UDC 530.145 + 678.9 DOI: 10.15222/TKEA2025.3-4.09

Volodymyr KOVALCHUK[1], *Diana POPRYAGA*[2], *Dmytro DYACHOK*[2]

Ukraine, Odesa, [1]Odesa Technological University IT STEP;
[2]South Ukrainian National Pedagogical University named after K. D. Ushynsky
E-mail: lslvvvas@ukr.net

FILM HETEROJUNCTION WITH NANOCLUSTER SUBSYSTEM FOR NEW TYPE OF PHOTOCELLS

The paper describes the manufacturing technology and presents the results of studies of a pCu2S–nSi heterojunction (HJ) and an HJ based on it, containing a nanocluster (NC) subsystem. It is shown that the presence of an NC subsystem at the interface between the p-type Cu2S film and the n-type Si substrate significantly increases the overall sensitivity of the samples under high illumination conditions. The operating mode of such an HJ as a highly sensitive valve photocell has been determined. It has also been demonstrated that these transitions are photoelectrically active in different spectral regions. The observed effects are extensive in nature, being largely determined by the geometry and morphology of the nanocluster centers rather than by the type of atoms from which they are formed.

Keywords: heterojunction, film, nanocluster, subsystem, photocell.

The technological component of modern functional electronics is increasingly focused on the study of material properties at the nanoscale. The transition to nanostructures opens new opportunities for practical applications ranging from electronics to photonics. In this context, quantum-sized systems attract particular attention, with atomic nanoclusters (**NC**) occupying an important place [1].

Using modern technological methods and techniques, it is possible to form NC centers of various geometric shapes and sizes on the surface and even within the volume of individual crystals. The influence of NC morphology on the mechanical, electrical, and optical properties of the matrix in which they are formed is currently being actively studied theoretically and experimentally [2], [3]. NCs not only exhibit properties that distinguish them from the corresponding macroscopic substance, but also enable effective control of the physicochemical characteristics of the matrix in which they are embedded. For example, the experimentally observed red shift in the color of the silicon crystal matrix is associated with an increase in the size of NC centers [4]. In this case, an analogy can be drawn with the stages of the photographic process in alkali-halide compounds, where centers of a latent image are formed and developed under the action of light [5].

Therefore, from our point of view, a promising direction is the creation of heterostructures in the form of film heterojunctions (**HJ**), that incorporate NCs, forming a nanocluster subsystem (**NCS**). [6].

This paper presents results from a study on the properties of the $p\mathrm{Cu_2S}-n\mathrm{Si}$ HJ with silicon NCs introduced by implantation.

Manufacturing Technology of the Heterojunction under Study $p\mathrm{Cu_2S}-n\mathrm{Si}$

At the initial stage, a film-type $p\mathrm{Cu_2S}-n\mathrm{Si}$ HJ was fabricated. To remove the oxide film, the silicon substrate was etched with an active solution. By means of thermal evaporation in a vacuum ($\approx 10^{-6}$ Torr), copper sulfide (Cu_2S) powder of the ChDA grade was deposited on the (111) face of an *n*-type silicon crystal (*n*Si). The silicon was doped with phosphorus atoms, and its resistivity was 0.01 Ω·cm. To create omic contacts, tin was used on the sulfur copper side, and an alloy of silver and antimony (20%) was used on the semiconductor side. The samples were manufactured in two modifications according to the surface area of the heterojunction: approximately 1 mm^2 (for measuring characteristics in the valve photocell mode) and 40 mm^2.

We found that the structure of the film layer is determined by the conditions of its deposition. When the substrate temperature (*n*Si) was varied from room temperature to 400°C, two phase transitions were clearly observed in the Cu_2S film: from α-Cu_2S (orthorhombic phase) to β-Cu_2S (hexagonal or tetragonal structure). In addition to these phase changes, the high volatility of sulfur led to a violation of the sample's stoichiometry, which in turn resulted in the formation of a complex mixture of phases. Therefore, to develop a laboratory technology for obtaining Cu_2S films, the stoichiometry of the copper sulfide layer was studied using X-ray emission spectra of copper in the composition of the copper-sulfur compound. X-ray structural analysis was employed to perform quantitative evaluation of the elements both in the bulk and on the surface of the sample. We also used this approach to study the composition of cluster phases within the NCS when investigating diffusion processes and constructing diagrams of the composition of the studied HJ.

