MODERN METHODS OF Ta_2O_5 COATINGS DEPOSITION FOR BIOMEDICAL APPLICATIONS

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The study of e-beam evaporated Ta_2O_5 film structure and properties effect on cell/material response was performed. The surface properties and structure of e-beam evaporated Ta_2O_5 films were investigated by means of XPS and XRD methods. The cytotoxicity and cytocompatibility were estimated by in vitro tests. Films of Ta_2O_5 are bio- and chemically inert, which allows their use in various medical applications, e.g., in diagnostic and treatment techniques employing short-range quasi-static electric fields for stimulation of positive biological processes in live organisms.
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1. INTRODUCTION

The interest to dielectric materials and coatings applications has considerably increased in various areas of science and technique in recent years. Coatings based on Ti, Al oxides exhibit unique properties: high inductivity, density and fusion temperature, together with high electret characteristics. Tantalum has a high potential in the biomedical field. Ta-based implants show high fracture toughness, corrosion and wear resistance, chemical stability. The results of the animal implantation test of Ta in both soft and hard tissue of rats showed good biocompatibility and osteogenesis of this metal [1]. TaC and TaN materials posses relatively high hardness due to the covalent nature of their bond [2] and demonstrate high thermal stability and superior corrosion resistance [3]. The blood compatibility of TaN films was shown to be better than those of TiN and Ta [4]. Films of Ta_2O_5 are also bio- and chemically inert, which allows their use in various medical applications.

In the paper new Ta pentoxide ceramic coatings are presented as perspective biomaterials for biomedical applications like dental implants, coronary stents or prosthesis. The study of e-beam evaporated Ta_2O_5 film structure and properties effect on cell/material response was performed.

2. MATERIALS AND METHODS

The samples were formed on glass substrates. The electron beam evaporator consists of a heated tungsten filament apertured by screen, surrounding the filament (Fig.1). Both the apertured anode and the crucible are at a ground potential. Accelerating voltage U_a is applied to the filament and to the screen. The magnetic field is created by an electromagnet. The evaporation power P_{ev} needed to heat the crucible containing the evaporated metal is the product of the anode current I_a and U_a (7kV).

The evaporation process was carried out at initial vacuum of 7×10^{-6} Torr, operational-mode vacuum of 3×10^{-5} Torr, anode current of 50 mA and calculated evaporation power of 350 W [5]. The layer thickness and the deposition rate were controlled by a digital thin-film deposition monitor MSV-1843/H MIKI-EEV operating at 6 MHz. The deposition rate at those conditions was 50 nm/min. The control module consists of: a control unit, a pulse time modulator, a ramp generator and a final control element (FCE).

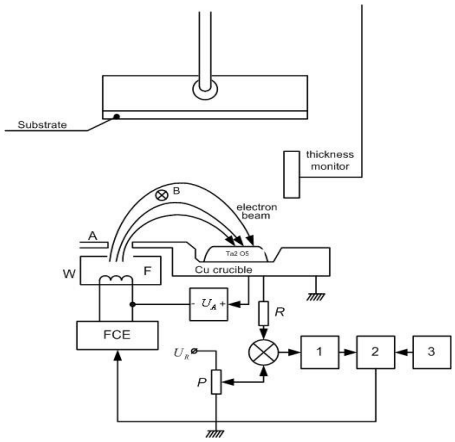

Fig.1. Electron beam evaporator: control unit, pulse time modulator, ramp generator and final control element

The surface properties and structure of e-beam evaporated Ta_2O_5 films were investigated by means of XPS and XRD methods. X-ray photoelectron spectroscopy was carried out using ESCALAB MkII (VG Scientific) electron spectrometer at a base pressure in the analysis chamber of 5x10-10 mbar (during the measurement 1x10-8 mbar), using AlKalpha X-ray source (excitation energy hn=1486.6 eV). The instrumental resolution measured as the full width at a half maximum (FWHM) of the Ag3d5/2, photoelectron peak is 1 eV. The energy scale is corrected to the C1s - peak maximum at 285 eV for electrostatic charging.

The analysis of surface parameters such as wettability, surface free energy was made. The contact angles were measured by Wilhelm's method in Kruss K12 Tensiometer at temperature 20°C [6]. For next calculations of surface free energy (SFE) were used the values of advancing water contact angle by Roberson equation, which is in a good agreement with values obtained by means of Owens-Wendt-Rabel-Kaeble' method.

