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Nanocrystalline Cerium Oxide Films for Microelectronic Biosensor Transducers

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The physical properties of thin nanocrystalline cerium oxide films have been studied with the purpose of their application as a functional material of different microelectronic transducers for biosensors: high-performance photoresistors and photodiodes for bioluminescence registration, ion-selective field-effect transistors (ISFET) and MOS-varactors indicating the pH changes as a result of biochemical processes. The effect of technological factors on the photoelectrical, optical, temperature and electrophysical properties of cerium oxide films has been studied. We established the technological conditions which allow to obtain CeO_x-films with desired functional characteristics. On the basis of the synthesized nanocrystalline CeO_x-films obtained by the "explosive evaporation" method we developed new types of photodetectors for registration of bioluminescent signal (photoresistors and photodiodes) with enhanced photosensitivity (310-330 mA/lm·V) in the visible range. Application of cerium oxide based photoresistors in the bioluminometers instead of photomultiplier tubes and avalanche photodiodes allows to significantly reduce the cost of bioluminometer and increase its sensitivity when measuring at alternating signal.

On the basis of nanocrystalline CeO_x-films obtained by the "metallic mirrors oxidation" method we developed potentiometric biosensory transducers (ion-selective field-effect transistors and MOS-varactors) with CeO_x as gate dielectric. It yields higher sensitivity and stability as compared to the use of the SiO_2 and Si_3N_4 films.

Keywords: Nanocrystalline cerium oxide films, CeO_x, CeO_2, Ce_2O_3, Thin-film photoresistors, Photodiodes, ion-sensitive field-effect transistors, ISFET, MOS-varactors, Microelectronic biosensors.

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1. INTRODUCTION

On the basis of biosensors analysis [1, 2] it was found that one of the promising trends related to the modern biosensors for detection of toxic substances are bioluminescent and potentiometric methods. Bioluminescent methods are typically based on the measuring of changes in intensity of bioluminescence with the help of photomultiplier tubes (FMT) and avalanche photodiodes. Potentiometric biosensors determine the change in charge in the solution using ion-sensitive bulk electrodes. To reduce the size of biosensors, simplify the application of biological membrane on the transducers surface and to save expensive biological materials the bulk biosensor transducers should be replaced with the film ones. Thus the tasks of finding new sensitive materials, its investigation and the development of film transducers of biosignals with increased sensitivity, stability and reduced cost are of urgent interest. The aim of this work is to obtain and study the physical properties of cerium oxide films to create effective biosensor transducers.

2. FABRICATION AND EXPERIMENTAL TECHNIQUES

Thin films of cerium oxide were obtained by various technological methods, depending on their application in sensors: CeO_x films for photoresistors and photodiodes by the method of vacuum flash evaporation (the "flash" method) and films of the external gate dielectric of ion-selective field-effect transistors by the technology of "metallic mirror" oxidation [1, 3].

Microstructure of the obtained CeO_x films was studied by scanning electron microscope JEOL JSM 6490LV (accelerating voltage of 20 kV), transmission electron microscope ПЕМ У-М (resolution of 0.21 nm, accelerating voltage of 125 kV) and X-diffractometer DMAX - B Japan [4].

The structural properties of films of cerium oxide have been studied using X-ray photoelectron spectroscopy (SERIES 800 XPS, Kratos Analytical) [7]. An X-ray tube with a magnesium anode (U = 12 kV, I = 30 mA) with nonmonochromatic MgK [3].

CeO_x-films surface morphology was studied by atomic force microscope NanoScope IIIa (DI, USA) using the Periodic contact silicon probe with the nominal tip radius of 5-10 nm.

Electrophysical properties of the structures based on the cerium oxide films were studied by the I-V characteristics [5], the study of optical and photoelectric properties - with the help of absorption and transmission spectra, spectral photosensitivity and lux-ampere characteristics. The method of high-frequency C-V characteristics was used to study the cerium oxide film/single-crystal silicon interface [4].

3. CERIUM OXIDE FILM AS AN ACTIVE MATERIAL OF MICROELECTRONIC TRANSDUCERS

The problems of using of the photoelectron multipliers and avalanche photodiodes in the bioluminescent sensors, and also ion-selective field-effect transistors and MOS-varactors in potentiometric sensor transducers have been analyzed. In particular these are limited dynamic range, high cost, high-voltage power of the FMT; problems with the supply voltage stabilization, probabil-

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ity of uncontrolled breakdown, low sensitivity to the short-wave boiluminescent radiation of avalanche photodiodes. As for the drawbacks of the potentiometric transducers based on the ion-sensitive MOS-varactors and ISFET with SiO_2, Si_3N_4 and Ta_2O_5 gate dielectrics it is the lack of sensitivity and instability of the informative signal due to mobile charges in the dielectric film and charge states at the oxide-semiconductor interface.

To eliminate the drawbacks of luminescent biosensors we decided to develop a new type of photodetectors of the luminescent signal – highly sensitive, microminiature, stable, low-voltage and low-cost photoresistors and photodiodes based on cerium oxide films.

To improve the characteristics of potentiometric MOS-sensors we followed a fundamentally new way – application of a new material as gate dielectric. The requirements for such material are following: close to the silicon crystal lattice parameters and hence the minimal number of charge states at the insulator-semiconductor interface, increased value of the dielectric permittivity, the highest possible number of pH-sensitive centers at the dielectric surface, thermal and chemical stability and biocompatibility. To meet the above requirements we proposed to use cerium oxide films as a functional material of the microelectronic sensor transducers (thin-film photoresistors, photodiodes, MOS-varactors and ISFET) because of the favorable combination of optical and electrical properties of cerium oxide.

