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TITANIUM OXIDE REACTIVE MAGNETRON DEPOSITION PROCESS USING PULS DC POWER SUPPLY.

- J. Kazuss, V.Kozlov, E.Machevskis
  SIDRABE Inc, Riga, Latvia

Why titanium oxide?

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 dioxide coatings

From ceramic target

Advantages:
- Simple control process
- No need high speed control
- Low oxygen flow
- Lower sputtering rate

Disadvantages:
- Worth heat transfer
- Higher (~30%) price
- Indirect cooling
- Complicate production
- Lower sputtering rate

From metallic target

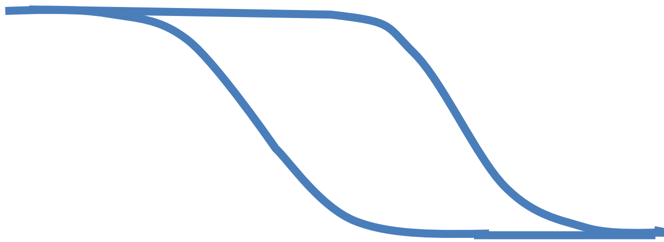
Advantages:
- Better heat transfer
- Lower (~30%) price
- Direct cooling
- Easy production
- Higher sputtering rate

Disadvantages:
- Complicate control system
- Need high speed control

•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 often used in the magnetron sputtering processes.
•It is characteristic for titanium dioxide that the coefficient of ion induced secondary electronic emission (ISEE) 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.

Two types of hysteresis loops



Si

Ti

$\gamma_{Si} < \gamma_{SiO2}$.

$\gamma_{Ti} > \gamma_{TiO2}$.

Experimental

- All experiments were carried out on vacuum machine UV-80 equipped with winding device for flexible substrate winding.
- Substrate width – 600 mm.
- Planar Ti magnetron target length – 800 mm.
- Vacuum machine equipped with optical measurements system, mass-spectrometer for gas analyse and with control system for technological process control.
- For TiO_2 deposition of the Pulse DC power supply was used.

- Power of the source was 10 kW, maximum 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 fig. 1. Voltage hysteresis during reactive sputtering of Ti metal target has number of differences comparing to sputtering of silicon, fig. 2 [8].

