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Д.В. Сокольский атындағы «Жанармай,
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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
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АО «Институт топлива, катализа и
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НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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METHOD FOR MANUFACTURING THIN FILMS OF CUBI$_2$O$_4$ FOR PHOTOELECTROCHEMICAL APPLICATIONS

Abstract. A method has been developed for producing thin semiconductor films of a complex copper-bismuth system ($CuBi_2O_4$) with reduced roughness and increased photoactivity.

The application process is carried out under standard laboratory conditions from aqueous solutions of salts, takes advantage of centrifugation to evenly distribute the coating over the surface, is characterized by low material consumption, and allows the thin nanocrystalline layers formation with a given thickness. Polyethylene glycol (PEG) is used to improve the spraying of solution droplets over the entire surface of the $CuBi_2O_4$ film, which allows the dense uniform films deposition.

Scanning electron and atomic force microscopy data demonstrate the ordering of the growth of $CuBi_2O_4$ particles (size ≈200 nm) and a 1.5-fold decrease in the roughness of the relief when polyethylene glycol is added to the solution. Micrographs show the growth of uniformly sized rounded crystallites.

In a comparative analysis of the XRD diagram of the samples, an increase in the number and intensity of peaks corresponding to the crystalline phase of Kusachiite ($CuBi_2O_4$) with the introduction of PEG into the initial solution is observed.

Based on the photoelectrochemical measurements results, it was found that the addition of polyethylene glycol to the electrolyte helps to increase the photoactivity of the samples by 2 times.

The obtained thin polycrystalline $CuBi_2O_4$ films are promising for use in photoelectrochemical converters.

Keywords: Solar energy material, spin coating, $CuBi_2O_4$, polyethylene glycol.

Introduction. A fundamental condition for a hydrogen economy is the ability to renew, purify, and efficiently produce hydrogen.

Currently, non-renewable methods for producing hydrogen, such as steam methane conversion, are cheaper than photoelectrolysis. However, the methane process leads to CO_2 emissions and is ultimately limited to natural gas reserves. On the contrary, photoelectrolysis of water does not lead to environmental pollution, sunlight and water can be considered inexhaustible resources, and with an increase in the efficiency of use of solar energy, it can be expected that internal costs will continue to decrease [1].

A significant advantage of the hydrogen obtained by photoelectrolysis is the relative ease of storage. If necessary, hydrogen can be stored and then converted into electricity in a fuel cell, which makes it particularly advantageous as a fuel for transport or in remote locations without electricity. In addition, it can simply be burned as fuel for heating or cooking, making it a promising alternative to natural gas.

However, despite significant research efforts over the past decades, fundamental problems still impede the commercial use of photovoltaics. Such problems include the low efficiency of sunlight, the corrosive instability of most semiconductors in aqueous solutions, the complex and expensive designs of PEC elements, etc. Obviously, to achieve progress, innovation is needed in both device design and material development.

One of the materials that can provide a high photocurrent density and a large overvoltage of the process of water photolysis is $CuBi_2O_4$, which was first proposed as a possible photocathode material in

2007 [2]. However, relatively little is known about this compound, especially in comparison with such more studied metal oxides as TiO_2, Fe_2O_3, $BiVO_4$, Cu_2O [3] and complex copper chalcogenides (($Cu_2ZnSnS(Se)_4$) [4].

$CuBi_2O_4$ is a p-semiconductor and has many promising physico-chemical properties including magnetic susceptibility, dielectric constant, high-temperature heat capacity, electrochemical capacitance, photoelectrochemical ability and catalytic properties [5-7]. $CuBi_2O_4$ has a small energy of the band gap of 1.5-1.9 eV, and, therefore, can largely absorb the visible parts of the solar spectrum [8-11]. The potential of the conduction band of $CuBi_2O_4$ is more negative than the redox potential of H^+/H_2. Due to this, $CuBi_2O_4$ is widely studied for use as a photocathode for solar energy and decomposition of water with evolution of hydrogen [12-17]. $CuBi_2O_4$ can be used as a promising photocatalyst for the decomposition of organic pollutants and dyes [17].

