Correlation of the surface density and size of FeS nanoinclusions with the electrophysical and photoelectric characteristics of the heterophase material CdS:Fe

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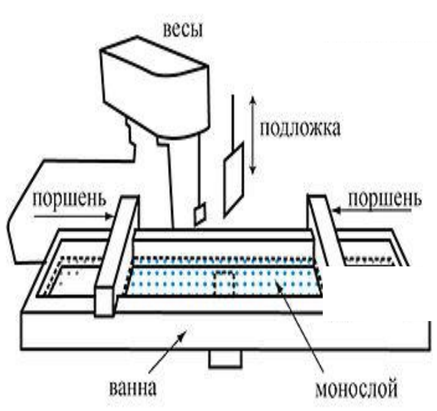
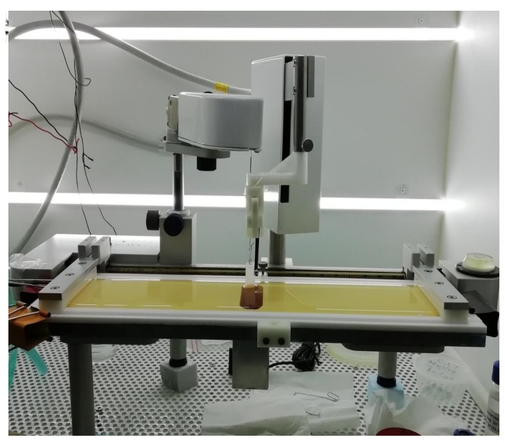
Relevance and purpose

Modification of previously known materials allows changing their properties, which can be controlled by various external influences. In this aspect, a promising material is CdS, the alloying of which with metal atoms makes it possible to obtain structures with improved characteristics. As shown, Fe atoms diffuse from the metallized coating into the CdS film during the high temperature annealing process and form a solid solution CdxFe1−xS. But due to the limited solubility of Fe in CdS, several processes — precipitation, diffusion, and surface oxidation competed, leading to the formation of several kinds of phases unevenly arranged on the surface and in the volume. Thus, FeS and Fe2O3 phases recorded, due to which the material exhibited the properties of a semi-magnetic semiconductor. At the same time, due attention was not paid to the study of the photoelectric characteristics and the surface density and size of FeS nanoinclusions of the heterophase structure of CdS-FeS. [*P.G. Kharitonova, E.G. Glukhovskoy, A.V. Kozlowski, S.V. Stetsyura, Semiconductors, 7, 2023*].

Production technology (*Langmuir-Blodgett technology*)





1. Organic matrix - arachidic acid, **C**= 10^{-3} mol/l, **V**=50 µl.
2. Iron source - $FeCl_3$, **C**= 10^{-3} mol/l.
3. pH of subphase -4.2±0.05.
4. Substrate - CdS.
5. Film transfer - Langmuir-Schaeffer method.
6. Number of transferred monolayers - 25.

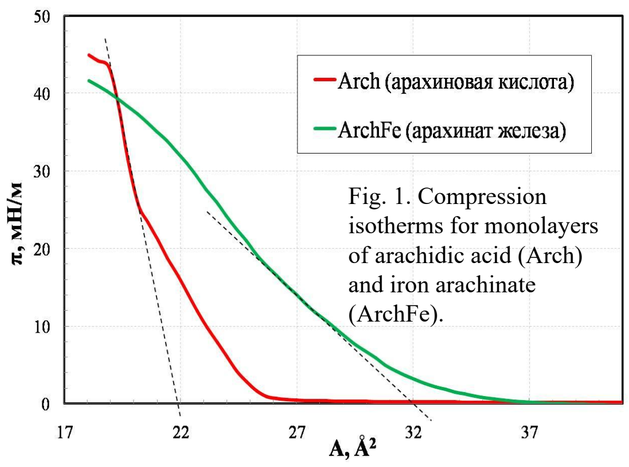


Fig. 1. Compression isotherms for monolayers of arachidic acid (Arch) and iron arachinate (ArchFe).

