

PHOTO RECEIVER WITH NANOCLUSTER SUBSYSTEM

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Abstract. The paper considers the effects associated with a change in the properties of a film heterojunction as a result of the introduction of a nanocluster subsystem. Such a modified heterojunction exhibits a spectrally invertible photo ventile effect. A design of a photocell containing two successively coupled p-n transitions of counter action, photoactive in different regions of the spectrum, is proposed.

Keywords. Hetero transition, film, nanocluster, subsystem

1. Introduction and motivation of the problem. Studying the properties of hetero transitions (HT) deserves attention on the way to solving the problems of functional diagnostics of new coating devices. Such studies are relevant in the development of effective photo ventile elements [1-3]. The task was to consider the possibility of manifesting new properties of pCu₂S-nSi film HTs, into which a sub colloid dispersion cluster raster in the form of a nanocluster subsystem (NCS) is introduced, and also to determine the optimal modes of operation of such a hetero-photocell.

2. Results and interpretation. The transition from an individual atom to a macro state is characterized by the formation of structures such as quasi molecular clusters, sub colloid and colloidal nanoclusters (NC), which are extensive in nature because they change their properties sequentially up to the properties of the corresponding macroscopic substance [4]. The latter is very important to take into account when using quasi metallic nanocrystals as an alloying principle for individual materials and hetero structures (HS) [5].

It is well known that the size of the individual crystals special processing methods can be created metallocluster centers very large sizes – up to colloidal particle size up to 1000 angstroms. Theoretically and experimentally studied the influence of different NC sizes on the optical and some other properties of crystals («red shift» coloring of matrix material upon consolidation centers, etc.) [6]. It is appropriate analogy with the different stages of the photographic process in silver-dispersing materials and on semiconductors [7]. In addition, in the monocrystalline matrix has the ability to widely vary the size of NS [4,8].

Taking into account the specifics of the us system is considered HT (pCu₂S-nSi), in the structure of the NC was introduced by means of implantation: application of cluster raster islet structure on the silicon substrate before layer deposition of Cu₂S.

By varying the speed of formation of NC and the temperature of the substrate, we were able to implant in pCu₂S-nSi-HT cluster centers in the form of nanocluster subsystem (NCS) of silicon. Thus evolved HT type pCu₂S-(Si-NCS)-nSi. For this HT was observed «extensive» effects: spectral-invert effect (SIE). It should be noted that the creation of the NCS HT as implantation of the material can also be used transition metals (Fe, Ni, Co, etc.). The results did not change significantly (even if the one metal the other). The latter is a good confirmation that the observed effects is largely due to the presence of NCS, not their material.

Common property barrier solar cells based on Si, Ge, Se, CdS and other is the preservation within the entire active region of the spectrum unchanged polarity of photo-EMF, in which, according to the usual scheme of valve photoelectric effect, in the light of p-region is negatively charged relative to the p-type

region. However, the possibility of treatment of inversion of the polarity of the gate photo-EMF when changing the wavelength along the active region of the spectrum.

This option allows the solar cell to optimize the solution of some important problems of optoelectronics: monitoring and measuring the colour temperature of radiation sources, detection of colour images, etc. However, the known methods of implementation of the SIE in practical terms represent little value, because they significantly limit the efficiency of photovoltaic energy conversion.

Key recommendations boil down to the introduction into the region of the p-n junction of various impurities (Fe, Ni, Co, etc.), playing the role of the traps and centres of recombination of no equilibrium electron-hole pairs or to the performance of solar cell based on complex HT from various materials containing two consistently articulated the p-n-transition of counter operation, photoactive in different spectral regions. In both cases, the photosensitivity of the device obtained is low, and the spectral distribution of the photovoltaic effect, is strongly asymmetric around the point of inversion of the polarity of photo-EMF. In the first case is obtained, apparently due to the insufficiently high efficiency of these impurities as centres of recombination, and the second because of the complexity of opto-photovoltaic conditions in HT with a serial chain of transitions.

We have considered the possibility of creating a valve of the SIE of $pCu_2S-Si(NCS)-nSi$, structurally, a combination of semi film p-n-HT that occurs at the contact between the film Cu_2S (p-type conductivity) and c-Si (p-type), with ultra small disperse clustered raster Si (NCS) distributed in the plane of the junction. Cluster raster forms a «discontinuous» structure, which is organically included in the structure of the heterojunction and, in particular, is embedded in a film of sulphide of copper.

