

Ўзбекистон

# **K**ompozitsion **M**ateriallar

Ilmiy-texnikaviy va amaliy jurnali



Ўзбекский научно-технический и производственный журнал  
**Композиционные материалы**

туркумига кириши аниқланди. Шунингдек уни керамика саноатида энгил суюқланувчан флюс сифатида ишлатиш мумкинлиги ҳам аниқланди.

**Ключевые слова:** Гидрослюдистая глина, легкоплавкая глина, легкоплавкий флюс, керамическая масса, химико-минералогический состав.

В результате комплексного исследования характеристики глины Кулатауского месторождения расположенного в Нижнеамударьинском регионе установлено что, Кулатауская глина относится к классу сильноспекающегося сырья с низкотемпературным спеканием. Также установлена пригодность в керамической промышленности в качестве легкоплавкого флюса.

**Key words:** Hydromica clay, low-melting clay, low-melting flux, ceramic mass, chemical and mineralogical composition.

As a result of a comprehensive study of the characteristics of the clay of the Kulatau deposit located in the Lower Amudarya region, it was established that the Kulatau clay belongs to the class of highly sintered raw materials with low-temperature sintering. It has also been shown to be suitable for use in the ceramics industry as a low-melting flux.

**Эминов Ашрап Мамурович** - д.т.н., проф. заведующий лаборатории ГУП «Фан ва тараккиёт» при ТГТУ им. И.Каримова

**Бойжанов Ислон Ражабович** - к.т.н., доц. докторант кафедры «Химической технологии», УрГУ,

**Джабберганов Джахонгир** - базовый докторант кафедры «Химической технологии», УрГУ.

UDC. 541.64:539.2

## DEVELOPMENT AND STUDY OF THE PROPERTIES OF A COMPOSITION BASED ON THE COMPOSITION $\text{Cu}_2\text{ZnSnS}_4$ AND POLYCRYSTALLINE SILICON

A. Yusupov, A.V. Umarov, D.K. Dzhumabaev

Tashkent State Transport University, 1 Temir yulchilar, Tashkent, Uzbekistan. [abusalom@inbox.ru](mailto:abusalom@inbox.ru)

**Introduction.** Quite a lot of works have been devoted to the preparation and investigation of heterostructural compositions based on  $(\text{Cu}_2\text{ZnSnS}_4)$  CZTS [1–3]. Most of them are devoted to the study of structures based on heterostructures of CdS /  $\text{Cu}_2\text{ZnSnS}_4$  compositions. This is due to the fact that CdS is an interesting composite layer for obtaining a barrier transition in solar cells (SC), has a high optical absorption coefficient and a suitable band gap.

It is known that in the formation of semiconductor heterostructure composite materials, the choice of the matrix material is of great importance. In most cases, researchers use various types of glass, quartz and sapphire to obtain thin composite layers of CZTS, as a matrix. At the same time, it should be noted that glass and the above materials are far from ideal as a matrix for industrial designs of solar cells, which is due to a number of reasons. Firstly, glass is a rather fragile material, which is especially pronounced when synthesizing solar modules with a large area, the thickness of the glass substrate is at least 1 mm, which significantly increases the weight of the solar cell, and secondly, accurate control of alkaline fillers in the glass substrate is almost impossible. Alkaline fillers impair process reproducibility. In addition, being an amorphous substance, glass has poor adhesion to many metal films used as back contact.

Silicon is the most common semiconductor material in electronics and photovoltaics. More than 85% of the world's solar panels are produced on its basis. However, the main problem for reducing the cost of solar cells based on monocrystalline silicon is the high cost of the technology for its production. Therefore, the use of cheap polycrystalline silicon is relevant. Effective SCs with p – n junctions based on polycrystalline silicon have been obtained [4]. Recently, there has been a growing interest in semiconductor heterojunction composite materials (HPCM) due to a number of their advantages over homojunction composite materials. Currently, HPCM are actively used in photovoltaics, electronics, and lasers [5, 6]. It is of great interest to study the electrical properties of HPCM based on polycrystalline silicon and CZTS. The use of polycrystalline silicon as a matrix makes it possible to reduce the cost of solar cells.

**Object selection and technology.** In this work, we study the creation of anisotypic HPCM  $\text{Cu}_2\text{ZnSnS}_4 / \text{Si}$ , on a matrix of polycrystalline Si.

