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ON THE OPTOELECTRONIC INFORMATION TRANSFER PHENOMENON AT THE INTELLIGENT INTERFACES OF SOME MIXED MULTILAYER (BIO)STRUCTURES

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This paper presents the experimental results concerning the study of the photoelectric behaviour of a multijunction type multilayer mixed heterostructure with photosynthetic pigments (Chl) having the form: S_nO_x/nCdS:pChl-p^+Chl-p^+Cu_xS-Al-Chl/Cu. Being constituted from more series-superposed and vertically-illuminated semiconductor junctions, the respective photosystem allows the selective usage of a part as large as possible from the spectrum of the solar radiations which is of interest for the photovoltaic conversion and optoelectronical devices. The paper presents a means by which such a heterostructure could be used to detect some noxious elements favouring some neuroviral epidemics. There is also suggested the possibility of using the chlorophyll photopigments micro(nano)cristals and a Schottky nanostructure such as Metal/Chl:DNA/Metal in the photodynamic treatment of neuroviral affections.

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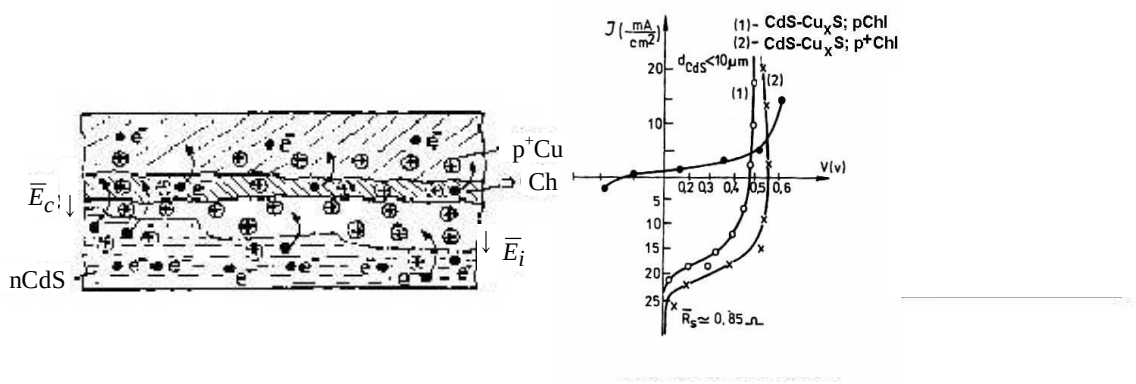
1. Introduction

The studies dealing with the photosynthetic pigments, known as chlorophyls (Chl), proved that these organic compounds possess two important properties necessary for a material used in the preparation of an efficient photovoltaic device, namely a strong absorption in the visible range and an activation energy of 1...2 eV, where the calculated efficiencies of the photovoltaic devices are maximum. The considerable photoconductor and photovoltaic properties of the microcrystalline chlorophyll thin films (Chl) are mentioned in the literature. Taking into account the above mentioned considerations, we carried out the study of the influence which a Metal/pChl/Metal-type Schottky barrier structure could have on some tandem-type heterojunctions based on II–VI, semiconductor compounds, with a view to improve their photovoltaic performances. One presents the results of the experimental researches on the study of the photoelectric and photovoltaic behaviour of a tandem-type mixed multiplayer heterostructure (a tandem cell system) of the following form: Al/pChl-Cu-nCdS-pCu_xS/Cu. The suggested photovoltaic system is made up of a Schottky barrier semi-conductor structure of the Al/pChl/Cu type found in interaction with a nCdS-pCu_xS type heterostructure and in series with it. The photoelectric characteristics of the Schottky barrier made evident in a series of works in this domain (for a Metal/pChl/Metal-type structure) reveals the important role which could be played by the introduction in the Metal/pChl interface region of a n^+n-type guard semiconductor structure (with an adjacent surface field) with a view to accomplish the increase of the ϕ_B height of Schottky barrier at the Metal/pChl intelligent interface.

2. Experiment

The CdS-Cu_xS heterojunction was produced by the method of liquid phase reaction [3,5] on glass substrates of 3×7 cm on which semitransparent SnO_x thin films were previously formed by the same method, these films representing the negative electrodes of the heterojunction [3,5]. As positive electrode, a cooper grid covered later with a 0.2 μm thin A1 film for avoiding the oxidation process was deposited by vacuum evaporation [3, 5, 8].