In recent years, many methods of obtaining $CuBi_2O_4$ have been used. Crystalline $CuBi_2O_4$ nanoparticles were synthesized using various methods, including solid-phase reactions [8,9,18], mechanochemical treatment [19-20], hydrothermal crystallization [21-23], thermal decomposition and complexation [24,25], microwave synthesis [6], ultrasonic method [16], electrochemical synthesis [13,26], magnetron sputtering [28], floating zone method [29], and sol-gel method [30]. Most of these methods are not widely used due to complexity, the use of high temperatures and low reproducibility.

In this work the spin coating method was used, which is carried out under standard laboratory conditions from aqueous salt solutions, uses the advantages of centrifugation to uniformly distribute the coating on the surface, is characterized by low material consumption, allows the formation of thin nanocrystalline layers with a given thickness. It is known that the addition of polymers is often used to the uniform distribution of solution droplets over the entire surface of the deposited films when using the spin-coating method. In this work polyethylene glycol (PEG) is used for this purpose. The investigations of photoelectrochemical properties of $CuBi_2O_4$ thin films are important for the creation of effective photocathodes.

Experimental procedure. A solution for depositing $CuBi_2O_4$ films was prepared by mixing copper nitrate trihydrate and bismuth nitrate pentahydrate (at 0.05M and 0.1M, respectively) with acidification with concentrated (65%) nitric acid. Subsequently, the resulting mixture was evaporated without boiling to an amount of 1/5 of the original volume and cooled to room temperature. The preparation of solutions containing polyethylene glycol - 2000 (PEG) additives was performed after cooling the initial solution, adding PEG in the amount of 0.25 grams to each 5 ml of the solution. After that, the solution was subjected to treatment in an ultrasonic bath. The resulting mixture was used for at least an hour, but not later than a day after preparation.

Films of the complex system copper-bismuth were obtained by the spin coating method. The films were applied to pre-cleaned optically transparent electrodes, which are a fluorinated tin oxide glass (FTO), measuring 10*25 mm. During rotation of the FTO, the electrodes were fixed in the horizontal plane by a special holder, which avoided the displacement of the substrate and eliminated the influence of the position on the uniformity of film deposition. Rotation lasted 90 seconds at a frequency of 500 rpm.

After application, the films were annealed in a muffle furnace for 2 hours at a temperature of 600°C.

In the future, physico-chemical characterization of all samples was carried out.

With the help of an electronic scanning microscope from JEOL (Japan) with the capabilities of the micro analysis "JSM 6610 LV", surface micrographs were obtained. Analysis of the elemental composition excluded the presence of impurities.

The structure and morphology of the surface were studied by atomic force microscopy (JSPM-5200 (JEOL)). During the measurements, images of topography and contrast images for the phase regions were recorded. During scanning, a region measuring 500x500 nm was examined.

The crystal structure was confirmed by X-ray diffraction on the X-ray diffractometer DRON-4-07.

Photoelectrochemical studies were performed in real time in a solution of 0.2 M Na_2SO_4 + 0.1 M phosphate buffer + 10 mM H_2O_2 under modulated illumination with a wavelength of 465 nm in a GillAC (ACM Instruments) apparatus using a quartz cuvette and a silver chloride reference electrode.

Results and Discussion. Figure 1 compares the results of electron microscopy for $CuBi_2O_4$ films deposited on FTO/glass from solutions without organic constituents (Fig. 1a, c) and from solutions containing PEG (Fig. 1b, d). Microphotographs of the samples surface show that the addition of polyethylene glycol to the solution contributes to the ordered growth of identical in size and shape grains

(190-210 nm), while precipitation from the primary solution observed the development of chaotic formations ranging in size from 85 nm to 820 nm and the presence of significant relief changes.