The formation of a thin CZTS composite layer on a Si matrix was carried out in two stages. At the first stage, the base layers of the composite components were formed on a polycrystalline Si matrix by the method of vacuum deposition. The process was carried out on a VUP-5M installation, at

a vacuum of (2-5)  $10^{-5}$  mm Hg. The ratio of the components of the compositions in the base layer was taken in accordance with the stoichiometric composition of the compound. The latter was calculated based on the atomic weight of the components and the layer thickness of each component of the composition.

At the second stage, the base layer was sulphurized from an unlimited source, in a closed volume. For this, samples of polycrystalline Si with the components of the compositions deposited on the surface were placed in a vacuum pumped to  $(1-3) \cdot 10^{-5}$  mm Hg. vacuum quartz ampoule. To ensure uniform sulphurisation and prevent the evaporation of sulfur from the formed film, sulfur was placed in the ampoule, in an amount providing the required pressure inside the ampoule. The formation of the CZTS composite layer was carried out by thermal annealing of samples with base layers in an SUOL-4 furnace. To study the process of the formation of CZTS layers on Si, the components of the compositions were deposited sequentially or in parallel; during sequential deposition, the sequence of deposition of the components of the composition was varied. The thickness of the films after each stage of deposition was controlled by the metallographic method. Thermal firing of the components of the compositions was carried out at temperatures of 400 – 620 °C, the firing time was within 15 - 90 minutes. The heating rate was 15 - 30 deg / min. After firing, the samples were cooled to 200 °C at a rate of 10 - 15 deg / min, and then brought to room temperature by removing the ampoules from the oven or together with the oven.

**Results and research.** The study of the morphology of the grown layers of the composites, depending on the preparation mode, showed that a smoother surface is provided when the components are deposited in the sequence tin - zinc - copper and annealing temperatures of 550-565 °C (Fig. 1). With other sequences of spraying of components and an increase in the annealing temperature, some roughness of the surface of the films is observed, which, apparently, is associated with the volatilization of individual components of the compositions. Taking this into account, further thermal annealing was carried out at a temperature of 560 °C.

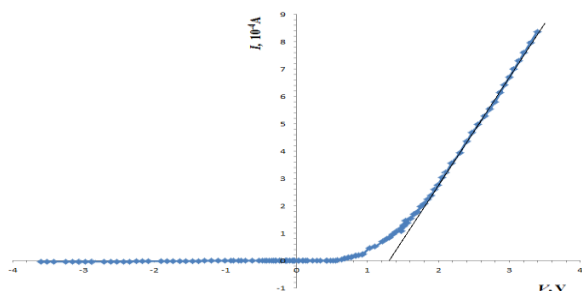


**Figure 1. Micrograph of the surface of the czts layers of the compositions**

Studied the X-ray reflection spectra in the layers of the CZTS compositions. The spectra exhibit peaks corresponding to planes (112), (200), (312), (008). The intensities of these peaks differed somewhat depending on the temperature and time of sulfonation. The largest peaks of the (112) planes corresponded to the samples that underwent thermal annealing at 550-560 °C for 30 minutes or more. The study of the microstructure of the films showed that the sizes of crystallite grains depend on the annealing temperature and the quenching mode. With an increase in the annealing temperature and the cooling rate of the samples, an increase in the size of the crystallite grains is observed.

Measurement of the electrical parameters of the obtained compositions showed that all samples obtained without special doping have a hole-type conductivity. This is apparently due to the fact that the formation of layers of the CZTS composition results in the formation of such structural defects as a vacancy of copper atoms –  $V_{Cu}$  and the substitution of a copper atom for the zinc site –  $Cu_{Zn}$ . These defects with shallow acceptor levels determine the type of conductivity of the formed layers of the composition. The ionization energy  $V_{Cu}$  is ~ 0.02 - 0.08 eV, the ionization energy of  $Cu_{Zn}$  is ~ 0.10 - 0.15 eV [7]. The surface resistance of the CZTS films was in the range of 30-55 Ohm sq.