The secondary spectrum was excited by a braking (white) primary beam of a sealed X-ray tube of the BXB-I type with a tungsten anode (30 kV, 20 mA) with voltage fluctuations within $\Delta V = 0.1$ kV, on a X-ray spectrometer using a scintillation counter (quartz crystal, oriented to the (1011) facet). The choice of crystal for spectral analysis was determined by the wavelength K_α for Cu. The results of monitoring the thickness and density of the Cu_2S film during deposition indicated that the weight concentration is proportional to the intensity of the characteristic radiation excited in the HJ.

Calibration was performed in two ways: by comparison with a calibration graph based on reference samples with a known copper content in the range of 60 – 70% and by analyzing the dependence of HJ photosensitivity on the temperature of the silicon substrate during the growth of the Cu_2S layer. This made it possible to determine the composition of the Cu_2S film that corresponded to the maximum photoactivity of the $p$$Cu_2S$ – nSi HJ. It was found that the highest photosensitivity is exhibited by HJs in which the Cu_2S films contain a slight excess of sulfur (≈ 1.1%): that is, the Cu_2S layer should contain 34.4% sulfur (the stoichiometric composition of Cu_2S corresponds to 33.3% sulfur).

Based on the results of structural studies of copper sulfide films sulfur copper films, a technology was developed for producing HJ with textured mosaic-type Cu_2S layers. The optimal mode for obtaining such a HJ is as follows. A substrate with a temperature of about 300°C was placed on a mask above an evaporator with a copper sulfide mixture and cooled to a temperature of 150°C within 10 minutes. The transition layer of copper sulfide was formed within an hour. The stability of the evaporation process was ensured by the use of an additional sulfur emitter with a temperature of 100 – 120°C, which maintained a constant partial pressure of its vapors. Under these conditions, it was possible to grow the Cu_2S film required for the HJ. The specific resistance of the films was 1 – 10 Ω·cm. They exhibited a mirror-smooth surface with good adhesion to the silicon substrate. Microscopic studies revealed a mosaic structure with a grain size of 20 – 50 μm. It should be noted that when Kikuchi lines appeared on the electron micrographs of Cu_2S films, the reflections from the twins disappeared at the same time, which indicates a high degree of perfection of the grown film.

Zone Diagram and Characteristics of a Heterojunction *p*Cu_2S – *n*Si

To predict the possible properties and practical applications of the $p$$Cu_2S$ – nSi compound, it is advisable to construct a band diagram to obtain additional information about this compound. As shown in **Fig. 1**, the resulting band profile is smooth, and moreover, the valence band has practically no gap. When evaluating the band profile of a HJ, special attention should be paid to cases of sharp asymmetry in the doping levels of contacting materials. The electron affinity of copper sulfide (3.74 eV) is inherently lower than that of silicon (4.5 eV). From the diagram, the gap values can be obtained: in the conduction band, $\Delta E_C \approx 0.76$ eV, and in the valence band, $\Delta E_V \approx 0$.

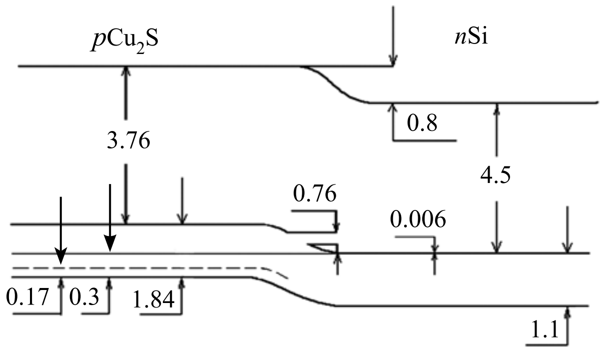


Fig. 1. Zone diagram of the $p$$Cu_2S$ – nSi compound (the numbers correspond to energy in eV)

It should be noted that due to the difference in the structures of the substrate (Si) and the Cu_2S layer, there is a high probability of forming an HJ with a high density of mismatch defects at the interface. Such defects are capable of localizing charge carriers around themselves, i.e., acting as traps or recombination centers for electrons and holes. The presence of boundary states can clearly affect the band profile of the transition and significantly determine its properties.