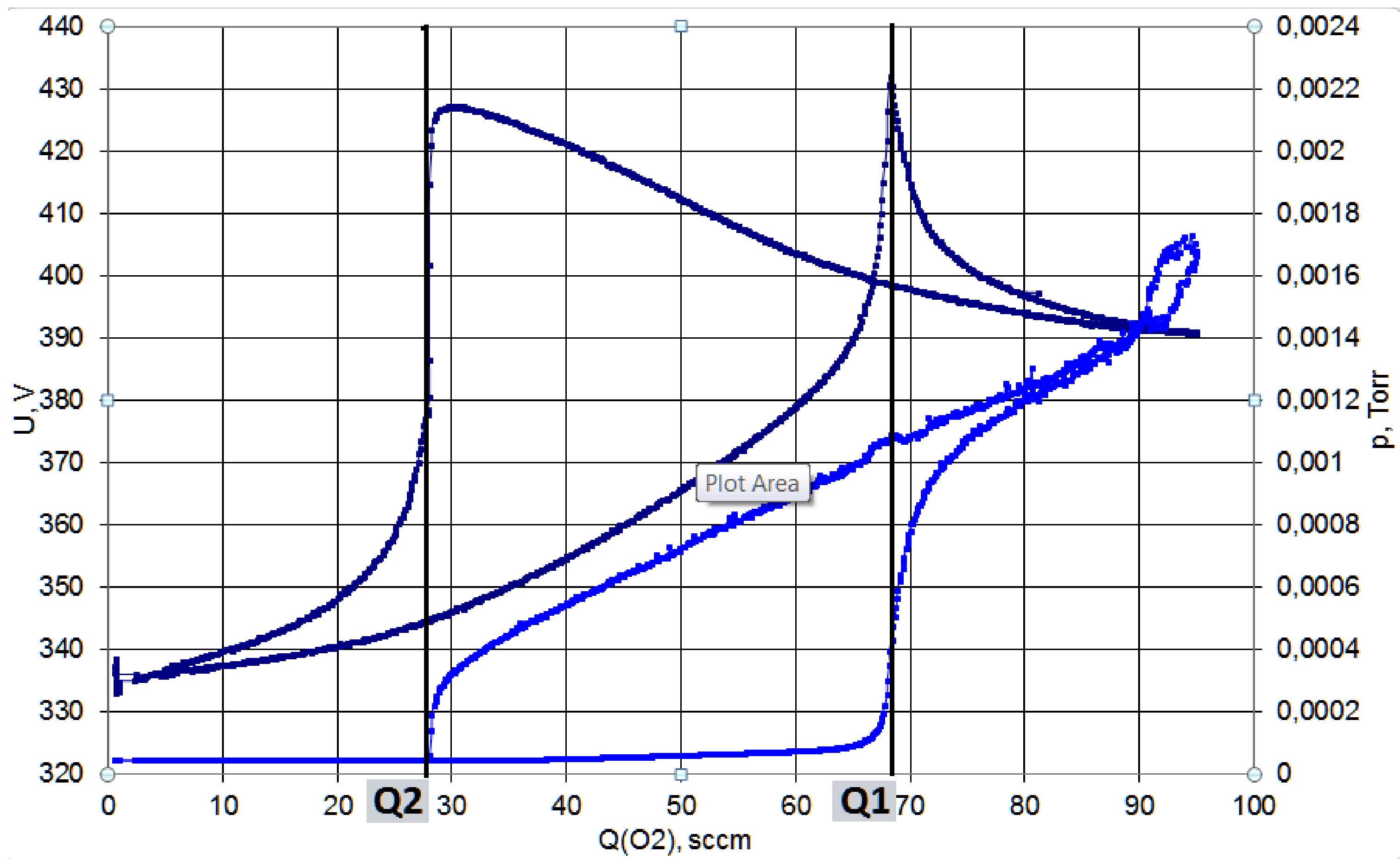
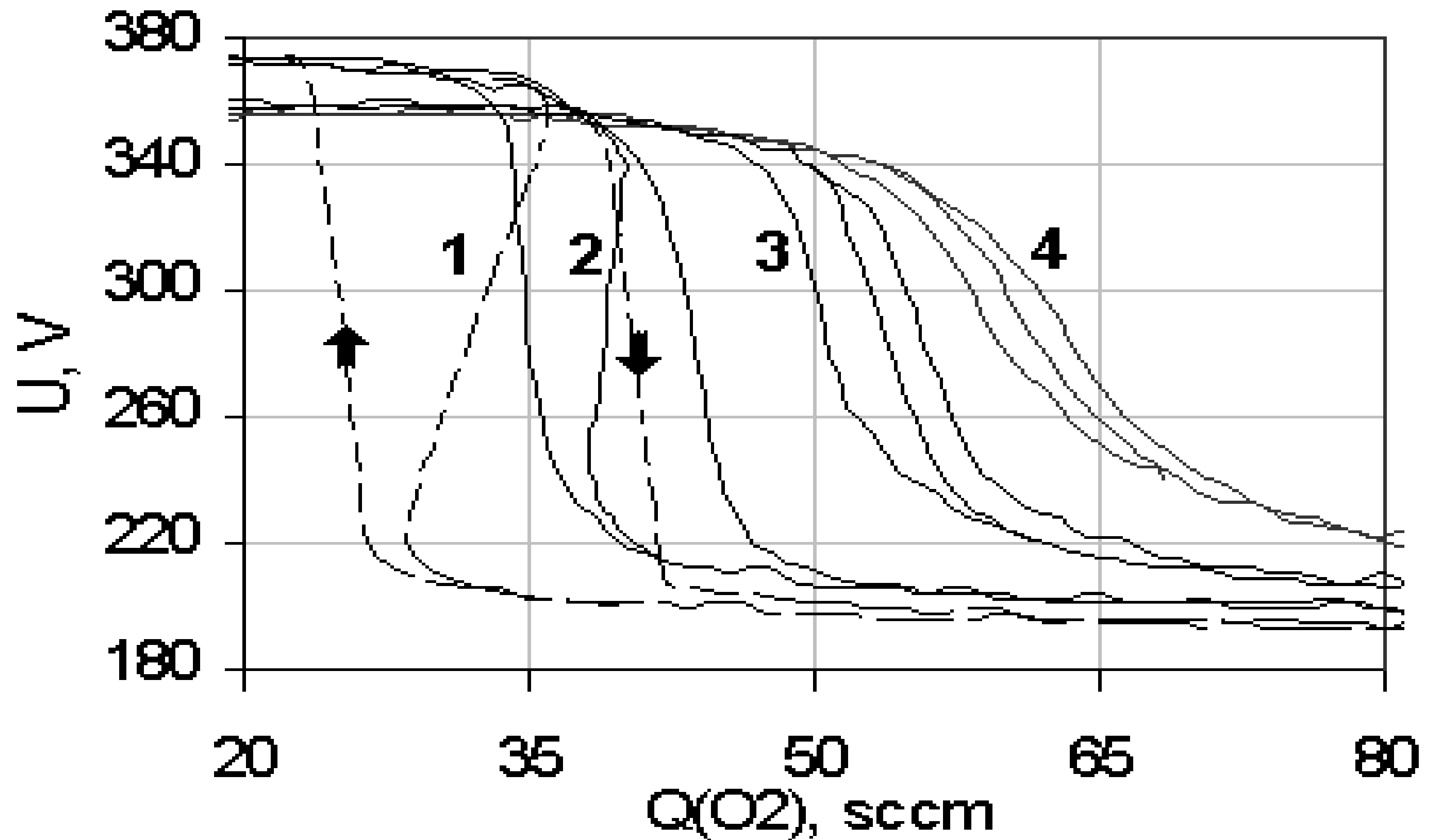