The effect of the applied voltage on the current through the created  $Cu_2ZnSnS_4 / Si$  HPCMs was measured at room temperature. Ohmic contacts to the structures were obtained by applying a eutectic composition of an indium-gallium alloy. The forward and reverse branches of the dependences of the current on the applied voltage  $I(V)$  of heterostructural composite materials are shown in Fig. 2. It can be seen from the figure that heterostructural composite materials have pronounced diode characteristics.



**Figure 2. Effect of the applied voltage on the current of the  $\text{Cu}_2\text{ZnSnS}_4$  / Si HPCM at  $T = 300$  K**

Moreover, the flow direction in all HPCMs is observed when the positive polarity of the external bias is applied to the CZTS composite layer, which is consistent with the band model of the studied HPCM [8]. Other compositions were previously explained by this model [9, 10]. Straightening coefficients in the best structures for  $|V| = 1-2$  V were reached up to  $K = 65-110$ . The relatively small  $K$  values obtained are apparently associated with imperfections in the transition region of the heterojunctions.

The temperature dependence of the resistivity of the composite CZTS layer on a silicon matrix in

the temperature range of 300-450 K. was studied. Depending on the specific resistance from the temperature, in the temperature range above 350 K, there is a certain increase in the value of the resistivity, apparently, this is due to a decrease in the mobility of carriers with an increase in temperature.

To measure the mobility of holes in polycrystalline composite layers of CZTS, the Hall coefficient and resistivity were measured. The Hall mobility of holes in CZTS polycrystals with a hole concentration of about  $10^{16} \text{ cm}^{-3}$  was in the range of  $17-23 \text{ cm}^2/\text{V}\cdot\text{s}$ .

Thus, the analysis of the results of the study of the basic electrical properties shows that the results obtained in the work are, in general, in good agreement with the literary results

**Conclusions.** Thus, a composite CZTS layer on a silicon matrix was formed by the method of thermal vacuum evaporation and subsequent sulfonation in a closed volume and  $\text{Cu}_2\text{ZnSnS}_4$  / Si HPCM were created. The best structures are obtained at an annealing temperature of 550-5600C for 45 minutes.

#### REFERENCES:

1. G. S. Babu, Y.B. Kumar, et. all. Solar Energy Materials and Solar Cells, 2010, 94, 221-226.
2. H. Araki, Y. Kubo, et. all. Phys. Status. Solidi. 2009, 6, 1266-1268.
3. Wang W., Winkler M. T., Gunawan O., Gokmen T., Todorov T. K., Zhu Y., Mitzi D. B. Advanced Energy Materials, DOI: 10.1002/aenm.201301465.
4. T.M. Razykov, C.S. Ferekides, D. Morel, E. Stefanakos, H.S. Ullal, H.M. Upadhyaya. Solar Energy, 85, 1580 (2011).
5. J.I. Alfyorov. Fizika i tehnika polyprovodnikov, 32, 3 (1998). (in Russian)
6. A.L. Fahrenbruch, R.H. Bube. Fundamentals of solar cells. Photovoltaic solar energy conversion (N. Y., 1983).
7. M.S. Guk. Spectri kombinatsionnogo rasseyaniya, elektricheskkiye i fotoluminescentniye svoystva polyprovodnikovix materialov  $\text{Cu}_2\text{Zn}(\text{Sn}, \text{Ge}, \text{Si})(\text{S}, \text{Se})_4$ , Kishinev, 2014. (in Russian)
8. A. Yusupov, K. Adambayev, Z.Z. Turayev. «Geliotechnika», 2015, №3, p. 74-79. (in Russian)
9. Magrupov, M.A., Umarov, A.V., Khamidov, Sh.R., Makhmudov, R.Kh., Electrical conductivity of a sitall // Glass and Ceramics, 1992, 49(7), p. 313-314. <https://doi.org/10.1007/BF00677447>
- Abdurakhmanov, U., Umarov, A.V., Zainutdinov, A.Kh., Magrupov, M.A. Electrical conductivity of semiconductor pyropolymers in an alternating electrical field// Polymer Science U.S.S.R., 1989, 31(6), p. 1323-1330.

**Abstract.** Anisotypic heterojunctions based on the  $\text{Cu}_2\text{ZnSnS}_4$  / Si composition have been obtained by sulfonation of base metal layers previously deposited onto a polycrystalline silicon matrix. The mode of obtaining the  $\text{Cu}_2\text{ZnSnS}_4$  / Si heterojunction is established. The dependences of the current on the voltage of the heterostructure compositions have been studied and their main parameters have been determined.

