

Magnetron sputtering of copper on thermosensitive polymer materials of the gas centrifuge rotors

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Abstract. Magnetron sputtering is the well-known and widely-used deposition technique for coating versatile high-quality and well-adhered films. However, the technology has some limitations, caused by high temperatures on the coating surface. The paper is devoted to the experimental development of a process of magnetron sputtering of copper on a surface coated with a thermosensitive polymer made of carbon fiber with epoxide binder. This process is applied for balancing a rotor of a gas centrifuge for isotope separation. The optimum operating parameters of the process are found and discussed. They were in quantitative agreement with data obtained by means of non-stationary modeling based on a global description of plasma in the typical geometry of the magnetron discharges obtained in independent research. The structure of the resulting layer is investigated.

1. Introduction

The development of magnetron sputtering paved the way for the coating of various substrates with materials that previously were impossible by thermal and ion sputtering. The main advantage of this technique is that bombarding the substrate with high-energy electrons becomes unnecessary for that leads to uncontrolled heating of the substrate and damages structures.

According to expert evaluations, high-power pulsed magnetron sputtering (HPPMS) has not exhausted its potential in that it enables dense plasma with a high content of a target component to be generated [1-2]. To date, many polymer materials are greatly restricted in applications in HPPMS because of sensitivity to thermal loading. As is known, the general value of the substrate temperature during the sputtering process is above 500°C, which is not suitable for many kinds of thermosensitive materials. No doubt, that the substrate temperature can be lowered by cooling and lowering the deposition rate but it greatly increases the cost of the sputtering process. [3]. It is also important in our case that a reduction in the process temperature would avoid surface tensions in the substrate that result in damage and flaking [4-5].

We deal with balancing of the gas centrifuge rotors, which is a classical problem of a turbomachinery. Being unbalanced these machines start to vibrate and it can lead to catastrophic failure. The balancing of three-dimensional rotating bodies is the most difficult case because it demands to place the balancing masses in a few places on a rotating body surface simultaneously. Referring those who are interested in the details of the rotor balancing process to the paper [6], we will



focus on the development of the magnetron sputtering system and the search of its optimum parameters. Being intended for mass production, this technique should be simple and cheap enough. The additional limiting condition for it is a restriction on a surface temperature of a rotor caused by its surface coated with a thermosensitive polymer. In our case it is carbon fiber with epoxide binder.

Recently, a model analysis of HPPMS of copper by means of the non-stationary two-zone model on the effects of voltage characteristics on HPPMS of copper was done by Kozaket. al. [7-8], where the conclusion was made that the average target power density in a pulse is, in addition to the target voltage, a fundamental quantity determining the average ionized fraction of copper atoms in the flux onto the substrate and the normalized deposition rate. Another conclusion was that a compromise between a high degree of ionization of the sputtered target material atoms and an acceptable deposition rate should be found by tuning the average target power density delivered in a pulse. It was demonstrated that sufficiently long pulses (at least 100 μ s) are needed to achieve high target power densities in a pulse and, consequently, high degrees of ionization of the sputtered atoms. The results of our experiments are compared with that model analysis below in the section Results and Discussion.

The feature of our problem consists in balancing of the spinning at high speed rotor covered with thermosensitive polymer. The idea was born to adapt HPPMS of copper for that. We found a paper of Kozak [6], but decided to verify the results of this theoretical research because the temperature limitation on the HPPMS process was added as the used carbon fiber with epoxide binder is destroyed by heating over 70°C. This limitation led us to question of limiting the deposition rate to keep our material from harm but keeping it rather high to be industry efficient.

As the possible means to solve this problem, we propose a cheap and easy method to operate a balanced magnetron with a low current through the substrate that would enable magnetron sputtering to be used on thermosensitive polymer material without significant substrate heating ($t_{\text{sub}} < 70^\circ\text{C}$).