The experiments on study of cytotoxicity and cytocompatibility *in vitro* – in culture of fibroblasts were carried out [7]. In process of cell cultivation with coated samples the cell cytology, morphology and proliferation activity were determined by means of optical microscopy after 24h and 3, 5 days cultivation. Rat hypodermic cellular tissue was extracted for initial fibroblast culture obtaining. The suspension of extracted cells was centrifuged at 750 orb/min during 15 min. Sowing cell area was $3x10^5$ cell/ml density of cultural medium. The fibroblast cultivation at 3 ml of Dulbecco Modified Eagle's Medium (DMEM, Sigma) was made by methods of mono layer culture at thermostat condition (temperature 37° C during 5 days). After cultivation, fixation at the acetic acid and methyl alcohol (1:3) solution and azure-eosin coloration the cellular proliferation on the cover glasses was determined by optical microscopy (Micros). The experiments were triplicate.

3. RESULTS AND DIDCUSSION

The XPS survey spectra of the e-beam evaporated Ta_2O_5 films (initial, un annealed sample; sample annealed at 450°C in O_2) were obtained. All spectra consist of well defined XPS lines of Ta 4f, 4d, 4p and 4s; O 1s; C 1s. All binding energies of the high-resolution spectra were calibrated with a C 1s binding energy of 285.0 eV. Fig. 2 show the high-resolution Ta4f and 4 O1s XPS spectra of the investigated structures.

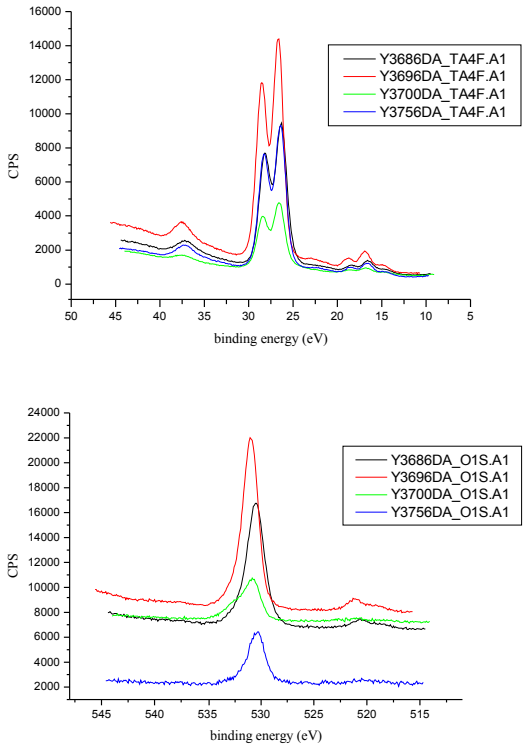

Fig. 2 The XPS high-resolution Ta 4f and 4 O 1s spectra of the e-beam evaporated Ta_2O_5 films

A relatively strong C1s feature is observed at 285 eV for the precursor and deposited films, most likely as a result of hydrocarbon adsorptions on the samples surfaces due to the exposure after the deposition to atmosphere air.(In situ surface cleaning using an ion –gun was not applied, in order to avoid the negative effects of the sputtering on the film composition). The carbon signal was used to take account the effect of the samples charging during the measurements.

Ta 4f doublets are typical for e-beam evaporated Ta_2O_5 and have two peaks: Ta 4f7/2 at ~ 26.3…26.6 eV and Ta 4f5/2 at the binding energy 1.9 eV higher. The Ta 4f lines of the deposited films agree well with the Ta 4f doublet representative of the Ta-0 bond in Ta_2O_5. The Ta4f7/2 peak is placed at 26.5 and 26.6 eV, and the Ta 4f5/2 one is at 28.4 and 28.5 eV for the annealed and un annealed films respectively. These results clearly demonstrate that the annealed films are more stoichiometric Ta_2O_5 composition. The O1s spectra further support this assumption. The O 1s peaks of the deposited layers are centered at binding energies of 530.9 and 530.8 eV for the for the annealed and un annealed films respectively, which is consistent with reported data for Ta_20_5 [8]. The FWHM of both peaks is 1.9 eV. The O/Ta ratio estimated from the spectra is ~ 3 for all samples (see Table bellow).