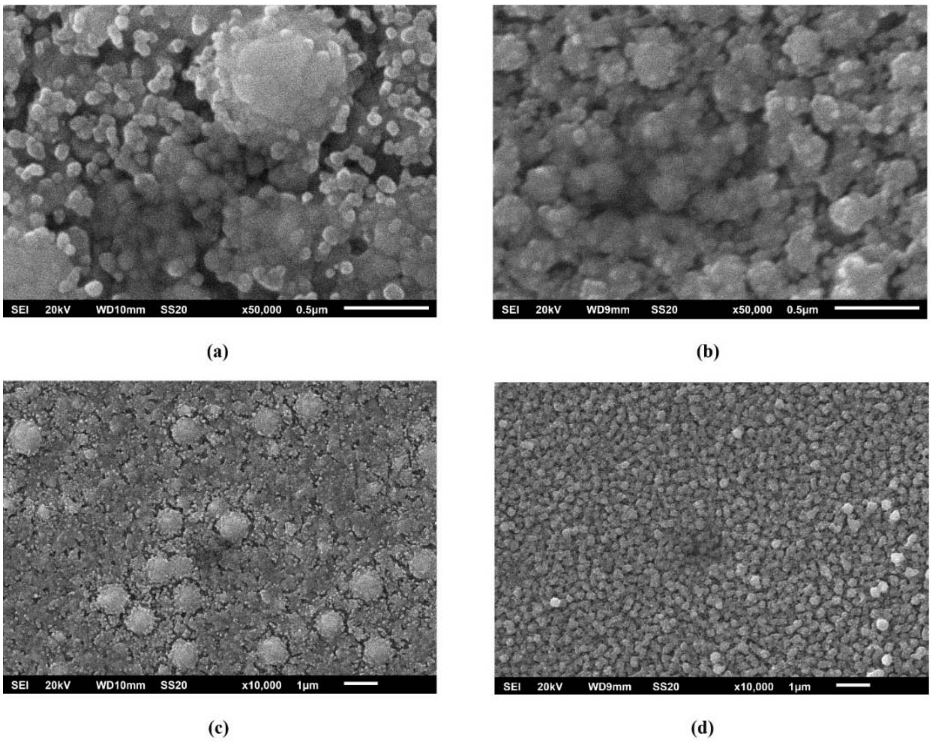

Figure 1 - SEM micrographs of the surface of deposited $CuBi_2O_4$ films a, c) without using PEG; b, d) in the presence of PEG

The results of elemental analysis show that the elemental composition of the films corresponds to the composition of the $CuBi_2O_4$ precipitate with an accuracy of ± 2 at %. The introduction of polyethylene glycol into the solution does not affect the composition change and does not contribute to the appearance of impurities in the composition of the precipitate.

Figure 2 shows the results of films investigation on an atomic force microscope. On scans in 3D format, growth figures up to 146 nm (figure 2a) are formed from the initial solution, whereas for films deposited from solutions with polyethylene glycol content only growth up to 94 nm is observed (figure 2b). Experiments showed that when using a solution with PEG, the roughness of the surface decreases by a factor of 1.5, and the crystallites have a rounded shape characteristic of the $CuBi_2O_4$ compound.

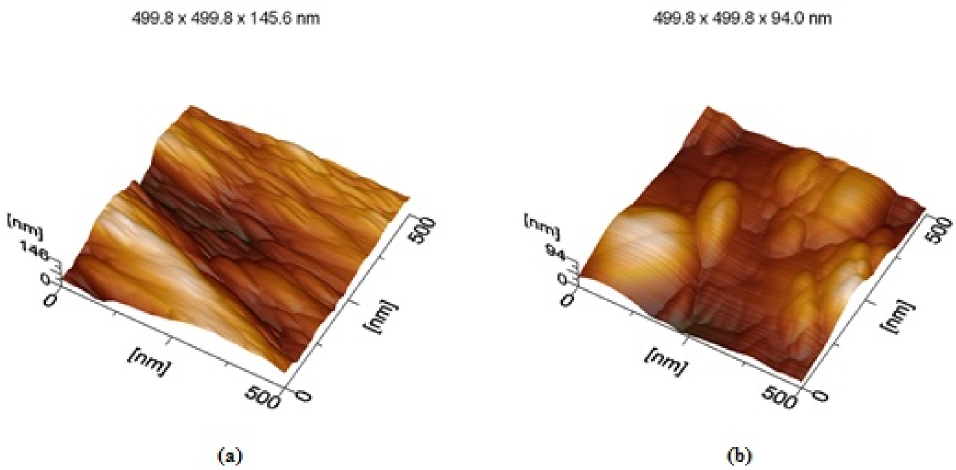

Figure 2 - Micrograph of surface obtained on AFM
for deposited $CuBi_2O_4$ films a) without using PEG; b) in the presence of PEG