As is well known, oxides and nitrides of titanium and aluminum are the most frequently used materials in magnetron sputtering. The choice of usage copper instead of the above-mentioned materials was dictated by the fact that copper has one of the highest sputtering coefficients, and, of course, it is much cheaper than they are. In addition, we realize that magnetron sputtering of copper may be used in various applications for creation of electrical and thermo-conductive layers on thermosensitive plastics [9-11].

2. Description of stand and method

The experimental stand we propose for the magnetron sputtering with copper of polymer materials consists of a vacuum camera with flanges for the magnetron modules. The modules are situated at five balancing planes to provide the rotor to come through resonant frequencies without destruction (see figure 1). Carbon fiber covered with epoxide is used as the substrate because it is widely used and easily obtained. The major limitation imposed on the process is a substrate temperature that should not exceed 70°C.

The material for the vacuum camera walls is stainless steel. Two pumps are used in the stand: a backing pump of pumping speed 5.5 l/s and a turbomolecular pump of pumping speed 150 l/s (for N_2). The vacuum camera is pumped down to a pressure of 1.3×10^{-3} Pa. The balanced magnetron is used with a cathode made of copper M1 with surface area of approx. 7570 mm². The magnetron sputtering modules are connected to a power supply, which generates powerful pulses of negative polarity with maximum voltage of 3 kV for durations of 50–300 μ s. A thermocouple sensor and a vacuum gauge trigger shutting of the valve and to measure pressure. Pure argon (of 99.998% purity) is used as the process gas. The argon flow rate of 4.72×10^{-5} l/s is controlled by an analog flow meter. The total volume of the vacuum camera is 100 l. The weight scales have an accuracy of ± 0.5 mg giving a measurement limit of 420 g and ± 10 mg; a measurement limit of 4.200 g is used for the sputtered mass measurements.

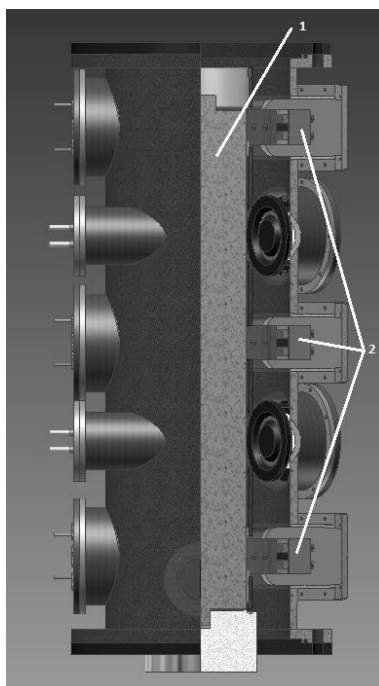


Figure 1. Design of the stand. 1 – polymer material of the rotor, 2 –magnetron modules

For sustained work for a magnetron, a constant pressure needs to be maintained. Indeed, this is not an easy task because the pressure to supply a constant argon flow to the installation must not fall below 10^{-3} Pa, otherwise the magnetron operation mode changes. Moreover, a good vacuum without a trace of oxygen is needed for magnetron sputtering with copper. Non-compliance with this condition leads to reactive deposition of copper oxide, for which adhesion is much worse. Additionally, the results from copper oxide sputtering are much worse compared with that for pure copper.

3. Special Requirements of the magnetron design

The optimal settings which are described below were found in a series of experiments yielding a sputtering speed of about $8.82 \mu\text{m}/\text{mm}^2\cdot\text{h}$ that produced a sustained and predictable mode of operation for the magnetron. If the magnetron design (figure 2) does not follow these requirements, negative effects take place, the most unpleasant being the discharge ignition behind instead of in front of the target. A “rear” discharge glows brightly and large currents are realized in this mode, although gradually front discharge pulls over the magnetic field to the region above the target. Concurrently, the current drops by one order of magnitude and subsequently sputtering speed decreases. Simultaneously, the vacuum camera pollution is very fast; the maximum deposition rate achieved in this case does not exceed $6.05 \mu\text{m}/\text{mm}^2\cdot\text{h}$.