The Al films had a 0.5...1.5 μm thickness while the thickness of the p^+Chl diffused layer was between 0.2...0.3 μm [9]. The thin microcrystalline Chl films have been prepared by sputtering, electrodeposition and dipping methods [3-5,8] these films having a 0.5...5 μm thickness and an average value of resistivity of 3×10^{11} Ωcm. The CdS-Cu_xS heterojunction has been superposed on the Al/pChl-Cu structure by alternative deposition of the component photoconductor films [7-9], finally results a mixed multijunction-type heterostructure (tandem cell system), made up of two connected photojunctions (Al/p^+pChl and nCdS-Cu_xS respectively) and having the form S_nO_x/nCdS-pp^+Cu_x:pp^+Chl-Al-Chl/Cu (Fig. 1).



a b

Fig. 1. The structure of nCdS/pChl:p^+Chl/Cu_xS photosystem (a); (b) – The "I–V" photovoltaic characteristic of CdS/pChl:p^+Chl/Cu_xS structure.

We mention the fact that the mixed tandem-type photoelement which finally resulted, being made up of more semiconductors characterized by various values of the forbidden band [2,7-9] has the possibility of using a great part of the solar radiation spectrum, at the same time, a bifacial illumination which improves the increase of the collecting efficiency. Simultaneously, in the presence of the superficial field adjacent to the Al/p^+Chl contact, by means of the action of the dopped n^+ diffused layer, the minority photocarriers will be turned back and directed towards the separating field of the barrier region, thus contributing to the increase of the short-circuit current density by increasing the collecting efficiency. Accordingly, by using as a sublayer the Al/p^+pChl (non-rectifier contact) and taking into account the fact that the thin films of microcrystalline Chl present remarkable photoelectrical properties characteristic for the p-type photoconduction [3-9], a Schottky barrier heterostructure of the Al/pChl-p^+Chl/Cu form has been accomplished [1-10].

3. Results and discussion

The photoelectrical measurements as well as the analysis of the photovoltaic characteristics evidenced the fact that the studied system has the behaviour of an optoelectronic device with Schottky barrier. Thus, the system is considered as being made up of a Schottky-type structure in series with a "n-p"-type photojunction, the electrooptical processes from the photoactive contact areas being strongly connected by the electrooptical processes from the photosynthetic pigments (Chl) film. The optoelectronic operation of the system is explained by taking into account the fact

that, in the photoactive area of the pChl/p^+Cu_xS, an important role is played by the formation of an "intelligent" nanojunction pChl/p^+Chl having the function of a "nano-actuator" which accomplishes the intersyste-mical communication of the entire device.

The photoelectrical measurements carried out at room temperature for all the studied samples, have also made ecident an interesting aspect of the photovoltaic behaviour, Fig. 1b, at the Al/p^+pChl-Cu heterostructure, namely, the appearence of a negative photoconduction phenomenon, corresponding to an illumination time of the sample ranging in the interval 1.5...2 min. During the experiments and for all the samples, it has been noticed that after their continuous illumination for a time interval of approximately $t \approx 2$ min, the negative photoconduction phenomenon undergoes a saturation process, passing in a positive photoconduction regime with the establishing of the photovoltaic parameters Figs. 2, 3.

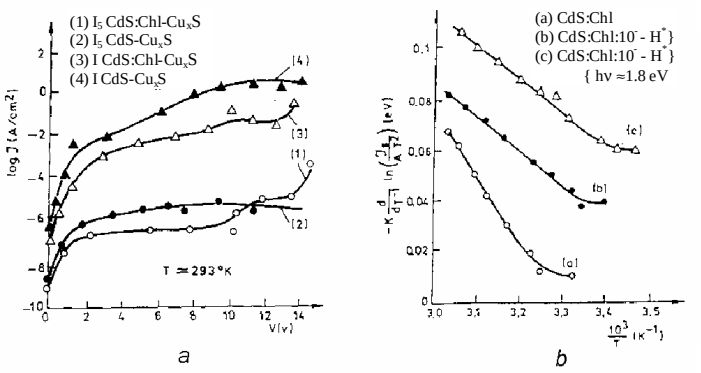


Fig. 2. The photoelectrical ``I–V" characteristic and J_S *vs.* 1/T Arrhenius diagram.