**Аннотация.** Анизотипические гетеропереходы на основе состава  $\text{Cu}_2\text{ZnSnS}_4$  / Si были получены сульфированием слоев основного металла, ранее нанесенного на матрицу поликристаллического кремния. Установлен режим получения гетероперехода  $\text{Cu}_2\text{ZnSnS}_4$  / Si. Исследованы зависимости тока от напряжения составов гетероструктур и определены их основные параметры.

**Annotatsiya.**  $\text{Cu}_2\text{ZnSnS}_4$  / Si tarkibiga asoslangan anizotipik getero-o`lishli polikristal kremniy matritsiga metall qatlamlarini sulfirlash orqali olingan.  $\text{Cu}_2\text{ZnSnS}_4$  / Si getero-o`lishni olish rejimi o`rnatildi. Elektr toki oqimining geterostrukturali kompozitsiyalardagi kuchlanishiga bog`liqligi o`rganiladi va ularning asosiy parametrlari aniqlanadi.

## 3. Разработка и технология получения композиционных материалов

С.С. Негматов, К.С. Негматова, М.Э. Икрамова, С.У. Султанов, У.Қ. Қобилов, Х.Ю. Рахимов, М.А. Бабаханова, А.Ш. Насридинов, М.М. Машарипова. Разработка эффективных составов машиностроительных антикоррозионных композиционных полимерных материалов и покрытий на основе местного сырья и промышленных отходов.....	93
Ж.М. Бекпулатов, М.М. Якубов, Х. Ахмедов, Б. Садуллаев, А. Нормуродов. Современные способы интенсификации цианирования золотосодержащих руд.....	96
Ф.Р. Норхужаев, Ж.М. Усмонов. Иккиламчи алюминий чиқиндисини механик майдалашда технологик кўраткичларни кукунининг гранулометрик таркибига таъсири.....	98
А.М. Эминов, И.Р. Бойжанов, Дж.С. Джабберганов. Исследование глины кулатауского месторождения как легкоплавкая флюсующая добавка в составе керамики.....	101
A. Yusupov, A.V. Umarov, D.K. Dzhumabaev. Development and study of the properties of a composition based on the composition $Cu_2ZnSnS_4$ and polycrystalline silicon.....	104
Ю.С. Юсупова, Ш.М. Шакиров. Графит ва углеграфит-кремний асосли композицион материаллар.....	107
Ф.Р. Норхужаев, Ж.М. Усмонов. Шарли тегирмонда иккиламчи алюминий чиқиндисидан кукун олиш жараёнида алюминий кукун таркибидаги алюминий оксидининг микдорини бошқариш.....	109
M.S. Xudayberganov, F.G. Rahmatkarieva. Mahalliy xom ashyolardan modifikatsiyalab olingan mikrog'ovakli adsorbentlarda suv bug'i adsorbsiyasi.....	111
T.O. Kamolov, X.T. Sharipov, F.A. Nurxanov, F.S. Axmedova, A.N. Bozorov, A.P. Saфарov. Исследование и разработка технологии получения железа из отходов металлургического производства.....	113
С.А. Ахмаджанов, А.М. Искендеров, Э.У. Тешабаева. Технология получения и модификации монтмориллонита.....	117
E.A. Egamberdiyev, Y.T. Ergashev, X.N. Xaydullayev, D.A. Xusanov, G'R. Rahmonberdiyev. Bazalt tolasi ishtirokida qog'oz namunalari olish va xitozan tabiiy yelimini qog'oz sifatiga ta'sirini o'rganish.....	121
Б.М. Сайдумаров, Т.Н. Ибодуллаев. Современные технологии производства прокатки листа.....	124
S.O. Ramazanov, M.X. Arifova. «Yolg'izbuloq» ohaktoshi asosida portlandsement olish texnologiyasi.....	127
Ш.И. Мамаев, А.С. Ибадуллаев, З.Г. Мухамедова, Д.И. Нигматова. Магистрал тепловозларнинг тортув узатмаларидаги тортув моторлари тебранишини сўндирувчи элементни тайёрлаш учун композицион материаллар яратиш.....	130
J.A. Sherbo'tayev. Metallkompozitsion uglerodli po'latlardan quyib olingan quyma detallarning tarkibi va xossalari.....	134
С.И. Соипов, А.Н. Ризаев. Махаллий хом ашё асосида композицион релс суртмасини олиш ва синовдан ўтказиш....	138
Т.С. Халимжонов, С.Н. Асатов. Получение компактных крупногабаритных молибденовых заготовок методом гидростатического прессования.....	141
К.С. Негматова, Ш.Н. Жалилов, Р.Х. Пирматов, С.С. Негматов, Н.С. Абед, Д.К. Холмурадова, Р.Х. Солиев, М.Э. Икрамова, Д.Н. Ходжаева, М.Б. Бойдодаев. Исследование процесса отверждения модифицированной с реакционноспособными соединениями мочевиноформальдегидной смолы и определение их оптимальных режимов отверждения.....	143
T.O. Kamolov, M.G. Bekmuratova, N.Sh. Rahmatova, A.N. Bozorov, E.I. Turapov. Фторидная переработка золошлаковых отходов ТЭЦ.....	147