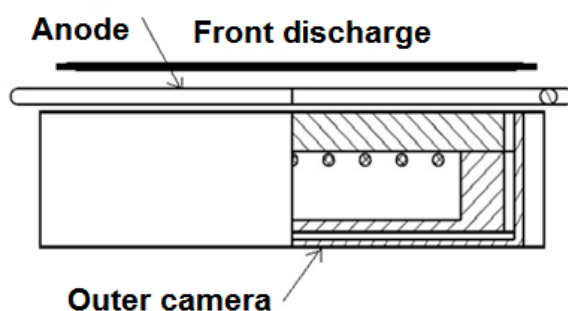


Figure 2. Design of the magnetron.

4. The optimum regime of the magnetron

During testing of the magnetron sputtering system the discharge voltage vs applied voltage graph was obtained at various pulse durations (100, 200, and 300 μs) at a frequency of 200 Hz (see figure 3).

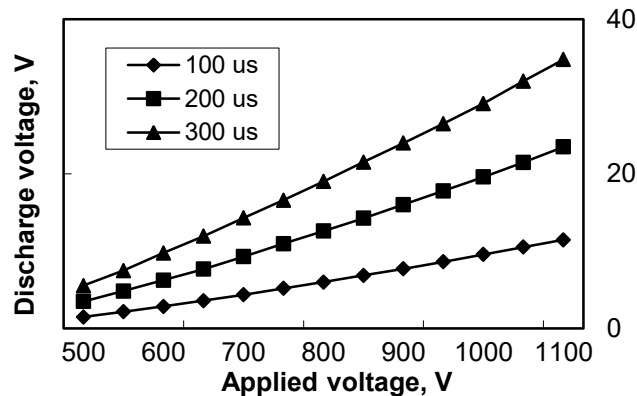


Figure 3. Discharge voltage vs applied voltage for various pulse durations.

The voltage dependence of the discharge ignition delay is shown in figure 4. The delay time is inversely proportional to the supplied voltage and is nearly 30 μs at low voltage. Hence, we concluded that the pulse duration of 100 μs is not optimal because a considerable amount of that time (up to 1/3) is spent on discharge ignition. Note that the value obtained for the delay time from these experiments is consistent with that in the work of Anders et al. [12]. The pulse duration of 300 μs is also not optimal because of heating of the polymer substrate and dissipating resistor. The experiments were therefore performed with the 200 μs pulse duration.

Additionally, discharge voltage vs applied voltage dependence at different pulse frequencies with pulse duration of 200 μs was obtained in experiments. These results are presented in figure 5. Clearly, from the data obtained, a higher pulse frequency leads to greater sputtering of the target and to greater heating of the substrate. As one can see the pulse frequency of 400 Hz and 600 Hz leads to great deposition rate, but these sputtering conditions totally destroy the substrate.

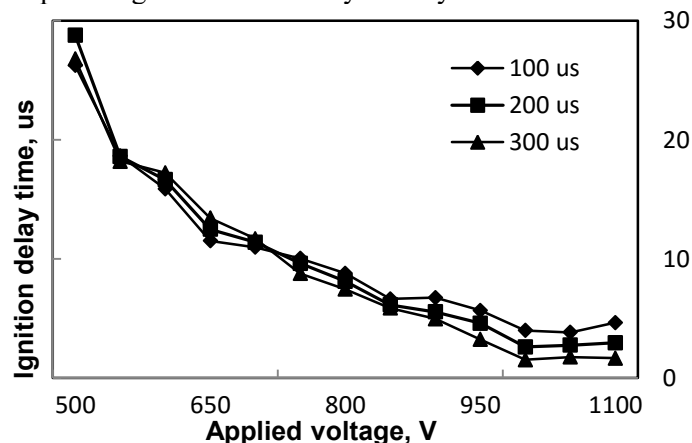


Figure 4. Voltage dependence of discharge ignition delay.