The characteristics shown in **Figs. 2, 3** indicate that the proposed HJ variant is quite promising for photoelectric

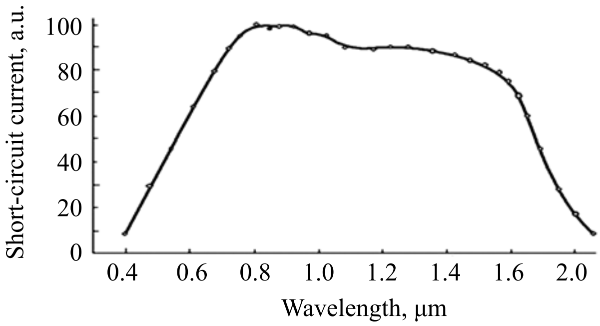


Fig. 2. Spectral dependence of the short-circuit current of the $p$$Cu_2S$ – nSi photovoltaic cell (source: tungsten lamp with a color temperature of 2900 K)

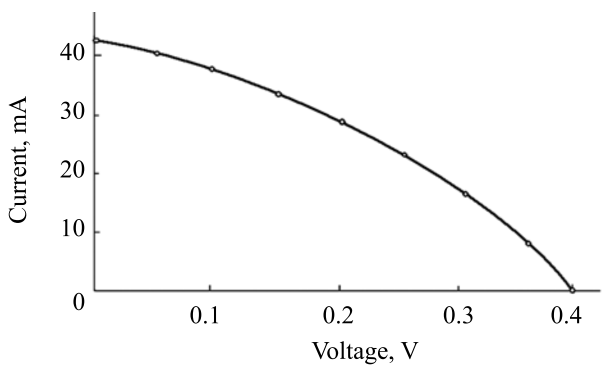


Fig. 3. Load characteristic of the $p$$Cu_2S$ – nSi photocell (illumination: $5 \cdot 10^4$ lux)

ISSN 3083-6530 (Print)
ISSN 3083-6549 (Online)

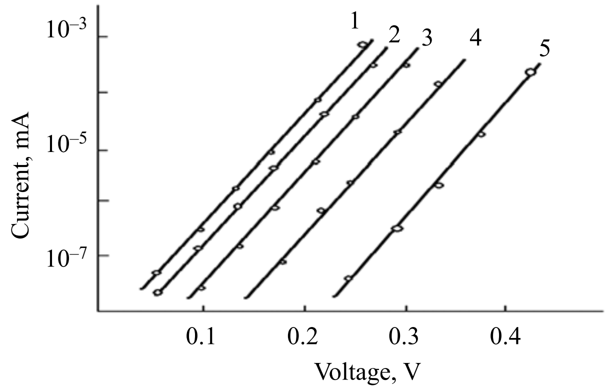


Fig. 4. $I-V$ curves of the pCu$_2$S$-n$Si at different temperatures (°C):
1 — 150; *2* — 75; *3* — 20; *4* — minus 97; *5* — minus 195

applications of semiconductor heterostructures, for example, in the manufacture of efficient photocells based on it.

The polarity of the valve electromotive force arising in the samples when illuminated corresponds to the forward bias on the HJ. A wide spectral range is active: from 0.4 to 2.0 μm (**Fig. 4**), which is explained by the participation of the HJ constituent materials — copper sulfide and silicon — in the photoelectric effect. The operating frequency band of the pCu$_2$S$-n$Si HJ under modulated illumination is approximately 1 MHz. Thus, as a solar converter, a pCu$_2$S$-n$Si photocell with such characteristics is capable of generating an open-circuit voltage of 0.6 V and a short-circuit current of 40 mA/ cm^2 with an efficiency of up to 4%.

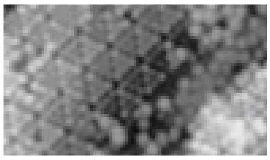
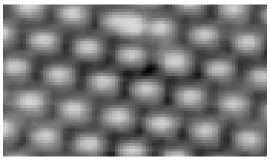
It should be noted that the determined properties of the pCu$_2$S$-n$Si compound are not typical for such systems with zone profiles containing potential breaks in the form of teeth or pockets.

