Ar 50 sccm, 2,5 mTorr, 0,5 m3/s. Low frequencies.

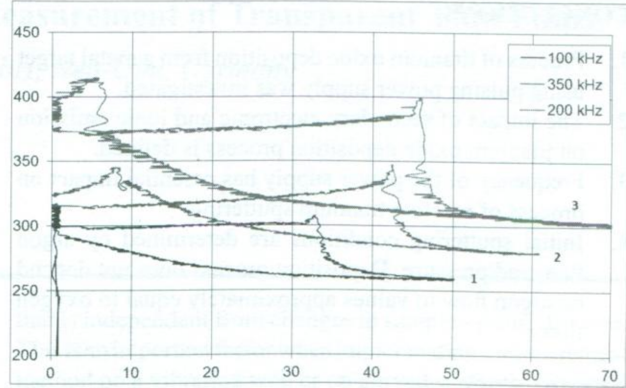

Figure 4: Change of a hysteresis loop during reactive sputtering of Ti. Ar 50 sccm, 2,5 mTorr, 0,5 m3/s. High frequencies. 1 – 100 kHz, 2 – 200 kHz, 3 – 350 kHz.

At further increase of the discharge frequency character of the hysteresis loop does not change, and they move to area of higher voltage and higher oxygen flows. The increase of the oxygen flow at which there is a transition from metal to oxide mode shows increase of the deposition rate. It corresponds to conclusions presented in other works [7-8]: increase of impulse frequency for more than 100 kHz causes growth of TiO_{2-x} deposition rate. At discharges with short impulses with length ~ 2 microsec intense ionic bombardment of isolated substrate and coating provides possibility to formulate nanostructured TiO_{2-x} coatings.

The same transformation of a hysteresis loop was observed at high argon flows and, respectively, at higher pumping speeds, Figure 5. At a frequency of 50 kHz change of the hysteresis character is observed.

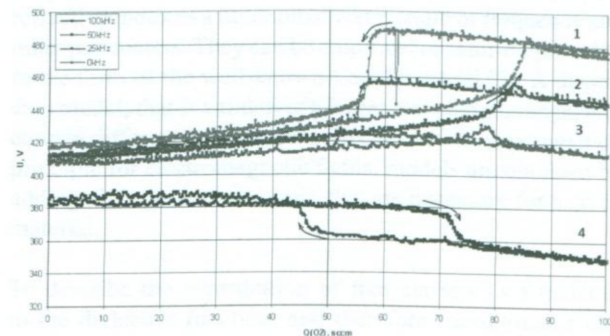

Figure 5: Change of voltage hysteresis loop depending on frequency of the Puls DC power supply. Ar 200 sccm, 3,4 m3/s. (1 – 0 kHz, 2 – 25 kHz, 3 – 50 kHz, 4 – 100 kHz)

CONCLUSIONS

1. Process of titanium oxide deposition from a metal target using pulsing power supply was investigated.
2. The impact of secondary electronic and ionic emission on titanium oxide deposition process is defined.
3. Frequency of the power supply has essential impact on process of reactive titanium sputtering.
4. Initial sputtering conditions are determined by argon flow and pressure. Deposition process does not depend on argon flow to values approximately equal to oxygen flows.

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