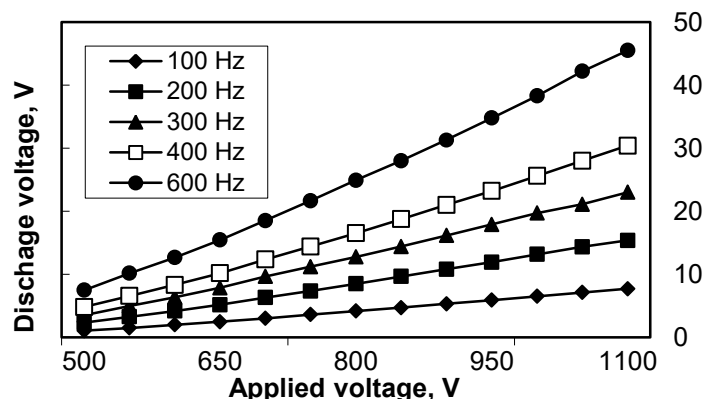


Figure 5. Discharge voltage vs applied voltage for various pulse frequencies.

The dependence of the substrate temperature T_{sub} on sputtering time t_{sput} under optimal operating settings ($V_{\text{imp}} = 1$ kV, $t_{\text{imp}} = 200$ μs , $f_{\text{imp}} = 300$ Hz) is exhibited in figure 6. One sees substrate temperatures being restricted to about 63°C ; short breaks in magnetron use (up to 30 s) leads to a sharp decrease in substrate temperature. The temperature was occasionally measured by a thermocouple which was situated next to the center of the sputtered spot. It was protected from the copper ions to prevent errors.

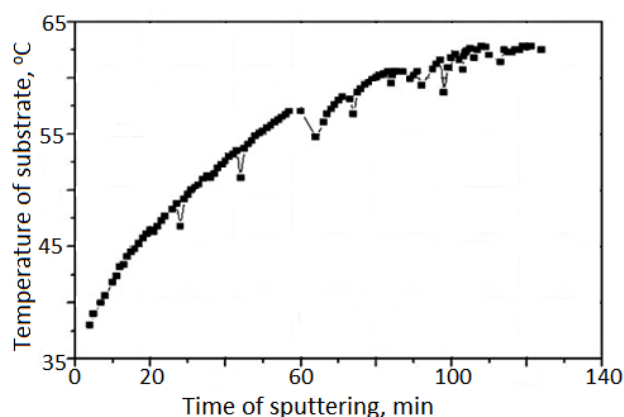


Figure 6. Dependence of a substrate temperature on sputtering time.

We believe that it differs from the regular mode of the conventional DC magnetron, using which we would be unable to operate with such low temperatures of the substrate.

According to [7], the high degree of ionization of the sputtered copper atoms leads necessarily to lower deposition rates when compared with DC magnetron sputtering at the same target power density. Due to this fact, we were able to carry out sputtering at a temperature limited by the properties of a polymeric substrate.

5. Results and discussion

The copper film was studied by TESCAN scanning electron microscope VEGA3 at NRNU MEPhI. As one can see in figure 7, the surface consists of four layers: the bottom is the layer of carbon fiber; next layer is epoxide binder; then goes the layer of dense copper and the upper layer is copper of the columnar morphology. The total thickness of a copper film is approx. $15 \mu\text{m}$.

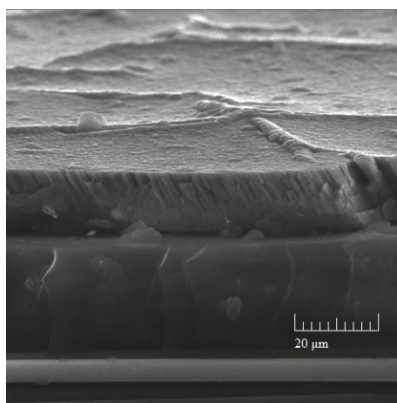


Figure 7. SEM photo of the surface.