Figure 3 shows the X-ray diffraction patterns of $CuBi_2O_4$ films deposited on glass / FTO from the initial solution (figure 3a) and solutions containing PEG (figure 3b). Crystallographic analysis of X-ray data and EDAX measurements confirm the presence of the Kusachiite phase ($CuBi_2O_4$). The peaks of SnO_2 from the substrate on the diffraction diagrams are due to the small thickness of deposited $CuBi_2O_4$ films (less than 500 nm).

From the results of XRD it is obvious that the introduction of polyethylene glycol into the solution positively affects the film structure. There is an increase in the diffraction peaks and their intensities.

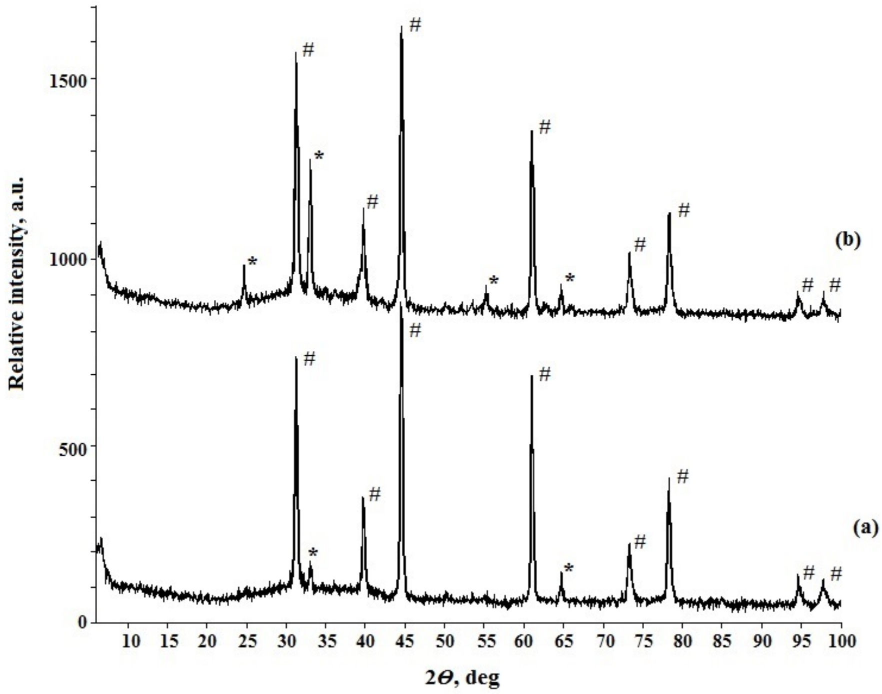

Figure 3 - XRD diagram of deposited $CuBi_2O_4$ films a) without using PEG;
b) in the presence of PEG: # FTO; * $CuBi_2O_4$

The photosensitivity of the deposited $CuBi_2O_4$ films was studied by photoelectrochemistry with modulated illumination with a wavelength of 465 nm (a solution of 0.2 M Na_2SO_4 + 0.1 M phosphate buffer + 10 mM H_2O_2). Figure 4 shows the photocurrent curves for samples of $CuBi_2O_4$ thin films.

