The surface parameters modifications at nano scale for biomedical applications

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Abstract. Functional coatings deposition is an effective way of surface modification with direct control of stoichiometry, impurity elements, functional groups and surface charges. Modified surface properties such as composition, roughness, wettability have effect on the most important processes at biomaterial interface. The aim of present study was the analysis of surface roughness and surface free energy parameters of oxide Al₂O₃ and Ta₂O₅ coatings and the possibility to separate the influence of such factors on the regularities and mechanisms of nano materials interactions with the biological objects.

1. Introduction
Material surface properties such as composition, roughness, topography, wettability can influence events at material interface and play a basic role at processes of dyeing, penetration, chemical absorption, biocompatibility and others. The coatings deposition is an effective way of surface modification with direct control of stoichiometry, impurity elements, functional groups and surface charges. Coatings based on Ti, Al, Zr, Ta oxides exhibit unique properties: high inductivity, density, bio- and chemically inertness, which are very important for next implant and tissue engineering applications. Cell/biomaterial interaction process and direct cell adhesion to a biological surface creates many important phenomena providing vital functions of a living organism on different levels of its organization. The effects of substrate material composition, surface chemistry and surface energy on cell adhesion and proliferation processes have been largely studied [1-4]. The interpretation of data on cell contact formation is crucially dependent on the actual area of membrane region involved in adhesion. The distance between phospholipid bilayers of membranes is in the order of 20-40 nm [5]. The characteristic size scale of cellular receptors interaction is a few 100 nm. Thus the surface relief modifications should be also controlled at a nanometer-submicronic level. The important task of cell/biomaterial interaction research is separation of different factors influenced on process such as surface chemistry, surface energy and roughness.

2. Materials and methods
At the present study the samples were glass substrates (Petri dishes), uncoated and oxide coated (Al₂O₃ (MS) magnetron sputtered and Ta₂O₅ (EB) e-beam evaporated) with different roughness parameters – 20, 200 and 400 nm. Al₂O₃ (MS) coatings deposition was performed in high vacuum

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pumping system with the base pressure about $10^{-3}$ Pa. The main process parameters were magnetron discharge power 1-8 kW, oxygen source power 1kW, deposition rate 8 µm/hour [6]. The Ta$_2$O$_5$ films evaporation process was carried out at initial vacuum of $9.3 \times 10^{-4}$ Pa, operational-mode vacuum of $4 \times 10^{-3}$ Pa, anode current of 50mA and calculated evaporation power of 350W [7]. The deposition rate under these conditions was 28nm/min. The layer thickness and the deposition rate were controlled by a digital thin-film deposition monitor MSV-1843/H MIKI-EEV operating at 6MHz.

The coatings adhesion properties, hardness and elastic modulus, thickness were evaluated by standard methods. The surface roughness was measured by means of profilometer Hommel T-2000. surface topography was estimated by AFM methods (Quesant Instrument Corporation,USA). The structure of Al$_2$O$_3$ magnetron sputtered and Ta$_2$O$_5$ e-beam evaporated thin 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 $6 \times 10^{-8}$ Pa (during the measurement $1.3 \times 10^{-6}$ Pa), using AlKalpha X-ray source (excitation energy $h\nu=1486.6$ eV). The instrumental resolution measured as the full width at a half maximum (FWHM) of the Ag3d5/2, photoelectron peak is 1 eV.

The contact angles were measured by means of tensiometric method in Kruss K12 Tensiometer at temperature 20° C [8]. Prior to contact angle measurements, samples were ultrasonically cleaned in acetone and deionised water and dried. The standard liquids with well-known values of surface tension, component of dispersion and polar interaction such as water, formamide, diiodo methane, ethylene glycol, α-bromo naphthalene and glycerol were used. Also the surface free energy (SFE) and its polar and dispersion components were determined by means of Owens-Wendt-Rabel-Kaelble methods [9].

3. Results and discussion
The coatings adhesion properties, hardness and elastic modulus were presented at Table 1. The surface roughness parameters were estimated by means of profilometer Hommel T-2000, at the range 20, 200 and 400 nm (table 2).

| Table 1. The mechanical properties of Al$_2$O$_3$ magnetron sputtered and Ta$_2$O$_5$ deposited by EB-evaporation method coatings on glass substrates. |
| --- |
| Coatings type | Hardness Hv [Mpa] | Hardness H [Gpa] | Young Modulus [Gpa] | Adhesion [N] |
| --- | --- | --- | --- | --- |
| Glass/ Al$_2$O$_3$ 20nm | 742.6 | 8594.8 | 203.7 | 33 |
| Glass/ Al$_2$O$_3$ 200nm | 747.5 | 8614.3 | 207.4 | 36 |
| Glass/ Al$_2$O$_3$ 400nm | 751.0 | 8105.2 | 209.8 | 37 |
| Glass/ Ta$_2$O$_5$ 20 nm | 129.35 | 1397.4 | 47.5 | 12.7 |
| Glass/ Ta$_2$O$_5$ 200 nm | 130.2 | 1412.7 | 48.8 | 12.8 |
| Glass/ Ta$_2$O$_5$ 400nm | 133.5 | 1452.4 | 49.3 | 13.1 |