Modification of Heterojunction pCu$_2$S$-n$Si

Improvements in the technology for obtaining the above-described HJ are aimed at enhancing the quality of these photocells. Therefore, our proposed modification of the pCu$_2$S$-n$Si HJ involves the introduction of a silicon nanocluster subsystem at the transition boundary. We define such a GP as pCu$_2$S$-$(Si-NCS)$-n$Si. The NCS is created before depositing of the copper sulfide layer by implanting Si NCSs, i.e., forming a cluster raster of an island structure, into the nSi substrate. Between the film and the substrate (along the interface), a clustered film is formed, consisting of stochastically distributed NCSs.

The manufacture of HJ from NCS involves applying a cluster raster of colloidal dispersion to the surface of a silicon wafer (at 100°C). This procedure was carried out by thermal evaporation of the corresponding element (silicon, chromium, nickel, iron, cobalt) in a vacuum (10^{-5} Torr) under conditions that ensures the formation of a colloidal layer that is clearly distinguishable using an electron microscope (see **table**). The process of introducing NCS into such a HJ is similar to that used by us to obtain copper sulfide films. By changing the rate of formation of NCS centers and the temperature of the crystalline silicon (c-Si) substrate, it was possible to implant Si-NCS into the pCu$_2$S$-n$Si HJ in the form of Si-NCS. Thus, a pCu$_2$S$-$(Si-NCS)$-n$Si type HJ was formed. It should be noted that transition metals (such as Fe, Ni, Co, etc.) can also be used as implanted material to create a similar type of HJ. We found that the results did not change significantly even when one metal was replaced with another. This indicates that the effects we observed are due to the presence of NCSs, rather than the type of atoms that form the NC.

Illustration of the layers of the Cu$_2$S$-$(Si-NCS)–nSi HJ

Electron microscope photo	HJ layer	Control and formation method
	pCu$_2$S	Thermal sublimation of Cu$_2$S powder in a vacuum (10^{-6} Torr)
	Si-NCS	Vacuum evaporation (10^{-5} Torr)
	nSi	Crucible melting method Cochralsky method

Properties of the pCu$_2$S$-n$Si Heterojunction with a Nanocluster Subsystem

Our research on HJ samples with NCS has made it possible to identify properties that are of practical interest for the development of elements in modern electronic devices.

Fig. 5 shows the voltage-ampere characteristics (**VAC**) for HJ pCu$_2$S-(Si-NCS)$-n$Si. At low voltage values, the forward branch of the VAC (*a*) is described by an exponential law (with a diode ideality factor $\beta \approx 2.0-2.5$). With increasing voltage, the current increases more slowly than in HJ without NCS.

On the reverse $I-V$ curve (*b*), three sections can be distinguished: pre-breakdown (*1*), sharp breakdown (*2*), high current (*3*).

Their comparison with the VAC obtained for HJ without NCS indicates a slight increase in the currents of the pre-breakdown region. This is explained by an increase in the concentration of charge carriers due to the presence of Si-NCS.

ISSN 3083-6530 (Print)
ISSN 3083-6549 (Online)