It was determined that properties of cerium oxide films and their quantitative relationships with the technological parameters (especially for their use as the active material for the sensor transducers) are studied insufficiently. On this basis it has been tasked to carry out a comprehensive study of formation of cerium oxide films with the desired functional properties for the creation of microelectronic biosensors.

Structural research of cerium oxide films has shown that at low substrate temperatures (T_s = 175 ^{0}C) cerium oxide films with nanocrystals in amorphous matrix are formed. The amorphous phase is represented by Ce_2O_3, while nanocrystalline – by CeO_2 with face-centered cubic crystal lattice. At higher substrate temperatures T_s the “explosive evaporation” method gave nanocrystalline films of CeO_2 with the CaF_2 structural type with no amorphous phase in it. Besides, such CeO_x films obtained at 200 ^{0}C and 300^{0}C had different grain size (close to 24 nm and 27 nm respectively), different shape of grains, and different preferred orientation.

It was revealed that increasing of the substrate temperature from 175 to 200 ^{0}C is accompanied by the growth in photosensitivity, electrical conductivity, coefficient of absorption in the short-wave visible range, reduction of temperature coefficient of resistance and decreasing of charge states density at the film-substrate interface. This is caused by the transition from amorphous to nanocrystalline phase and also by changes in film composition (from two-phase Ce_2O_3 and CeO_2 to single-phase CeO_2) of the cerium oxide films produced by the "explosive evaporation" technology. Further increase of the substrate temperature up to 250-300 °C leads to deterioration of the above properties due to the changes in the morphology and phase composition of the CeO_x films.

As the bioluminescent methods are usually used at 450-600 nm of wavelengths, the research of the photosensitivity of the photoresistors and photodiodes based on cerium oxide films was carried out in this wavelength range. Thus for the photoresistors with CeO_x films deposited on SiO_2/Si substrate a linear dependence of photocurrent density of luminous flux was observed unlike to this dependence for Si_3N_4/Si substrate. The research of the spectral photosensitivity of the CeO_x film photoresistors in the spectral wavelengths range 200-800 nm, has shown that maximum photosensitivity is observed in the range of 450-550 nm, which is typical for bioluminescent radiation.

It was experimentally determined that the best characteristics for the creation of photodetectors of bioluminescent signal had the cerium oxide films deposited by explosive evaporation at substrate temperature of 200 ^{0}C. These technological conditions promote formation of nanocrystalline CeO_2 films with a minimum number of the recombination centers (the value of the surface states density at the film-substrate interface N_{ss} on the level of $7 \cdot 10^{10}$ $sm^{-2} \cdot eV^{-1}$) and a maximum value of the absorption coefficient (~ 10^4 sm^{-1}), which also explains the increased photosensitivity (3-3,3 mA/lm).

Based on the synthesized thin nanocrystalline cerium oxide films we developed new types of photodetectors for the bioluminescent signal registration (photoresistors and photodiodes) which have an enhanced photosensitivity value of 310-330 mA/lm·V and have no typical deficiencies of the photoelectron multipliers and avalanche photodiodes (high cost, high-voltage power of FEM and problems of stabilization of the supply voltage, probability of uncontrolled breakdown, low sensitivity to short-wave boiluminescent radiation of the avalanche photodiodes).

Based on results of the research of the high-frequency C-V characteristics of MOS structures with the CeO_x films obtained in different technological conditions it was determined that for the manufacture of ion-sensitive potentiometric biosensor transducers it is advisable to use a low temperature technology of metallic mirrors oxidation at the T_s = 160 ^{0}C. In this case the highest value of dielectric permittivity (ε = 15) and of the capacitance overlap coefficient (13), the minimum value of density of surface states at the insulator-semiconductor interface (N_{ss} = $6.8 \cdot 10^{10}$ $cm^{-2} \cdot eV^{-1}$), and also the absence of mobile charges are achieved. This enables the raise of sensitivity and stability of potentiometric biosensor transducers with the CeO_x gate dielectric (ion-selective field-effect transistors and MOS varactors) compared to their counterparts on the basis of SiO_2 and Si_3N_4. As a result, the pH-sensitivity of the ISFET with CeO_x dielectric has risen by almost 10% compared to SiO_2-Si_3N_4 and has reached the value of 58 mV/pH, which is close to the maximum possible sensitivity to the semiconductor-insulator-solution structure - 59.2 mV/pH. In addition, the drain current pH sensitivity of ISFET with CeO_x dielectric has risen compared to SiO_2-Si_3N_4 more than twice.

Taking into account the high chemical stability of CeO_2 and simplicity of the dielectric films obtaining, cerium dioxide can be considered very promising for use as ion-sensitive material in ISFET – a basic element in the creation of the biosensors for various purposes.

On the basis of the efficient photodetectors developed in this work a new type of bioluminescent sensor – a portable electronic biolumenometric device for the detection of toxic substances – was developed and studied. The application of semiconductor photoresistors based on cerium oxide films in biolumenometric device instead of photoelectron multipliers and avalanche photodiodes allows to reduce the cost of biolumenometers and raise its sensitivity due to the extended sensitive surface area and highly sensitive bridge circuits using AC.

4. CONCLUSIONS

An urgent scientific problem of synthesis of the nanostructured cerium oxide films with the desired physical properties for the creation of highly efficient biosensors including multiparametric ones has been solved. Microelectronic transducers based on cerium oxide films developed in this work can be the basis for the creation of affordable, portable, highly sensitive and reliable biosensors for environmental monitoring, investigation of the effect of toxic agents on various chemical and biological processes and for other purposes, – instead of a costly, cumbersome and sophisticated analytical equipment used today.

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