The area per molecule (A) is **0.22** nm² for the arachidic acid monolayer and **0.32** nm² for the iron arachinate monolayer. This allowed us to estimate the density of Fe atoms in the monolayer **Ns**=3.125·10¹⁴ cm⁻².

The CdS/ArchFe structures were annealed at T=545±5 °C for 30, 40, 60 min. During annealing, Fe atoms diffuse into the CdS sample to form a solid substitution solution $Cd_xFe_{1-x}S$.

Morphology and surface composition of the studied samples

Atomic force microscopy

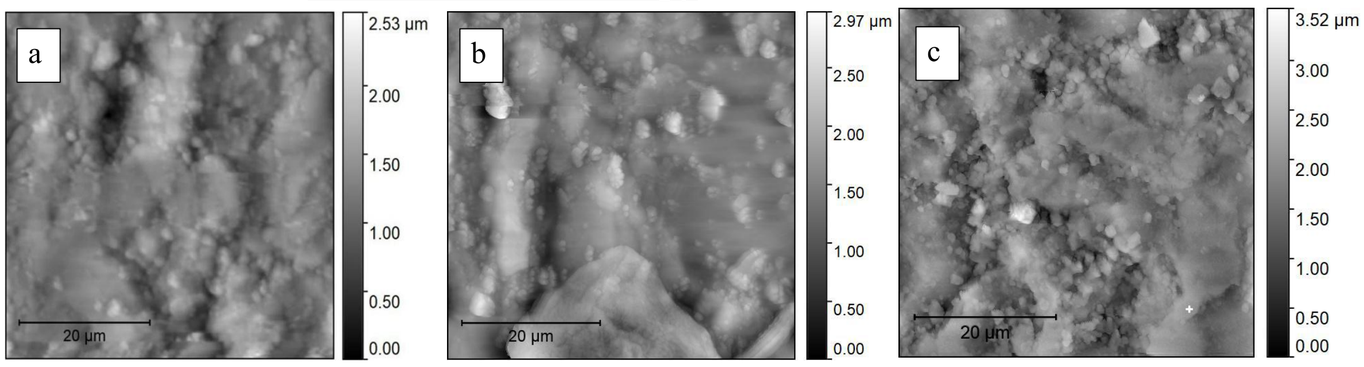


Fig. 2. AFM images of the surfaces of CdS (a), CdS/ArchFe (without annealing) (b) and the structure of CdS-FeS (after annealing of CdS/ArchFe) (c)

Study sample	Average roughness S_a, nm	Root-mean-square roughness S_q, nm
CdS	231.1	297.7
CdS/ArchFe	260.6	331.1
CdS-FeS	298.6	379.9

Energy-dispersive analysis

The obtained samples were studied before and after high-temperature annealing by scanning two sections of the sample measuring 50 by 50 µm at an accelerating voltage of primary electrons of 15 keV using a scanning electron microscope MIRA 2 LMU (Tescan).