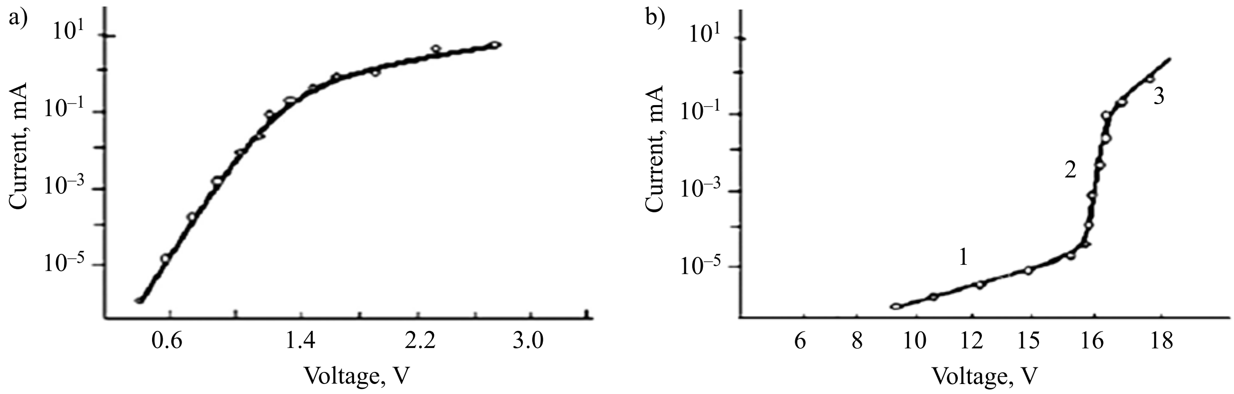


Fig. 5. Typical direct (a) and reverse (b) $I-V$ curves of the HJ pCu$_2$S – (Si-NCS) – nSi (with NCS center sizes greater than 2 nm)

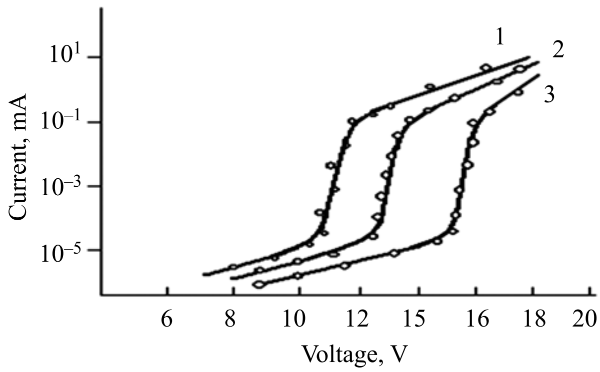


Fig. 6. $I-V$ curves of the HJ pCu2S-(Si-NCS)–nSi at different temperatures (°C):
1 — minus 193; *2* — minus 123; *3* — minus 93

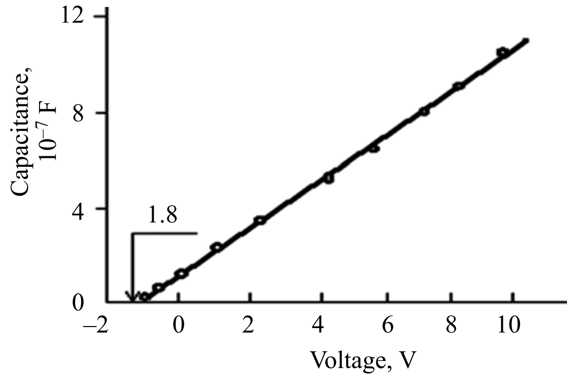


Fig. 7. Capacitance-voltage dependence ($V \sim C^{-3}$) of the HJ p-Cu$_2$S – (Si-NCS) – n-Si

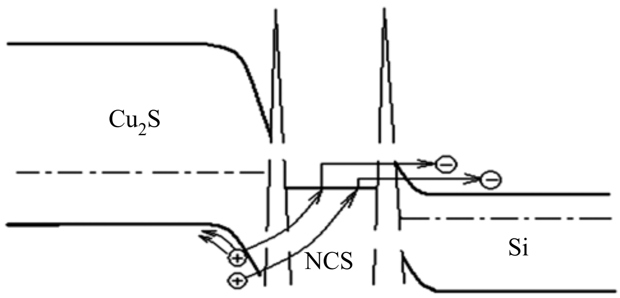


Fig. 8. Illustration of the mechanism of charge-carrier increase due to ionization of Si-NC centers under reverse current in the HJ pCu$_2$S – (Si-NCS) – nSi

The reverse $I-V$ curves for different temperatures shown in **Fig. 6** indicate that the breakdown voltage decreases with decreasing temperature. This behavior of the $I-V$ curve is opposite to that observed in the case of a diode without an NCS and, as is known, is characteristic of avalanche breakdown of a $p-n$ junction.

