Prethreshold Electron Emission towards Medical Applications: Characterization of Nanomaterials, Gas and Radiation Sensing (Review of Recent Results)

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Introduction. Rapid development of nano materials opens a wide horizon for their nanovolumed applications for medicine. Safe use of materials in a human organism requires reliable detection of their properties, surface features being very important.

To do not disturb gentle nanoobjects a contact less characterization is preferable. For this a low energy electron, having a nanoscaled mean free path (L) in a solid that could be employed. To detect such an electron emission the prethreshold mode, when an energy of the emitting electron is slightly higher that an electron work function (an energy threshold to escape the electron), should be employed.

A current (I) of the prethreshold single photon excited electron emission (PE) is described by the well-known formula

$$I = K(h\nu - \varphi)^m , \qquad (1)$$

where K- coefficient, $h\nu$ - energy of exciting photon, φ - electron work function (φ depends on the surface electrical charge density, in particularly), m-power index; $h\nu \geq \varphi$.

The values of φ are equal to several units of eV (~ 5 eV) [1], and therefore L of the photoelectron within the emitter is around 10-100 nm [2].

The results by the author and the team leaded by him directed to employ PE for characterisation of the thin (nanometric) surface layer of materials for medicine are reviewed in the present paper. The review covers the last decade achievements reached for the first time.

Experimental technique. To detect PE the home made spectrometers were in use [3, 4]. The specimens were located into the vacuum chamber (vacuum ~$10^{-3...-4}$ Pa). To excite PE the photons elected from the ultraviolet range (the monochromator was in use) illuminated the surface of the specimens. The emitted electrons were detected by the secondary electron multiplier (Hamamatsu (Japan) or VEU6 (Russia)) that was able to detect single electrons.

Results. Mechanical tensions at the nanolfilms/surface nanolayers control φ and could destroy molecular couples. In a case of a complicated loading of the material its surface becomes under the highest mechanical stress. Fig. 1 provides strain and electron emission diagrams of the composite material (epoxy binder mixed with carbon nano tubes) [5]. In contrast with monotone strain/load diagram at the elasticity area, the electron emission current demonstrates cog like regularity. This was explained as the indication of the single acts of molecular couples destruction [5] induced by deformation.

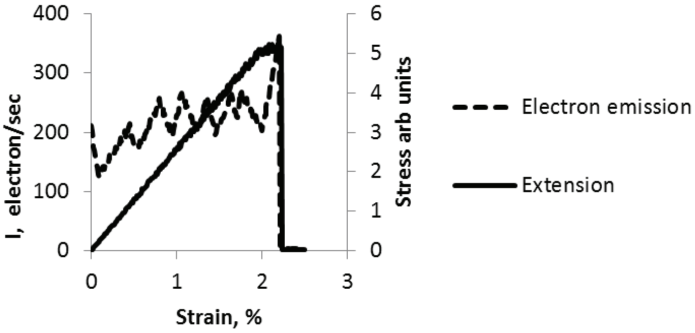

Fig. 1. Strain and electron emission diagrams of the composite material (epoxy binder mixed with carbon nano tubes) [5]

Hydroxiapatite (HAP) nano particles are widely in use for grafting of human bones, bioceramics, etc [6]. The HAP surface should have the specific properties to communicate with the human cells. The electrical interaction is the important channel for this [7].

It is known that mechanical surface tensions depend on a size of the spherical like particles. This could influence a density of the surface charge, particularly in a case of ionic crystals (HAP is partially ionic one), as the result φ should be affected. Fig. 2 [8] demonstrates a correlation of φ on a size (X) of the hydroxyapatite nanoparticles.

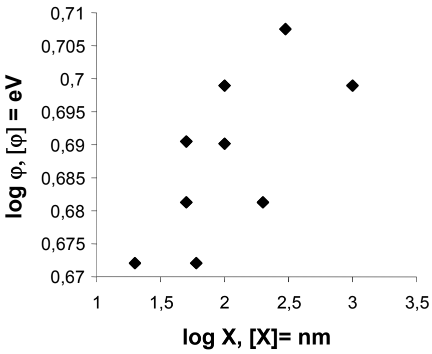

Fig. 2. Correlation of φ on a size of the nanoparticles [8]

To supply the antibacterial properties to the titanium implant coated with the titanium oxide the surface electrical potential of the latter was engineered because of imbedding of Cu nanodots into the titanium oxide substrate [9]. The Fig. 3 demonstrates that the value of φ was engineered because of the Cu nanodots density in the titanium oxide nanofilm coated the Ti substrate.