The technology for producing a spectrally invertible photocell with $pCu_2S-nSi-HT$ is generally similar to that described in the monograph [4], differing only in the fact that sample preparation begins with the execution of a metal-cluster (on a surface of $100^\circ C$) metal cluster raster of sub colloid dispersion, with the size of individual particles no more than 20 angstroms. HT clustering was performed by thermal evaporation in vacuo ($\sim 10^{-6}$ Torr) or by pyrolytic decomposition of compounds in the regime providing for the production of a sub colloidal monolayer of metal, clearly resolved by electron, on the control substrate, under the same conditions as the main substrate microscope (Fig. 1).

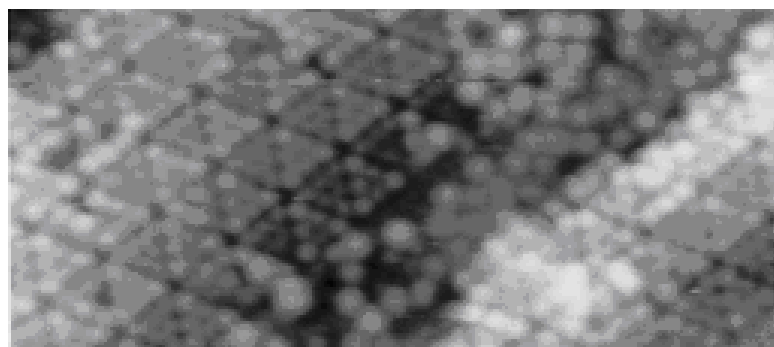


Fig. 1. Micrograph of a nanocluster raster on c-Si (NC shaded with carbon) [9]

The most important element of this design is a nanocluster raster, in which the degree of dispersion of nanocrystals is of particular importance. The result is a spectrally inverted photocell with a sensitivity distribution (Fig. 2).

The action of a spectrally invertible photocell of the $pCu_2S-(Si-NCS)-nSi$ type is ensured by a combination of two essentially different valve photoelectric effects in one HT separated by the corresponding active regions of the spectrum. The first of them implements the well-known trivial scheme of the gate photoelectric effect in the p-n junction (Fig. 2a), in which the p-region (silicon) is negatively charged under illumination. The spectral distribution of the photovoltaic effect in this case

(Fig. 2, a, b) corresponds to the photoactive absorption of light in both Cu_2S and Si materials, which contributes to the $\text{pCu}_2\text{S-nSi-HT}$ band diagram favourable for the photocell. The second mechanism (Fig. 2, b) is triggered in clustered sections of the HT, i.e. Where there are NC. Its spectral sensitivity corresponds to the optical absorption of light by nanocrystals (Fig. 2, b, c), and the result of the action is photo-EMF. (Photocurrent) direction opposite to that which corresponds to the first mechanism, i.e. Si appears to be positive in this region of the spectrum, and Cu_2S is negative.

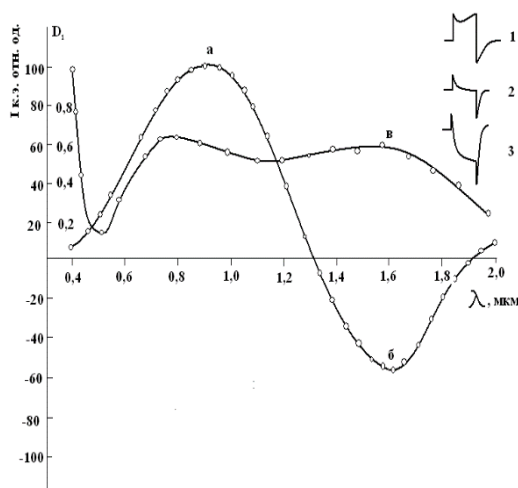


Fig. 2. The spectral distribution of the invertible photo ventile effect (with nanoclusters); a - area of the usual effect, b - abnormal.

Plots (top right) of the kinetics of the photo response:

- 1- in the region of the usual effect, 2- in the inversion point,
- 3- in the region of the anomalous effect;
- c - Optical absorption of the Cu_2S film.