Fig. 1. Voltage hysteresis (1) and hysteresis of partial pressure of oxygen (2) during reactive sputtering of Ti at I = const



Voltage hysteresis loop dependence on the pumping speed, SiO_2, Puls DC. 1 – 0.4 m^3/s, 2 – 0.8 m^3/s, 3 – 1.7 m^3/s, 4 – 3.4 m^3/s [8].

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$$U_{met.mode} < U_{ox.mode} \quad \text{for Ti}$$

$$U_{met.mode} > U_{ox.mode} \quad \text{for Si}$$

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, γ_{Ti} = 0,111. Assessment of the ISEE coefficient during reactive sputtering of Ti is made in [2]. 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.

Q_1 – transition from transition mode to oxide mode

Q_2 – transition from transition mode to metallic mode

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.

Voltage hysteresis at change of discharge frequency

- Pulse power supplies impact on reactive sputtering process.
- 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, fig. 3.

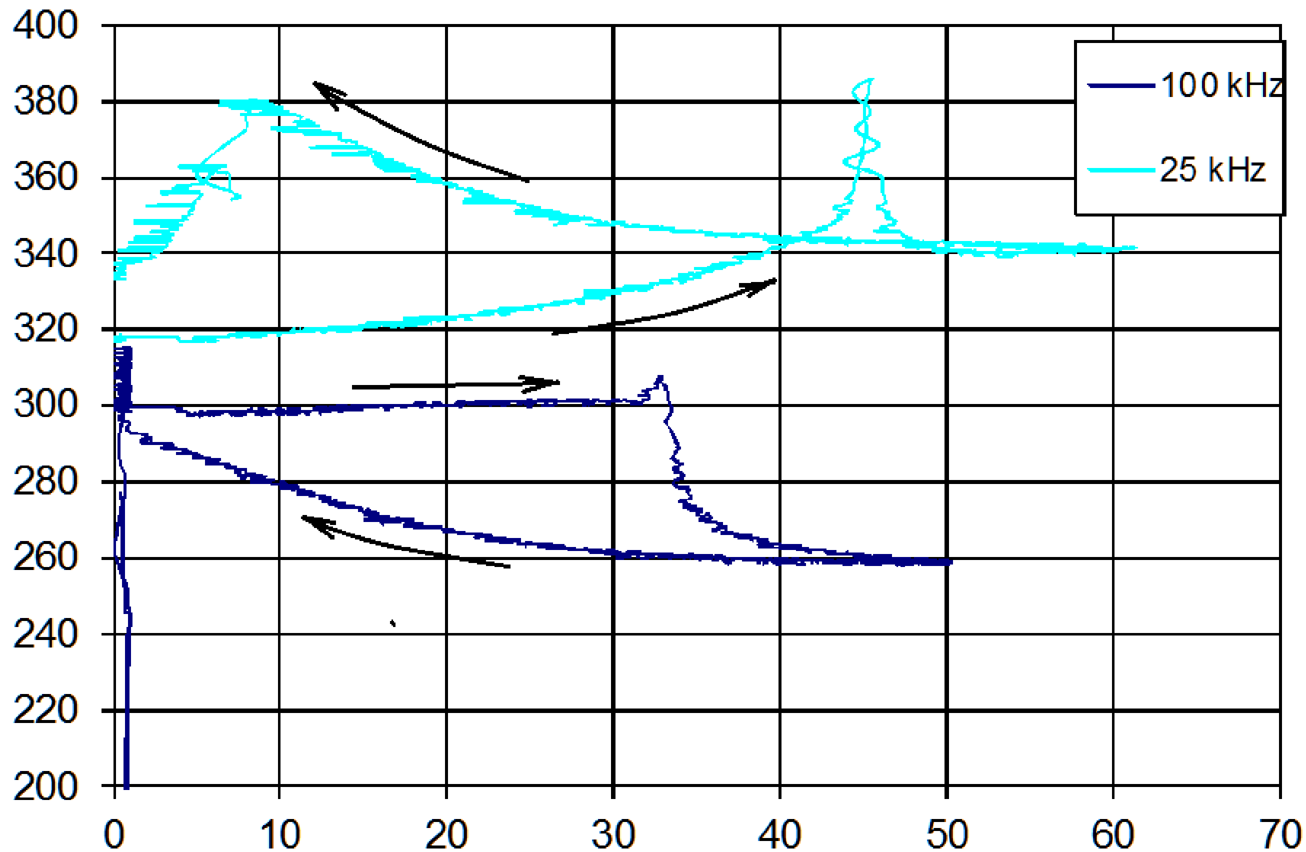

Fig. 3. Change of the hysteresis loop during reactive sputtering of Ti. Ar 50 sccm, 2,5 mTorr, 0,5 m3/s. Low frequencies.

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: $\gamma_{Ti} < \gamma_{TiO2}$.

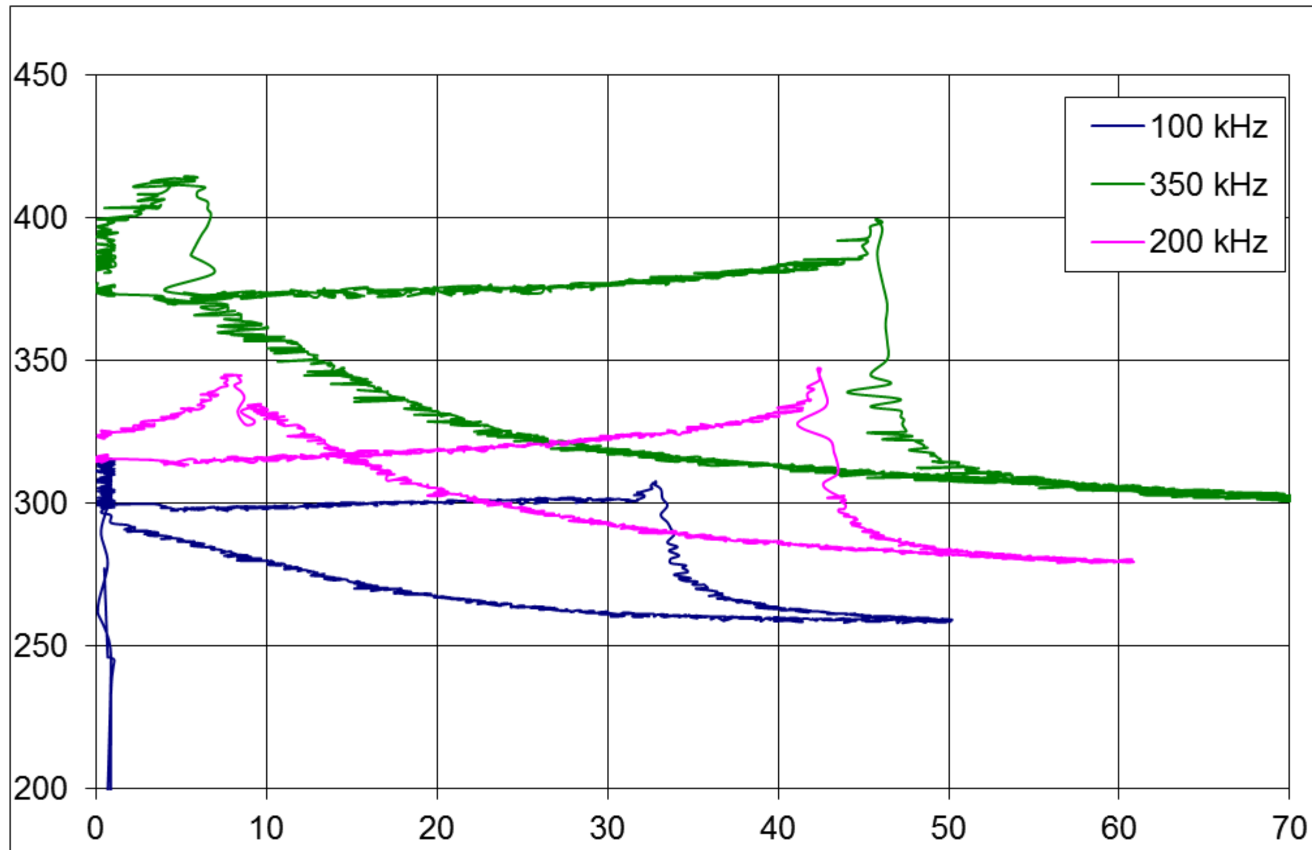

Fig. 4. Change of a hysteresis loop during reactive sputtering of Ti. Ar 50 sccm, 2,5 mTorr, 0,5 m3/s. High frequencies. 1 – 100 kHz, 2 – 200 kHz, 3 – 350 kHz.