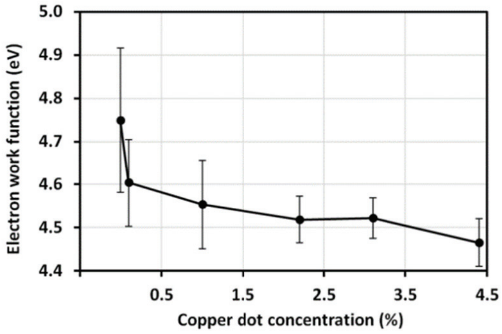

Fig. 3. The value of φ of Titanium oxide nanofilm coated the Ti substrate in dependence on the embedded Cu nanodots density [9]

Gas sensing and ionizing radiation are employed for cancer diagnostics and therapy, correspondingly [10].

Crystalline Si was deposited with benzene gases [11, 12]. Absorption of gas molecules altered φ and provided the response of *I*. Gas absorption altered I and correspondingly a total emitted charge indicated a volume of the molecules attached to the Si . Fig. 4 demonstrates the total emitted charge increment in dependence on benzene gases exposure. A sensitivity of the technique was evaluated as 10^{-5} gram of benzene for 1 cm^2 of the adhering wafer surface [12].

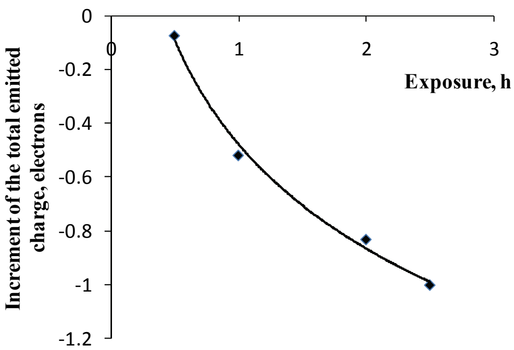

Fig. 4. Emitted charge increment versa exposure in benzene gas [12]

Modern radiation therapy (RT) technologies and the needs of molecular and micro radiobiology need detection of radiation absorbed by micro/nano volumes. There are several reasons for this: (i) biological effects caused by radiation depend on dose absorbed by nanosized DNA units; (ii) there is a trend in radiation therapy to apply high dose gradients (Gy/(µm…nm)) [13], surviving of the cells depending on the gradient value; (iii) nanoparticles as radiation scattering centers are expected to reach local micro- nano- scaled treatment that minimally influences risk organs/cells; (iv) radiation sensitive nanoparticles have ability to penetrate from the environment to a human body [14].

However, there are still no detectors that measure radiation in nanovolumes. The possibility to apply PE for this purpose is considered in [12]. An example is given, when PbS nanodots (~ 4 nm) imbedded in ZrO_2 nanofilm (thickness ~100 nm) were employed to detect radiation [12]. ZrO_2:PbS films were radiated with 9 MeV electrons. The values of *I* were measured before and after radiation. The corresponding increment of the derivation $\Delta[dI/d(h\nu)]$ recognized at 5.75±0.03 eV correlated with the delivered dose (Fig. 5).

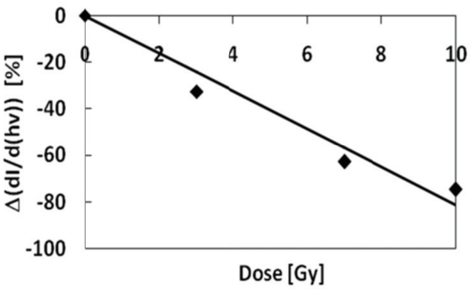

Fig. 5. Increment of Δ[dI/d(hν)] inspired by the delivered dose to the ZrO_2:PbS nanofilms[12]

Conclusion. Prethreshold electron emission is capable to supply sensitive, contactless technique to characterize biomaterials surface nanolayers, nanoparticles and to be in use for gas and radiation sensing inmedicine

The sensitivity of the chemical sensor, particularity to the benzole molecules is around 10^{-5} gram per 1 cm^2 of the Si substrate surface.

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Rapid development of nanomaterials opens a wide horizon for their medical applications in nanovolumes both of the human body and sensors. Safe employment of materials in a human organism requires reliable detection of their properties. Characterization of both nano materials and nano sensors should be supplied at the nanoscaled dimension. To do not disturb gentle nanoobjects their measurements due to contact less technique are preferable. Low energy electron has a mean free path in a solid that is in order of nanoscale. Therefore, a prethreshold (energy of the emitting electron is close to the electron work function) electron emission contact less spectroscopies could become a good instrument both for characterization of nanostructured materials and nanosensing. Weak emission ($\sim 10^{-15} \ldots 10^{-13}$ Q/cm^2) of electrons from a solid does not give a significant feed back to measurements in sense of the negligible inducted electrical charge at the material surface (a density of the surface electrons in the solid is around 10^{14} cm^{-2}). The paper reviews photo-, dual- and exo- electron emission fundamentals and their applications for characterization of focused to medicine nanoobjects (concentration of point like imperfections, their annealing, migration; surface charge of nanoparticles; energy gap; electron density of states; thickness of thin films and interfaces between them and the substrate) as well as gas and ionizing radiation nanodimensional sensing .