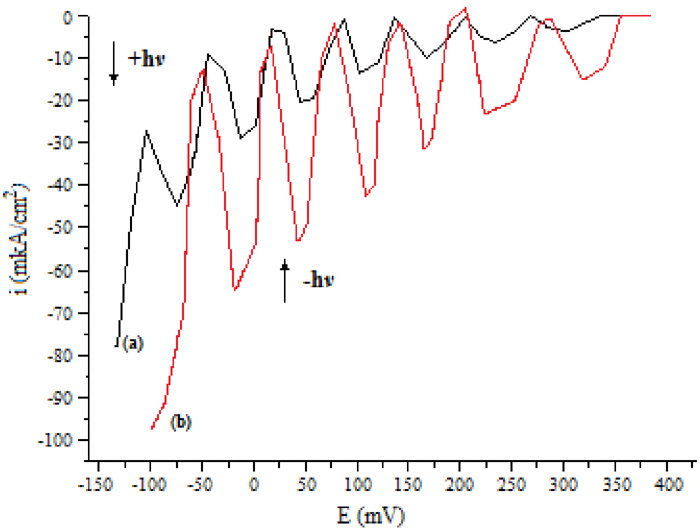

Figure 4 - Photopolarization curve under modulated illumination with a wavelength of 465 nm
in the "light off /light on" mode for the $CuBi_2O_4$ electrode without using PEG (a) and in the presence of PEG (b)

Photoelectrochemical study of deposited films showed that the photocurrents are negative, and the resulting semiconductor is characterized by a p-type conductivity. A comparison of the photocurrent values indicates that the photoelectrochemical activity of films deposited from solutions containing polyethylene glycol was found to be 2 times higher when switching from the light off mode to the light on mode (figure 4b) than the precipitated ones without the addition of PEG (figure 4a).

The developed method of deposition of a complex copper-bismuth $CuBi_2O_4$ system allows obtaining photocathodes with high photosensitivity.

Conclusion. A new composition of a solution for the thin films deposition of the copper-bismuth ($CuBi_2O_4$) complex system on FTO/glass by the spin coating method has been developed.

The physicochemical characterization of samples precipitated from solutions containing and without polyethylene glycol was carried out. The positive effect of the use of PEG is shown.

Surface micrographs showing the ordering of the growth of $CuBi_2O_4$ particles (size ≈200 nm) with the addition of polyethylene glycol to the solution were obtained by SEM.

The results of AFM indicate a 1.5 times decrease in the roughness of the relief and the formation of equidimensional rounded crystallites.

For all films, the XRD method confirmed the presence of the crystalline Kusachiite phase corresponding to the $CuBi_2O_4$ compound. Comparative analysis of the XRD diagram of samples obtained from solutions containing PEG and "pure" (without PEG) shows an increase in the number of peaks and their intensity in the first case.

Based on photoelectric measurements, it is established that $CuBi_2O_4$ films precipitated from solutions containing polyethylene glycol show a photoactivity of 2 times higher.

Thus, the developed method of deposition of a complex copper-bismuth $CuBi_2O_4$ system makes it possible to obtain polycrystalline films with high photosensitivity, p-type conductivity, which are promising for use in photoelectrochemical converters as photocathodes.

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ФОТОЭЛЕКТРОХИМИЯЛЫҚ ҚОЛДАНУҒА АРНАЛҒАН ЖҰҚА $CuBi_2O_4$ ПЛЕКАЛАРЫН АЛУ ӘДІСІ

Аннотоция. $CuBi_2O_4$ - су фотолиз процесін үлкен фототок тығыздығы мен үлкен асқын кернеумен қамтамасыз ете алатын материал болып табылады. Ол тыйым салынған аймағының энергиясы 1,6-1,8 эВ болатын р-типті металл-оксидті аралас жартылай өткізгіш болып табылады және стандартты сутекті электродқа қатысты потенциалы шамамен 1 В кезінде фототоқ басталады.

Қазіргі кезде қабықшаларды жасаудың түрлі әдістері белгілі және олардың әрқайсысына белгілі бір артықшылықтар мен кемшіліктер тән. Осы әдістердің көпшілігі күрделілігіне, жоғары температураны пайдалануына және нашар жаңғыртылуына байланысты кеңінен қолдануға болмайды.

Бұл жұмыста тұздардың су ерітінділерінен стандартты зертханалық жағдайларда жүргізілетін spinning coating әдісі қолданылады, үстіңгі беті бойынша жабынды біркелкі бөлу үшін центрифугалау артықшылық-тарын пайдаланады, аз материал сыйымдылығымен сипатталады, қалыңдығы белгілі жұқа нанокристалды қабаттарды қалыптастыруға мүмкіндік береді. $CuBi_2O_4$ қабықшаларының барлық бетіне ерітінді тамшыларын тозаңдануын жақсарту үшін полиэтиленгликоль (ПЭГ) қолданылады, бұл тығыз бір текті қабықшаларды тұндыруға мүмкіндік береді. Алынған $CuBi_2O_4$ жұқа қабықшалары фотоэлектрохимиялық қасиеттерін іргелі зерттеу үшін жақсы.