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.

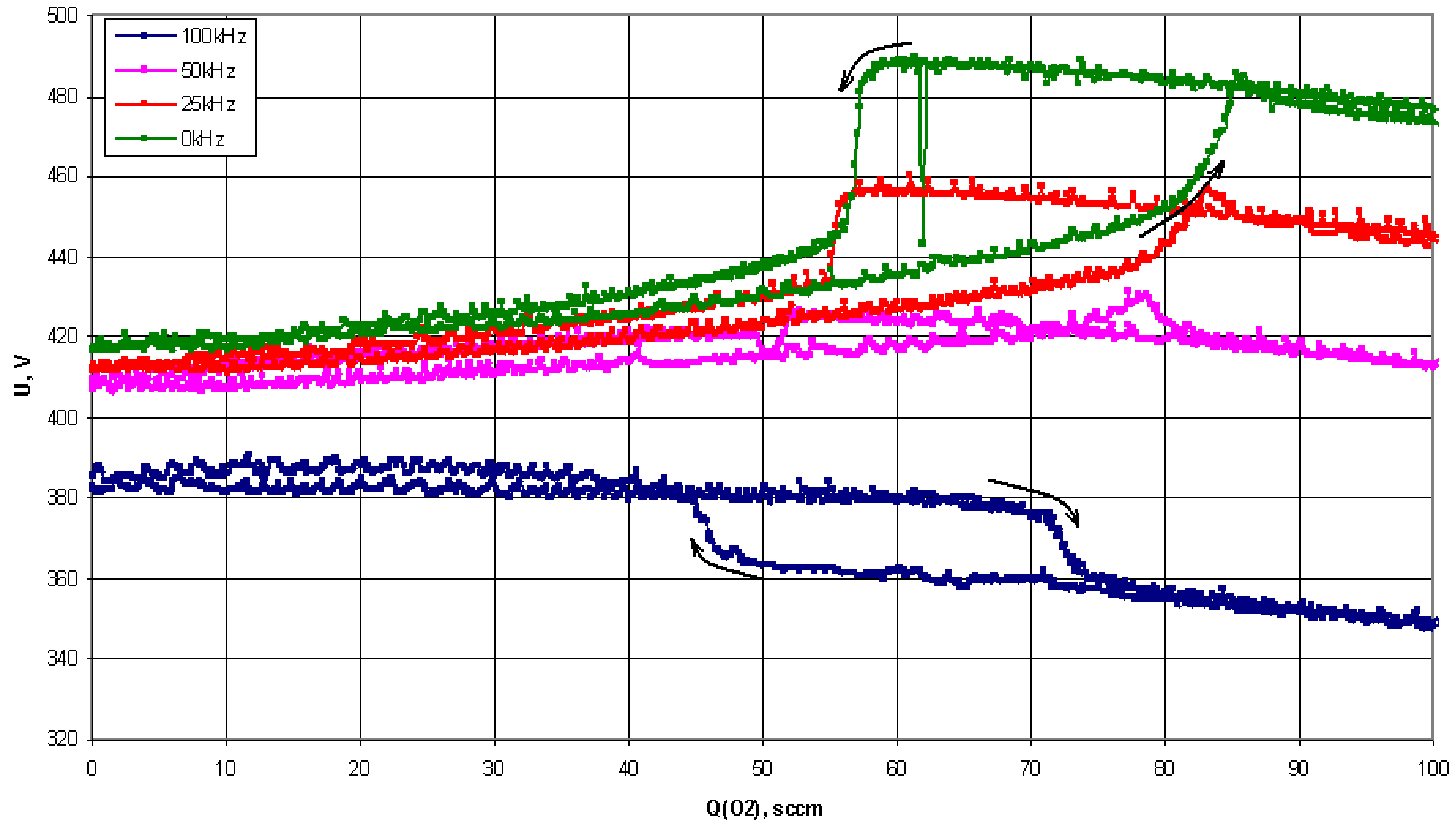

Fig. 5. Change of voltage hysteresis loop depending on frequency of the Puls DC power supply. Ar 200 sccm, 3,4 m3/s. (1 – 0 kHz, 2 – 25 kHz, 3 – 50 kHz, 4 – 100 kHz)

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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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Thanks for your attention!

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