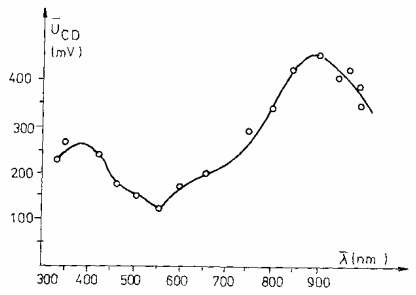


Fig. 3. The $U_{CD} = f(\lambda)$ spectral characteristic.

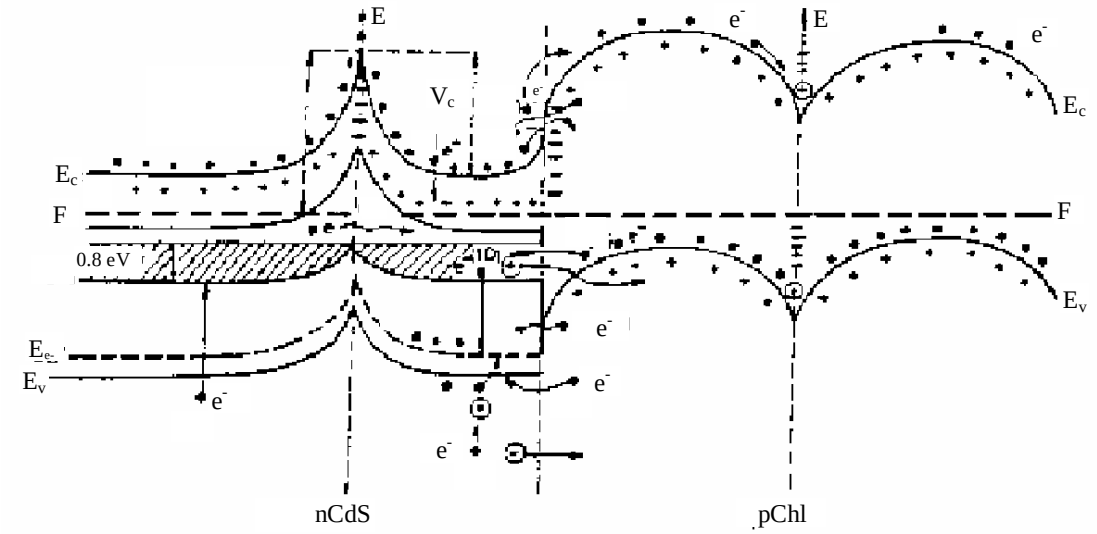


Fig. 4. The energy band diagram for nCdS/pChl:p^+Chl/p^+Cu_xS structure.

The interpretation of the volt-ampere characteristics J = f(V), J_S = f(V), as well as of the photovoltaic ones plotted at different temperatures $T \geq 295$ K, has rendered evident a "dispertion"' of the diode factor n which correlated both with the "dispertion"' of the potential fluctuation from the system interface regions and with the of values obtained for photocurrents and photopotentials, suggests the existence at the intergranular boundaries of a spatially electrical structurality [10] with an intense photoelectric activity in the photoactive region of the CdS:Chl/Cu_xS junction, Fig. 4. Thus, there was remarked the increase, Δ_{ϕ_B}, of the height of the energetic barriers in the areas with

intergranular boundaries, ((iB (0.09…0.1 eV. These increases compensate for the diminishing ((iB determined by the image forces at the interfaces, causing the increase of the diode factor "n" – implicitly of the photopotentials – and preventing the drastic diminishing of the photocurrent. From the view point of the photovoltaic performances, one can speak, in this type of structure, of a "positive" effect of the grains boundaries from the CdS/Chl and Chl/CuxS interface zones of the system, a compromise between the increase of the photopotential and the "convenient" decrease of the photocurrent.