The mechanism of the photovoltaic effect on nanocrystals seems to be closest to the scheme, which in English literature is called «feed in - feed out». This assumption follows from the analysis of the near-cluster energy situation, which can be determined taking into account specific conditions in the HT as follows. On the one hand, nanocrystals border on a strongly pronounced hole, and on the other, electronic semiconductors.

According to calculations of the electronic structure of Si nanocrystals by quantum chemical methods [4], in equilibrium, these systems tend to have some excess of negative charge, which is a condition for its stability and provides the possibility of further growth up to colloidal sizes.

Under such conditions, the presence of a high concentration of holes in Cu_2S should lead to a kind of «solvation» of nanocrystals by holes from the side of the Cu_2S film, resulting in a decrease in the effective work of the electron exit from the nanocrystals to the p-region, GP (Fig. 3). The latter determines the action of the «feed in-feed out» scheme (Fig. 3, b).

A photo excited electron breaks down from the nanocrystal deep into the Cu_2S film, where it is most likely captured by a system of attachment levels for electrons that is highly developed in this quasi monopolar semiconductor. Simultaneously with the photoexcitation of the first electron in a nanocrystal, another tunnelling occurs - from the silicon valence band, etc., i.e. the process that is the essence of the «feed-out» scheme is reproduced.

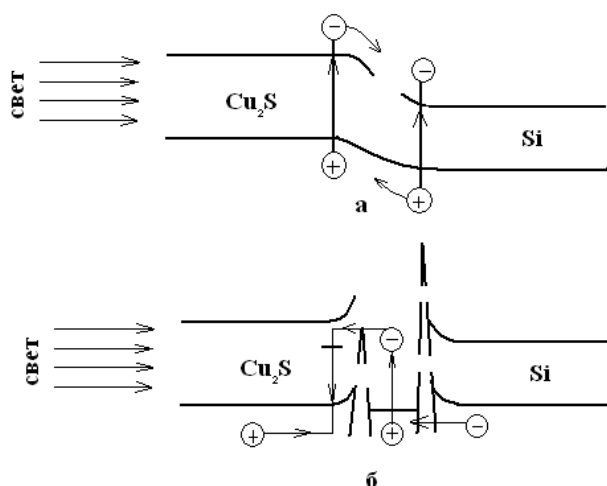


Fig. 3. Zone energy diagrams: (a) a nano crystalline-free HCS of the pCu₂S-nSi type and (b) a HT having an NCS – pCu₂S–(Si-NCS)–nSi HT

The region of spectral activity of the negative photovoltaic element (Fig. 2) determines the effective energy depth of the nanocrystals of 0.8 eV. This parameter is essential for the spectral inversion of the photoelectric effect, since it provides tunnelling contact with the valence band of silicon. When switching to a cluster raster with large NC (more than 20 angstrom), the «feed in - feed out» effect disappears, in other words, the spectrally inverted photovoltaic effect is not observed. This can be explained by the suppression of the solvating factors, which ensure the necessary «feed in - feed out» mechanism, the profile of potential barriers around the nanocrystals, as a result of the weakening of the Coulomb field of the nanocrystals upon transition to large sizes.

Direct confirmation of the above mechanism of the spectrally invertible photo ventile effect was obtained by parallel measurements of the photoconductivity kinetics in the base region of the solar cell — the Si plate. During illumination of the pCu₂S-Si(NCS)-nSi photocell with light from the spectral region creating an anomalous photo ventile effect (Infra-Red Light - 3 filter), the photo response of the element's base region is significantly smaller when the photocell is open (open circuit) than in the case of a short circuits (Fig. 4).

For a pCu₂S-nSi photocell that does not contain NCS, in such situations, the behavior will be the opposite in the entire active region of the spectrum. Our results are easy to interpret by comparing the two mechanisms of the photo ventile effect - the usual and «feed in - feed out». In the latter case, the extraction of electrons from silicon onto nanocrystals leads to a decrease in the photocurrent in the base circuit. Naturally, in the short-circuit current mode, such observations are less expressive due to the continuous restoration of the concentration of no equilibrium electrons in silicon through an external circuit. There are also other considerations confirming our proposed mechanism of spectral inversion of the photo ventile effect in pCu₂S-(Si-NCS)-nSi HT. The fact is that in this situation it would be possible to assume the participation in the spectrally inverted effect of the Schottky micro barriers at the «NC-matrix material» boundary, creating an electric field opposite to the barrier field in the heterojunction and providing an anomalous photofan effect, the latter, however, is unlikely in following reasons.