The wettability of films was evaluated by Wilhelm's method in Kruss K12 Tensiometer at temperature 20° C. The e-beam evaporated Ta_2O_5 films exhibited contact angles ranging from 49.3±0.5° for un annealed film to 52.5±0.6° for annealed film. The value of contact angle about 50° is considered as a positive indicator of good cell attachment, spreading and proliferation. In our study the values of water contact angle were measured in the range 49…52°, and evaluated by expression [6] meaning of SFE were in the range 40…45 mN/m.

After 3 days staying in the culture. fibroblast cells were well spread both on the control and coated surfaces. Any statistically significant dependence in the average area of cultivated cell was observed. The cell morphology was typical for cells on the coated surface. The cell structural organization corresponded to initial fibroblast. After 5 days cultivation the density of cell increased for all samples.

The concentration of O1s and Ta4f and binding energy annealed, un annealed and initial samples obtained from XPS spectra

Samples	C, at.% O 1s	C, at.% Ta4f	Ta/ /O ratio	Binding energy E (eV) O 1s	Binding energy E (eV) Ta 4f
Initial	68	32	0.471	530.4	26.3
Anneal. at 450 °C	69	31	0.449	530.9	26.5
Un anneal.	74	26	0.361	530.8	26.6

The most of cells were ripe fibroblasts with strongly marked phenotype. Fibroblast cells were well spread at all coated surfaces. The effect of the surface properties on cell proliferation is investigated by counting the cells attached to the glass surfaces after incubation. The mean cell counts vary when compared to uncoated glass samples (control, n = 72): cell numbers decrease by 18%

for un annealed film (n= 59) and by 11% for annealed e-beam evaporated Ta_2O_5 film (n = 64). The results demonstrated the good biocompatibility of e-beam evaporated Ta_2O_5 coatings especially in the case of annealed films with stoichiometric Ta_2O_5 composition.

4. CONCLUSIONS

The results show that the surface properties are strongly influenced by the preliminary treatment and the deposition conditions. The XPS analysis results clearly demonstrate that the annealed films are more stoichiometric Ta_2O_5 composition. The O/Ta ratio estimated from the spectra was ~ 3 for un annealed and initial samples (see Table), The e-beam evaporated Ta_2O_5 films exhibited contact angles, ranging from 49.3±0.5° for un annealed film to 52.5±0.6° for annealed film and evaluated meaning of SFE were in the range 40-45 mN/m. The cyto toxicity and cyto compatibility of Ta_2O_5 films were estimated by in vitro tests. The cell morphology was typical for cells on the coated surface. The results demonstrated the good biocompatibility of e-beam evaporated Ta_2O_5 coatings especially in the case of annealed films with stoichiometric Ta_2O_5 composition. The deposition process controlling allows one to control the surface parameters of the e-beam evaporated Ta_2O_5 films and the next positive biological response of live organisms.

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СОВРЕМЕННЫЕ МЕТОДЫ НАНЕСЕНИЯ ПОКРЫТИЙ Ta_2O_5 ДЛЯ БИОМЕДИЦИНСКОГО ПРИМЕНЕНИЯ

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Исследования структуры и свойств покрытий Ta_2O_5, нанесенных методом электронно-лучевого испарения, были проведены методами рентгеноструктурного анализа и фотоэлектронной спектроскопии. Цитотоксичность и цитосовместимость были определены *in vitro*. Пленки Ta_2O_5 являются био- и химически- инертными, возможно их применение для диагностики и лечения с использованием близкодействующих квазистационарных электрических полей, стимулирующих позитивные биологические процессы.

СУЧАСНІ МЕТОДИ НАНЕСЕННЯ ПОКРИТТІВ Ta_2O_5 ДЛЯ БІОМЕДИЧНОГО ЗАСТОСУВАННЯ

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Дослідження структури та властивостей покриттів Ta_2O_5, які нанесено методом електронно-променевого випарювання, було зроблено методами рентгеноструктурного аналізу та фотоелектронної спектроскопії. Цитотоксичність і цітосумісність були визначені *in vitro*. Плівки Ta_2O_5 мають біо- та хімічно- інертні властивості, що сприятиме їх застосуванню з метою діагностики та лікування з використанням близькодіючих квазістаціонарних електричних полів, які стимулюють позитивні біологічні процеси.