In evaluating the height of the energetic barriers at the CdS/Chl and Chl/CuxS interfaces, respectively, accomplished on the basis of the photoelectric measurements and the diagrams of the activation energy for the saturation currents, JS=f(1/T), T(295 K, (Fig. 2 a, b) we have taken into account the effect of the ``image forces'' which act in the region of the electrical field interface. There was evidenced the fluctuation of the potential barriers at the system interfaces, the average value (B of the energetic barrier in the "CdS:Chl/CuxS" photojunction region being (B (0.85 eV and the diminishing with ((iB of the height of the barrier due to the conjugated action of the image forces being evaluated as ((iB (0.03…0.05,

$$\Phi_B = KT \ln(A^* T^2 / T_S) = eV_B,$$

where A* ~ 3.2 (105 Am^{-2}, T ≈ 300 K, $I_S \sim 1.25 \times 10^{-8} - 0.98 \times 10^{-9}$ A,

We consider that in the photoactive area of the pChl/p^+Cu_xS interface, an important role is played by the formation of a pChl/p^+Chl interface, by the appearance, in the near vicinity of the p^+Cu_xS layer, of a p^+Chl film with a powerful "p"- type semiconduction because the Chl film is capable of restoring the nano-crystallites by the absorption of the H_2O molecules from the structural network of the p^+Cu_xS layer.

The formation of the p^+Chl film with a high degree of nano-crystallinity determines the appearance of a nano-junction pChl – p^+Chl, in contact with a "Schottky"- type structure – Al / pChl – and, therefore, in series, a fact which could explain the increase of the photopotentials and photocurrents in this device.

The pChl/p^+Chl nano-interface also creates, by the internal electrical field in the contact area pChl / p^+Cu_xS, a supplementary potential barrier which does not allow the photo-generated minor carriers to get to the contacts device where they could recombine themselves; this fact greatly contributes to the amplifying of the photoeffects, Figs. 5, 6.

At the same time, by the absorption of the H_2O molecules from the p^+Cu_xS layer, the p^+Chl film ensures its better chemical stability and photoconduction.

On taking into account all the above mentioned things, we consider that, from the view point of the information theory, the pChl / p^+Chl nano-interface plays the role of a "nano-actuator" in which the pChl film represents the "emission source", the contact area pChl-p^+Chl represents the "communication channel" of the information and the p^+Chl film represents the "receiver" of information capable of reorganizing itself when getting the photonic signals ("intelligent" internal field).

Consequently, the pChl / p^+Chl structure has the capacity of a system to select and process information, being a "nano-actuator" in which there intervenes the intersystemic communication function, necessary for the running of the entire systemic ensemble of the device.

The variation of the slope of the Arrhenius – Inσ – 1 / T diagrams renders evident, by its decrease, the appearance of the electrons donor – acceptor system (O^- - H^+) coming from the interface pChl / p^+Chl by the photolysis phenomena of the H_2O molecules.

We have to remark the fact that during all our experiments there was noted both an increase in the photovoltaic effects and an increase in the variation of the diagrams slope in the time periods in which was produced an increase in the atmospheric humidity correlated with an increase in the atmospheric pollution (heavy metals powders, etc.) as well as with the appearance of the heavily-loaded atmospheric fronts (strong variations of the electrical fields, E).

We could determine the fact that the formation of the O^--H^+ levels and their positioning in the forbidden band of the grains boundaries at the CdS/Chl interface – $E_{act\,O_2} \approx 0.15...0.2$ eV and $E_{act\,H_2} \approx 0.1...0.15$ eV, respectively [9,10] – is strongly correlated with the crystallinity of the

pigment film – $(Chl:H_2O)_n:O_2:H_2$ – which restores its polycrystalline structure by absorbing H_2O from the photojunction layers (CdS, Cu_xS).

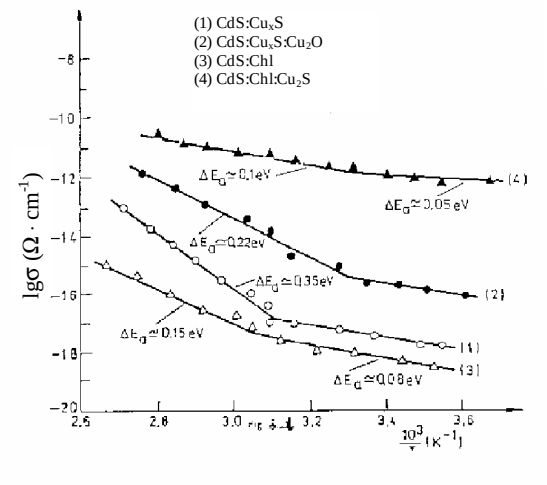


Fig. 5. The slope ΔE_a of the curved σ *vs.*1/T plots used to detect some noxious (HO, H_2O_2) elements.