An analysis was performed of the capacitive characteristics obtained for both types of HJ: with and without NCS. These results confirm the real possibility of generating additional charge carriers due to the ionization of NCS centers. At reverse voltages lower than the breakdown value, for HJ with NCS, the capacitance-voltage dependence was described by a power law: $V \sim C^{-3}$ (**Fig. 7**). Extrapolation of the curve to zero capacitance ($C=0$) indicates an increase in the diffusion potential to 1.8 V ($V_d \approx 1.8$ V) compared to the non-clustered HJ variant. This shows that the introduction of a nanocluster grid affects the HJ profile, which becomes more complex and, therefore, less distinct.

According to the physical model we propose, shown in **Fig. 8**, the mechanism responsible for increasing the concentration of charge carriers occurs precisely due to the ionization of Si-NC.

It should be emphasized that, in our opinion, an increase in the concentration of carriers in the NCS can lead to avalanche breakdown due to the cumulative effect of potential barriers created by the NC system itself. This is consistent with the collective barrier model for a photoconductor with quasi-macroscopic inclusions of high-resistance regions proposed by Prof. M. Sheikman [7].

The results of our study of the properties of HJ with a metal cluster grid indicate that, on the one hand, NCS changes the nature of the distribution of impurities and, on the other hand, significantly increases the potential barrier in the transition region. The mechanism for enhancing the photocurrent arises due to the interaction of hot photoelectrons with the electronic structure of NC centers blocked by asymmetric potential barriers in the HJ region.

ISSN 3083-6530 (Print)
ISSN 3083-6549 (Online)

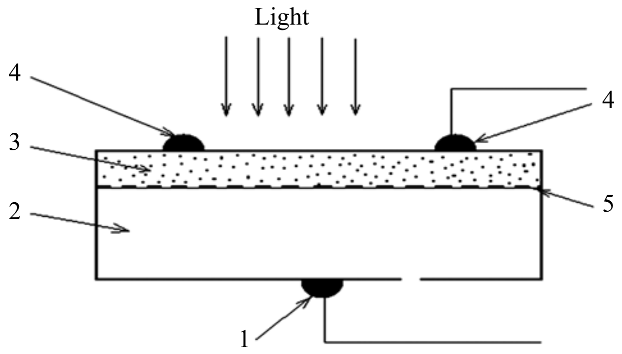


Fig. 9. Schematic representation of a hypersensitive HJ $p\mathrm{Cu_2S}$–(Si-NCS)–nSi:
1, *4* — thin removable contacts; *2* — silicon crystal; *3* — copper sulfide film; *5* — nanocluster grid

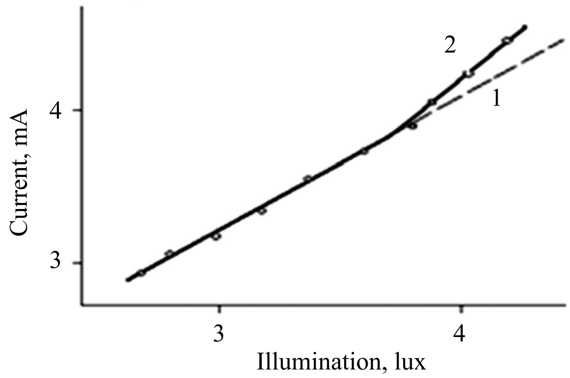


Fig. 10. Lux–ampere characteristics of different types of HJs:
1 — $p\mathrm{Cu_2S}$–nSi (linear); *2* — $p\mathrm{Cu_2S}$–(Si-NCS)–nSi (superlinear)

The phenomenon described above explains the superlinear photoelectric effect we observed in the HJ with NCS. Such an element has increased light sensitivity at high illumination. A schematic representation of such a hypersensitive heterophotovoltaic element is shown in **Fig. 9**.

We also investigated the lux-ampere characteristics (**LAC**) for both types of HJ at a temperature of 20°C (**Fig. 10**). As a result, it turned out that $p\mathrm{Cu_2S}$–nSi photocells always exhibit linear LAC (up to an illuminance of approximately $5 \cdot 10^4$ lux). In photocells with NCS, there is a sharp increase in LAC (curve 2) at illuminance levels of $8 \cdot 10^3$ lux and above. The values of the slope coefficients of the rectified sections of the LAC relative to the abscissa axis allow us to distinguish between linear (*1*) and superlinear (*2*) modes of operation of photocells without NCS and with NCS.