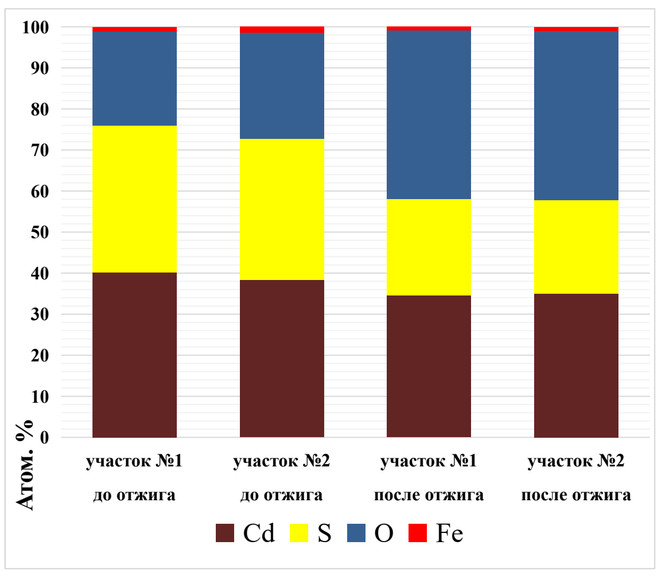
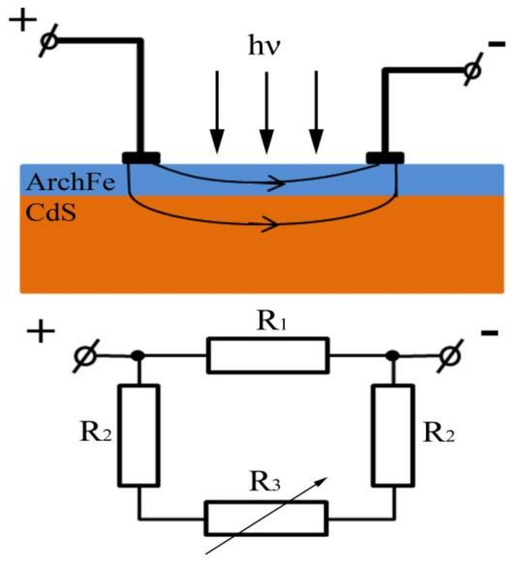


Fig. 3. Chemical composition of the surface of the CdS/ArchFe structure before and after annealing.

Photoelectric characteristics of the studied samples



1. Current-voltage curves was measured in the transverse mode of photoconductivity.
2. The distance between the contacts was kept constant at 800 µm

Fig. 4. Measurement and equivalent diagrams illustrating the transverse photoconductivity mode, where
R1 — resistance along the film ArchFe,
R2 — resistance across the film ArchFe,
R3 — photosensitive resistance of CdS.

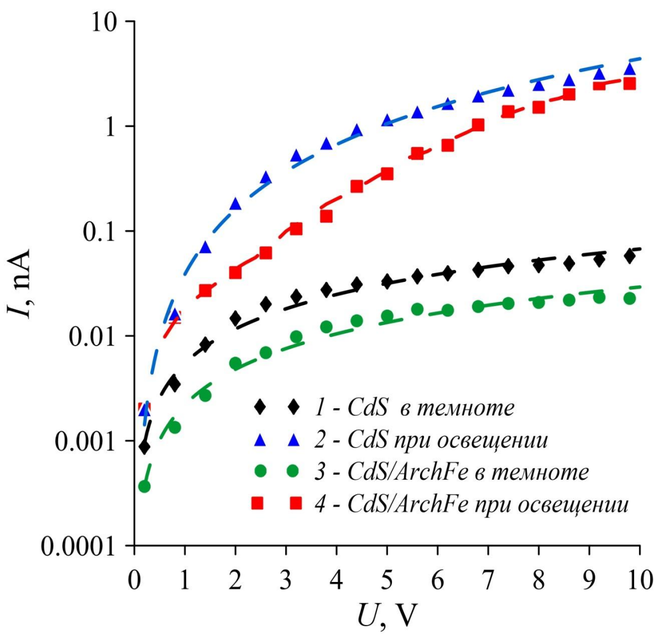


Fig. 5.Current-voltage curves of single-crystal CdS substrate and structure CdS/ArchFe, measured in the dark and under illumination in the transverse photoconductivity mode.

1. Character of current variation under illumination and in the dark does not change when ArchFe coating is applied.
2. The presence of the coating decreases the current both in the dark and under illumination, and the dark resistance of CdS/ ArchFe increased 2.5 times, and the current at the specified illumination decreased only 1.3 times in comparison with the CdS sample, i. e., the multiplicity of change in the light resistance of the hybrid structure CdS/ ArchFe remained at the same level.
3. Since ArchFe is not sensitive to wavelengths from the halogen lamp spectrum, and the CdS/ArchFe hybrid structure retains photosensitivity, this means that current flows not only through the iron-structured organic film, but also through the CdS near-surface layer, while overcoming the resistance of the film ArchFe along its nanoscale thickness.