## 4. Прикладные, экономические и экологические аспекты применения композиционных материалов

Е.И. Руклинская, М.М. Якубов. Использование техногенных отходов АО «Алмалыкский ГМК» в качестве сырья и восстановителя.....	150
G.Sh. Juraeva. Yuk avtomobillari uchun g'ildirak disklerini ishlab chiqarishda kompozit materiallarning qo'llanilishi.....	153
И.Р. Бойжанов, А.А. Мухамедбаев, С.Қ. Дўсчанов, Х.Ф. Машарипова, Ф.У. Тухтаназаров. Известняк учукасского месторождения – новое сырье для производства вяжущих материалов.....	155
Д.М. Хуррамова, М.Г. Хуррамов, Ш.А. Ганиева, З.Ш. Назиров, С.М. Хуррамова. Ресурсосберегающий первичный способ обогащения кислородом недостаточно очищенных стоков.....	158
Л.К. Уббиниязова, Г.Ж. Оразимбетова, А.Г. Нимчик, А.М. Кудайбергенова. Бурый железняк худжакульского участка в качестве минерализующей добавки при производстве портландцементного клинкера.....	161
Н.Н. Мирзаев, Р.К. Хамраев. Латуннинг хоссалари ва ишлаб чиқаришдаги афзалликлари.....	164
А.А. Абдумажидов, А.А. Миратаев, И.А.Набиева. Қоғоз саноатидаги иккиламчи толали ресурслар сифат кўрсаткичларига уларни қайта ишлаш жараён омилларининг таъсирини ўрганиш.....	167
Н.А. Исахожаева, З.М. Ахмедова. Исследование и выбор компонентов одежды для особой категории больных.....	170
Ш.Б. Холиёров, М.А. Жамолов, М.С. Юсуфов, А.К. Абдушукуров, Т.С. Холиқов, А.Д. Матчанов. Очистка отхода, выделенного из сепаратора-6401 шуртанского газохимического комплекса.....	173
Э.Э. Умурзаков, А.К. Сативалдиев, Ш.А. Сулаймонов. Роль фосфатирования металла в автомобильной промышленности.....	176
С.Т. Содиков. К вопросу перспектив обнаружения ртутных месторождений на территории республики Узбекистан...	179
А.Х. Аликулов, Ф.Р. Норхужаев, Д.А. Жалилова. Материалы, используемые в электродах, для точечной сварки...	182
Д.Ф. Ганиева, М.Б. Маматкулова, Р.М. Давлатов. Эффективность применения композиционного полимерного материала при модификации шерстяных волокон.....	184
B.R. Voxidov, A.S. Xasanov. Texnogen xomashyolardan platinoidlarni ajratib olish texnologiyasini yaratish.....	188
Sh.M. Munosibov, U.N. Fayazov. Oltinugurt oksidli oqova gazlardan gips olish imkoniyatlari.....	192
Ш.А. Аликобилов, Р.Х. Пирматов, Ё.С. Раджабов, Т.О. Камолов, Т.У. Улмасов, К.С. Негматова, Р.Х. Солиев, М.Б. Мухитдинов. Применение композиционных полимерных материалов в формах для повышения эффективности производства железобетонных строительных конструкций.....	195