Studies have shown that at low and moderate light intensities, the main characteristics of both types of photocells are practically the same, i.e., the NCS does not affect the photoelectric effect under such conditions. This can be explained by the presence of a specific Coulomb barrier for these centers, which limits their photoelectric activity and electron exchange interaction with the conduction band and valence band of the semiconductor.

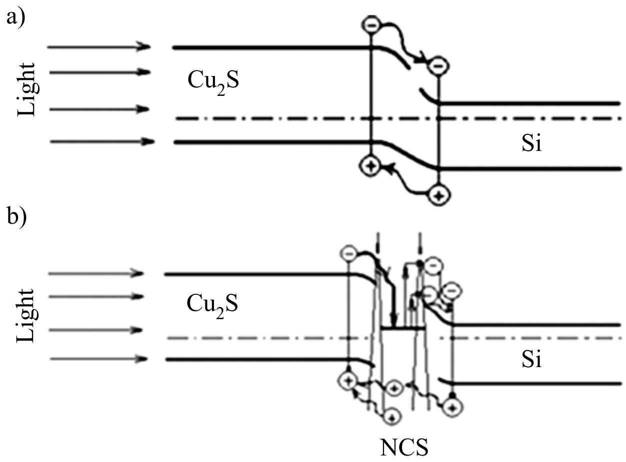


Fig. 11. Energy-band diagrams of different types of the HJs:
a — $p\mathrm{Cu_2S}$–nSi; *b* — $p\mathrm{Cu_2S}$–(Si-NCS)–nSi

The linear generation mode (about 10^4 lux) can be explained using the energy band diagrams of the PV cell shown in **Fig. 11**. They are based on measurements of the capacitance and I–V curves of the PV cell, as well as the electrical and optical properties of the base regions. As can be seen, a significant difference appears in the high illumination region, when a mechanism is activated in photocells with NCS that switches them to superlinear operation mode.

We propose a switching scheme between linear and superlinear modes, taking into account the specific structure of the sample. At high light intensity (10^4 lux), the conductivity of the $\mathrm{Cu_2S}$ photosensitive film increases significantly (by almost two orders of magnitude). The Debye screening length decreases, and the nanocluster center is solvated by mobile carriers, as illustrated in Fig. 11. As a result, the NC centers begin to participate in the process of electron exchange between the conduction band and the valence band.

The specificity of HJ with NCs is that the electrons entering the NC centers from the $\mathrm{Cu_2S}$ film are "hot" (Fig. 11, *b*). In this case, the excess energy, as in a bulk material, is either lost or scattered at the NC centers or upon collisions with electrons. Since the thermalization of charge carriers is more efficient than cooling, we obtain heating of the electron density in the NC centers. The latter, in turn, leads to the fact that the secondary radiation of electrons in the NC centers can exceed the intensity of the primary exciting electron flux. In this case, an additional current generation mechanism begins to operate. The effect is enhanced by the fact that the electron temperature is included in the Boltzmann exponential factor: $\exp(-\Delta E/kT)$, which determines the probability of electron emission from the NC center. Thanks to the introduction of NC into the base p-region of $\mathrm{Cu_2S}$, a significantly higher integral sensitivity was achieved at a high degree of sample illumination (<< $8 \cdot 10^3$ lux) in the valve photocell mode (2.4 mA/lux) compared to 1.8 mA/lux in the normal mode.

Conclusion

Thus, studies have shown that film heterojunctions with HCPs differ from non-clustered HCPs. The properties of pCu$_2$S$-n$Si with NCSs can be modified by implanting a cluster grid of an island structure onto a silicon substrate before depositing a layer of copper sulfide.

The proposed technology for manufacturing pCu$_2$S$-$(Si-NCS)$-n$Si-type HJ provides a predominantly smooth transition energy profile, which makes this structure a promising basis for photoconverters.

The effects identified are largely determined by the geometry and morphology of NC centers, rather than their chemical composition. When the size of the NC centers increases to hundreds of angstroms or more, the photoelectric effect not only does not intensify, but, on the contrary, disappears completely, giving way to another effect.

Thus, a superlinear mode of operation of photocells was discovered, in which there is an increase in sensitivity at high illumination of the HJ.