The best mechanical properties were obtained in the case of oxide coatings Al$_2$O$_3$ (MS) deposited by magnetron sputtered method. X-ray diffraction profiles of Al$_2$O$_3$ (MS) and Ta$_2$O$_5$ (EB) as-deposited coatings demonstrate the amorphous nature, no peaks were observed. The high-resolution Ta 4f and 4 O 1s XPS spectra show the investigated Ta$_2$O$_5$ structures. Ta 4f doublets are typical for e-beam evaporated Ta$_2$O$_5$ and have two peaks: Ta 4f7/2 at ~ 26.2 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$_2$O$_5$. The ratio Ta4f /O1s is nearly 0.37. These results clearly demonstrate that the investigated films have stoichiometric Ta$_5$O$_5$ composition. The O1s spectra further support this assumption. The O 1s peaks of the deposited layers are centered at binding energy of 530.6, which is consistent with reported data for Ta$_2$O$_5$ [10]. Some additional impurities have been observed at the XPS spectra of e-beam evaporated Ta$_2$O$_5$ (figures 1 and 2).
The surface topography was observed by AFM (figure 3).

**Figure 3.** Surface topography of Al$_2$O$_3$ (MS) coatings on glass substrates with roughness 20 (a), 200(b) and 400 (c) nm.

The standard liquids with well-known values of surface tension such as water, formamide, diiodo methane, ethylene glycol, α-bromo naphthalene and glycerol were used for tensiometric measurements. Also the surface free energy (SFE) was determined by means of Owens-Wendt-Rabel-Kaelble methods. The contact angles (water) and surface free energy calculated by means of Owens-Wendt-Rabel-Kaelble method for the uncoated glass substrates, Al$_2$O$_3$ and Ta$_2$O$_5$ oxide coated samples at various roughness parameters in the range 20, 200, 400 nm were evaluated (Table 2).

**Table 2.** The surface roughness parameters, the contact angles (water) and surface free energy for the uncoated glass substrates, Al$_2$O$_3$ and Ta$_2$O$_5$ oxide coated samples at various roughness parameters in the range 20-400 nm.

| Samples                  | Roughness $R_a$ ($\mu$m) | Water contact angles ($^\circ$) | SFE (mN/m) by Owens-Wendt-Rabel-Kaelble method |
|--------------------------|--------------------------|--------------------------------|-----------------------------------------------|
| Glass (Petri dishes)     | 0.017                    | 36.20±3.43                     | 57.71                                         |
| Glass                    | 0.18                     | 35.77±4.24                     | 58.05                                         |
| Glass                    | 0.37                     | 34.14±6.23                     | 58.28                                         |
| Glass (Petri dishes) /Al$_2$O$_3$ | 0.019               | 67.89±5.38                     | 43.76                                         |
| MS coatings              |                          |                                |                                               |
| Glass /Al$_2$O$_3$       | 0.21                     | 64.41±6.41                     | 44.97                                         |
| Glass /Al$_2$O$_3$       | 0.39                     | 69.92±4.02                     | 45.96                                         |
| Glass (Petri dishes)/ Ta$_2$O$_5$ | 0.021     | 65.35±7.22                     | 43.89                                         |
| EB evaporated coatings   |                          |                                |                                               |
| Glass/ Ta$_2$O$_5$       | 0.23                     | 62.41±6.43                     | 44.06                                         |
| Glass/ Ta$_2$O$_5$       | 0.38                     | 61.76±4.53                     | 44.14                                         |
The data demonstrate (table 2) that for the glass substrates contact angles (water) change in the range 34-36 °, 65-68 ° for Al₂O₃ coated samples and 61-66 ° for Ta₂O₅ coatings and surface free energy calculated by means of Owens-Wendt-Rabel-Kaelble methods changes in the range 57-60 mN/m for glass substrates and 43-45 mN/m for oxide coated samples at various roughness parameters in the range 20-400 nm.

4. Conclusions
The best mechanical properties were obtained in the case of oxide coatings Al₂O₃ (MS) deposited by magnetron sputtered method (table 1). The structure and composition of coatings was examined by XRD and XPS spectra. The Ta 4f lines of the deposited films agree well with the Ta 4f doublet representative of the Ta-O bond in Ta₂O₅. The results clearly demonstrate that the investigated films have stoichiometric Ta₂O₅ composition with some impurities (figure 1). The surface roughness and topography was observed by AFM (figure 2). The data demonstrate (table 2) that for the glass substrates contact angles (water) change in the range 34-36 °, 65-68 ° for Al₂O₃ coated samples and 61-66 ° for Ta₂O₅ coatings. The surface free energy calculated by means of Owens-Wendt-Rabel-Kaelble methods changes in the range 57-60 mN/m for glass substrates and 43-45 mN/m for coated samples at various roughness parameters in the range 20-400 nm. The results make the possibility to separate the influence of roughness and surface free energy effects on the regularities and mechanisms of nano materials interactions with the biological objects and open the perspective for a direct control of such parameters as adhesion, proliferation, differentiation of cells during their culturing.

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