It is known that significant contact barriers are formed as a result of the transition of $\sim 10^{15}$ electrons from one material to another, causing the curvature of energy bands. The appearance of Schottky barriers in contact with nanocrystals with a matrix substance is impossible due to the smallness of nanocrystals. Theoretical estimates presented in [4,5] show that ionization or capture of even one electron in an NCS leads to a sharp change in the position of the Fermi level of an NC by units of eV.

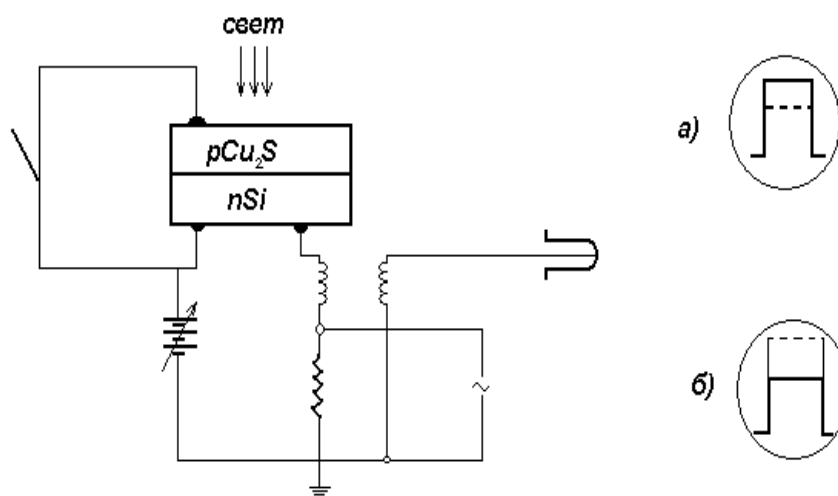


Fig. 4. The kinetics observation scheme (Infra-Red Light - 3 filter) in the low-resistance base layer of the photocell and the photocurrent kinetics diagram (the dashed line corresponds to the photocell short circuit mode):

a) pCu₂S-nSi - photocell; b) pCu₂S-(Si-NCl)-nSi – photocell

This fact, on the one hand, substantially complicates the further electronic exchange of nanocrystals with matrix material, and on the other hand, it is completely insufficient for curving the energy bands of the matrix crystal in this region due to the small charge involved in the exchange. The insignificance of the role of the Schottky barriers between nanocrystals and matrix material also follows from the experimental facts themselves. With NC sizes up to 20 angstroms, up to the formation of a network structure at the interface, the role of Schottky barriers should be strengthened, i.e. one would expect the anomalous photoventile effect to dominate or even the photoventile effect to completely reverse in the pCu₂S-(Si-NCS)-nSi HT from the usual to the anomalous one. But this actually does not happen, since with the increase in the size of nanocrystals to hundreds or more angstroms, the photoventile effect not only does not increase, but, on the contrary, completely disappears. The diffusion coefficient, for example, of Ni in Si at temperatures of ~ 100 ° C is negligible. In other words, atomic doping of Si with nickel in the process of obtaining pCu₂S-(Si-NCP)-nSi - photocells is effective.

3. Conclusion. A technology has been proposed for changing the properties of a film pCu₂S-nSi by introducing a cluster raster of subcolloid dispersion in the form of an NCS, which provides a smooth band-energy transition profile. It is proposed to use such a structure as the basis for photo ventile energy converters. The optimal operating modes of such a hetero photo element are determined.

A change in the HT can occur through the process of implantation of a cluster raster of an island structure on a silicon substrate before the deposition of a Cu₂S layer. Varying the rate of formation of nanocrystals and the substrate temperature opens up the possibility of implanting nanocrystals with sizes from 10 to 150 angstroms. For such a HT, spectrally inverted photo ventile effects were observed.

From our point of view, these processes are inherently extensive, because they are due, to a greater extent, to the geometry and morphology of nanocrystals, and not to their material. The results of the study deserve attention on the way to solving the problems of modern functional diagnostics of devices with NCS, as well as in the development of photofan elements [8].

So, the spectrally inverted photodetector described in the work, in addition to independent applications, can be used in the construction of bistable optocouplers, for example, a bichromatic LED with a controlled radiation frequency.

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