The mechanisms presented in the work are consistent with experimental observations and confirm the original properties of HJ with NCS.

The study showed that HJ with NCS have significant potential for creating new elements of modern functional electronic devices.

REFERENCES

[1] V. Kovalchuk, *Cluster Modification of Semiconductor Heterostructures*. Kyiv: Hi-Tech, 2007, 317 p.

[2] J. R. McBride, and S. J. Rosenthal, “Real colloidal quantum dot structures revealed by high resolution analytical electron microscopy,” *J. Chem. Phys.*, vol. 151, no. 16, p. 15128366, 2019, doi: 10.1063/1.5128366.

[3] R. Antoine, “Self-Assembly of Atomically Precise Nanoclusters: From Irregular Assembly to Crystalline Assembly,” Nanomaterials, vol. 13, no. 18, p. 2551, Sep. 2023, doi: 10.3390/nano13182551.

[4] V. V. Kovalchuk, “Optical properties of clusters,” *Journal of Physics and Electronics*, vol. 26, no. 1, pp. 29–34, 2018, doi: 10.15421/331804.

[5] O. M. Nazarov, and M. M. Nyshchenko, *Nanostructures and Nanotechnologies*. Kyiv: NAU, 2012, 248 p.

[6] V. Kovalchuk, and D. Popriaha, “Optical properties of the semiconductor nanoclusters,” *Technium: Romanian Journal of Applied Sciences and Technology*, vol. 28, pp. 35–42, 2025, doi: 10.47577/technium.v28i.12625.

[7] M. Sheinkman, “Properties and mechanisms of residual conductivity in single crystals CdS:Ag:Cl,” *Physics of the Solid State*, vol. 12, no. 11, pp. 3130–3140, 1970.

Received 12.11 2025

DOI: 10.15222/TKEA2025.3-4.09
УДК 530.145 + 678.9

Володимир КОВАЛЬЧУК[1], Діана ПОПРЯГА[2], Дмитро ДЯЧОК[2]

Україна,Одеса, [1]Одеський технологічний університет «ШАГ»
[2]Південноукраїнський національний педагогічний університет ім. К. Д. Ушинського

E-mail: lslvvvas@ukr.net

ПЛІВКОВИЙ ГЕТЕРОПЕРЕХІД З НАНОКЛАСТЕРНОЮ ПІДСИСТЕМОЮ ДЛЯ ФОТОЕЛЕМЕНТІВ НОВОГО ТИПУ

Наведено результати досліджень та описано технологію виготовлення плівкового гетеропереходу (ГП) типу pCu$_2$S$-$nSi з нанокластерною підсистемою (НКП), що формується стохастично розподіленими нанокластерними центрами на границі розділу. Показано, що атомарні нанокластери проявляють властивості, відмінні від макроскопічної речовини, та дозволяють ефективно керувати фізико-хімічними характеристиками матриці. Модифікація ГП здійснювалася імплантацією кластерного растра острівкової структури на кремнієву підкладку перед осадженням шару сульфіду міді, що забезпечує плавний профіль енергії переходу та відкриває можливості для створення фотоперетворювачів.

Досліджено фотоелектричні ефекти у модифікованому ГП pCu$_2$S$-$(Si-НКП)$-$nSi, зокрема спектральну інверсію, суперлінійні режими роботи та незвичайну люкс-амперну залежність. Встановлено, що введення НКП у базову p-область Cu$_2$S–Si значно підвищує інтегральну чутливість при високій освітленості, а геометрія та морфологія нанокластерних центрів відіграють вирішальну роль у формуванні властивостей ГП. Показано, що збільшення розмірів НК-центрів до сотень ангстрем призводить до зникнення фотоефекту та появи інших екстенсивних ефектів.

Запропоновано конструкцію фотоелемента з двома послідовно з'єднаними p–n-переходами протилежної дії, що забезпечує фотоелектричну активність у різних ділянках спектра. Отримані результати вказують на перспективність використання плівкових ГП типу pCu$_2$S – (Si-НКП) – nSi для розв'язання задач сучасної функціональної діагностики та створення нових елементів фотоелектроніки.

Ключові слова: гетероперехід, плівка, нанокластер, підсистема, фотоелемент.