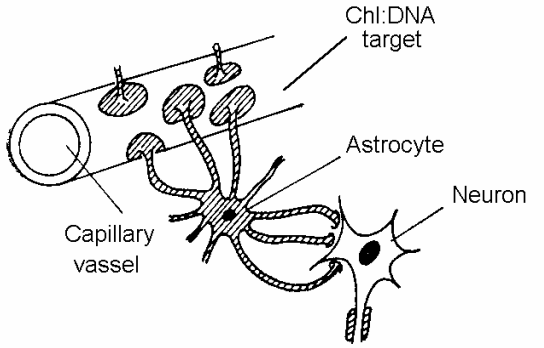


Fig. 6. Schematic photodynamic treatment – the (Chl:DNA) complex as target material to injection neuronal body.

The pChl/p$^+$Chl, as an "intelligent"' nanocrystalline interface, is responsible for the modulation of the ΔE_a slope of the Arrhenius curved and thus the photoelectrical signal could be used to detect some environment noxious elements, Fig. 5, favouring some neuroviral epidemics [11]. So, there is suggested the possibility of using the Metal/Chl:DNA/Metal nanostructure as intelligent target material in the photodynamic treatment of such affections.

It is possible the affecting of the nervous endings both directly and by forming, in the skin, of some active substances, such as the free radicals HO, H_2O_2; thus some reflex modifications are possible to appear in the entire body.

One of the most toxic free radicals, namely H_2O_2, is formed in large quantities in clean water (drinking water, mineral water, etc.) in the presence of the free oxygen dissolved in water as a result of air irradiation. The air irradiation determines, according to the pattern of the chain reactions, the formation of some toxic substances which are accumulated in tissues and organs with simultaneous penetration into the blood circuit.

The appearances of the noxes such as HO, H_2O_2 can be rendered evident by the variation of the slope of the Arrhenius diagrams – detection by photoanswer.

The study of the tissue biocompatibility phenomena in the case of the Schottky nano-structures with chlorophyllian photopigments (Chl) in the photodynamic treatment of some types of neuro-viroses, will have to take as reference point the fact that the "risk / profit" ratio should be as small as possible, aiming at the exclusion of all the risks and the keeping of all the advanges.

Therefore, the metal / Chl : DNA photosystem, used as target material, can determine the loss of the capacity of the neuro-virus to induce cellular patological effects.

The attachment of the complex Chl : DNA / metallic ion to the viral protein can influence both its spatial structure and the distribution of the electrical charges from the binding area of the cation. The formation of a Schottky barrier nanostructure of the metal / Chl : DNA type could lead to the perturbation of the viral sequence, and, implicitly, to the distortion of the genetic information. Thus, the metal / Chl : DNA system could be considered as an intruder in the virus – cell system, the result being the local alteration of the viral DNA structure and the possibility that the replicative cycle could be interrupted.

As a result of the oxidation reaction which takes place at the illumination of the system, local alterations of the structure of the viral DNA can be produced, so that the viral replication should be interrupted.

The question to be solved is if the virus, thus activated, could induce the appearance of some mutable effects in the cells from the near vicinity of the viral lesion.

On taking into account the fact that, in the etyogenesis of many diseases (e.g. recurrent viroses, self-immune illnesses), the genetic factors mingle with the environment ones, there can be foreseen, on using such a biosensor, a prophylaxis for the genetically-sensitive persons, by avoiding the propitious environment factors (powders of heavy and / or radioactive metals, sudden changes in temperature, humidity, strongly disturbing electrical fields, etc.).

4. Conclusions

We consider that a M_1/Chl:DNA/M_2 Schottky-type nanostructure can be capable of disturbing a viral sequence and so, there is suggested the possibility of using of a such nanostructure as intelligent target material in the photodynamic treatment of neuroviral affections. The structure can be an "intruder" in the (virus – cell) system having as consequences the local alteration of the viral DNA structure, as a result of which the replicative viral cycle could be interrupted under the influence of the inner electrical field of such an "intelligent" Schottky barrier. This fact will determine the disturbance of the distribution of the electrical loads from the viral sequence.

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