Calculation of the sizes of FeS nanoinclusions

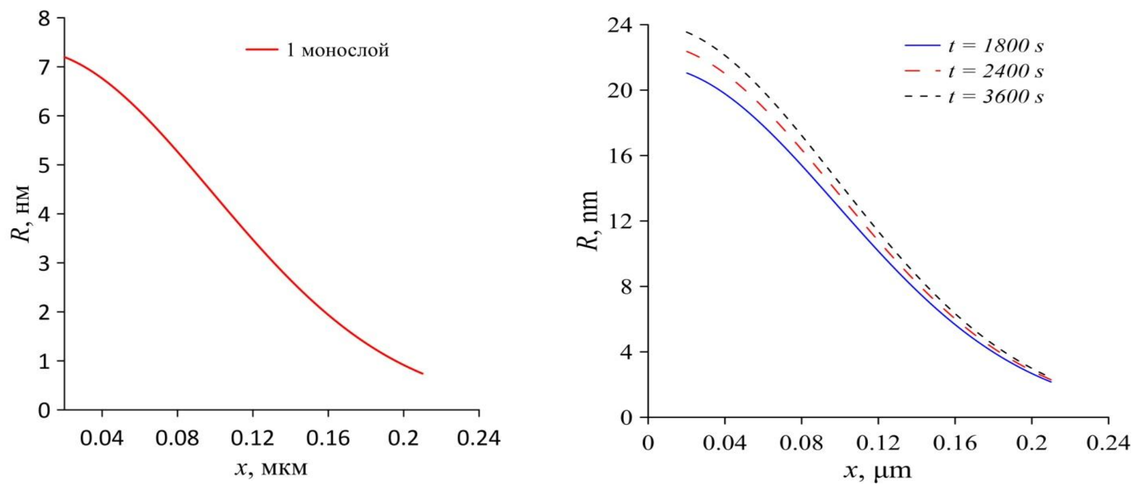


Fig. 6. Dependence of the average radius of the FeS precipitate on the depth of occurrence of precipitates for 1 and 25 ArchFe monolayers obtained at different annealing times.

$$R(t) = \frac{3V_0\langle i(t)\rangle}{4\pi}^{1/3}$$

$$< i(x,t) >= \frac{1}{N_C} \int_0^t \frac{\partial N(x,t)}{\partial t} dt$$

where ***N(x, t)*** — the Fe concentration at a depth *x* from the surface resulting from diffusion of Fe atoms from a surface confined source with Fe concentration ***Ns***, determined from the compression isotherms for ArchFe, over an annealing time t;
N_C -the concentration of precipitate nucleation centers along the axis direction *x*; V_0 - the volume of one molecule FeS.

To determine the growth rate of nanoclusters ***dN(x, t)/dt***, the model previously presented in [***S.V. Stetsyura, E.G. Glukhovskoy, A.V. Kozlowski, I.V. Malyar, Technical Physics, 60 (5), 746 (2015); S.V. Bulyarskii, V.V. Svetukhin, O.V. Prikhod'ko. Semiconductors, 33 (11), 1157 (1999)***].

According to the figure, it is evident that the size of FeS precipitates on the surface does not exceed 8 nm for one ArchFe monolayer, which is insufficient for the manifestation of new properties, including magnetic ones. Thus, to obtain a material with new properties, it is necessary to apply more monolayers (25 ArchFe monolayers) to increase the surface concentration of Fe.
For the investigated material it is shown that FeS phases with radius more than 5 nm are formed at a depth up to 165 nm for 30 min of annealing, and at 60 min this depth is 175 nm. The maximum size of precipitates at the surface does not exceed 21 nm at t = 30 min and 24 nm at t = 60 min. The obtained sizes and the distribution of nanoscale phases in depth are sufficient for the emergence of the material's new properties, while the photosensitivity of CdS practically does not decrease, which increases the functionality of the material and controllability of its properties.