The columnar structure is clearly visible on the surface layer of the film. The observed phenomenon of a column-like structure in sputtered deposited films has been written in a review of Windischmann [13]. In [14] it is explained by the presence of oxygen in the discharge area. The presence of oxygen on the surface and inside the copper layer in an amount of maximum 8% was detected by the conducted qualitative spectral analysis of the film and substrate. We attribute the reason of it by a weak leakage to our vacuum system.

They predict that when the amount of oxygen is reduced, the densification of the copper layer will take place. Bombarding ions will erase the peaks and fill the valleys further densifying the film, which in turn will lead to the upgraded mechanical properties of the film [15]. It will be one of the future goals in our further work on the problem to achieve more planar structure of a copper layer on a polymer substrate.

The interface between the carbon fiber, epoxy and sputtered copper is demonstrated in figure 8. At the lower side of the picture the yellow dots show carbon atoms; the carbon fiber at the bottom is clearly visible (compare with figure 7). The epoxide occupies the middle part of the picture. The amount of the carbon there is obviously lower. As for the upper side of the picture, where green dots represent copper, one can see that the bottom layer of the copper surface is very dense. There is a mixture of copper and carbon atoms near the outer side of the layer. The adhesion of the sputtered layer was tested by the stress test. No signs of destruction or flaking off were detected as a result of the test.

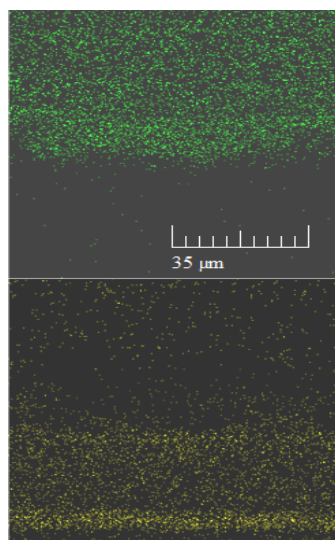


Figure 8. The distribution of the atoms on the surface cut. Green dots are cooper (upper) and yellow are carbon (lower).

Note that all physical regularities observed in our experiments are in qualitative agreement with that for the large currents (up to 80 A) applied in modeling [7-8]. As it was shown in the research of Kozak, the pulse length of 200 μs is very significant time mark as the average target power densities in a pulse, the average ionized fraction of the sputtered copper atoms in the flux onto the substrate as well as the normalized deposition rate reach their saturation by this time. The discharge parameters in [7-8] and in our research were obtained at different experimental stands and at various working conditions, nevertheless, they are in a good enough agreement. It allows us to assume that these parameters are general for this type of the discharge. This fact creates good and stable operational conditions for wide application, which is one of the purposes of this research.

6. Conclusions

The effective HPPMS of copper on the thermosensitive polymer material to balance the rotor of centrifuges for isotope separation is demonstrated at the specially designed experimental stand. Carbon fiber coated with epoxide was used as a substrate. The balanced magnetron, operating with pulse duration of 200 μs and pulse frequency of 300 Hz, enabled a sputtering speed of about 8.82 $\mu\text{m}/\text{mm}^2\cdot\text{h}$ to be achieved without significant heating of the substrate ($T_{\text{sub}} < 70^\circ\text{C}$, max $T_{\text{sub}} = 63^\circ\text{C}$). The dependence of substrate temperature on sputtering time was obtained. The dependence of magnetron discharge on various pulse durations and pulse frequencies were determined.

The experimental results obtained confirm the theoretical findings by Kozak et al. on the fundamental character of three process parameters namely, the average target power density in a pulse, the average ionized fraction of sputtered copper atoms in the flux onto the substrate as well as the normalized deposition rate. These parameters reach their saturation in 200 μs what also in good agreement with the model results for one of the considered values of the magnetic field. It seems that these parameters are general for the discharge regardless of the operating conditions.

The proposed method of non-destructive mass sputtering on thermosensitive polymer surfaces opens the possibility of a significant expansion of the range of materials used for HPPMS as well as application of the latter. The usage of HPPMS lead to the development of the gas centrifuge rotor balancing method which is cheaper and faster compared with the convenient one.

Acknowledgments

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