Қабықшаларды жағу үшін алдын ала тазартылған электродтар ретінде фторирленген қалайы оксиді (FTO) қабатымен жабылған оптикалық мөлдір шыны пластиналар қолданылды. Шөгу кезінде электродтың көлденең жазықтықта орналасуын арнайы ұстағыш қамтамасыз етті, оның конструкциясы айналғанда төсеніштің ығысуын болдырмауға және қабықшаның біркелкі жағылуына теріс әсер болдырмауға мүмкіндік берді. Айналу 90 секунд ішінде, минутына 500 айналым жиілігі кезінде жүзеге асырылды.

$CuBi_2O_4$ қабықшаларын жағуға арналған ерітіндіні дайындау бірнеше кезеңде өтті, ол мыс пен висмут азот тұздарын араластыру және концентрацияланған азот қышқылымен (65%) қышқылдандыру, ерітіндіні буландыру және температурасын бөлме температурасына дейін төмендету. Құрамында полиэтиленгликоль

(ПЭГ) бар ерітінділерден қабықшаларын тұндыру жөніндегі эксперименттер үшін ерітіндіге әрбір 5 мл ерітіндіге 0,25гр ПЭГ-2000 қосылды. Тиімді араластыру үшін ультрадыбыстық ванна қолданылды. Эксперимент нәтижелері дайындалған ерітіндіні тиімді пайдалану мерзімі дайындағаннан кейін бір тәуліктен артық болмауын көрсетті.

Соңғы кезекте муфельді пеште қабықшаларды 2 сағат бойы 600°С температурада күйдіру жүзеге асырылды.

Физикалық-химиялық зерттеулердің нәтижелері әртүрлі ПЭГ құрамы бар электролиттерден жасалған үлгілерде айтарлықтай айырмашылықтарды анықтады.

Сканерлі электрондық және атомдық-күш микроскопияның деректері $CuBi_2O_4$ бөлшектерінің өсуінің ретке келтіруін (көлемі ≈200 нм) және ерітіндіге полиэтиленгликоль қосылған кезде рельефтің кедір-бұдырлығының 1,5 есе төмендеуін көрсетеді. Микрофотографияда біркелкі өлшемді дөңгелек кристалдардың өсуі байқалады.

Бастапқы ерітіндіге ПЭГ енгізгенде үлгілердің XRD diagram салыстырмалы талдауында kusachiite ($CuBi_2O_4$) кристалдық фазасына сәйкес келетін шыңдар саны мен қарқындылығы көбейетіні байқалады.

Фотоэлектрохимиялық өлшеулердің нәтижелері негізінде электролитке полиэтиленгликольді қосу үлгілердің фотоактивтілігін 2 есеге арттыруға ықпал ететіні анықталды.

Осылайша, фотоэлектрохимиялық түрлендіргіштерде қолдану үшін перспективалы мыс-висмут $CuBi_2O_4$ күрделі оксидті жүйені тұндыру әдістемесі жоғары фотосезімталдығы р-типті поликристалды пленкаларды алуға мүмкіндік береді.

Тірек сөздер: күн энергиясы материалдары, spin coating, $CuBi_2O_4$, полиэтиленгликоль.

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СПОСОБ ИЗГОТОВЛЕНИЯ ТОНКИХ ПЛЕНОК $CuBi_2O_4$ ДЛЯ ФОТОЭЛЕКТРОХИМИЧЕСКИХ ПРИМЕНЕНИЙ

Аннотация. $CuBi_2O_4$ является материалом, который может обеспечить большую плотность фототока и большое перенапряжение процесса фотолиза воды. Он представляет собой смешанный металл-оксидный полупроводник *p*-типа с энергией запрещенной зоны 1,6-1,8 эВ и потенциалом начала фототока около 1 В относительно стандартного водородного электрода.

На сегодняшний день известны различные методы нанесения пленок и, каждому из них присущи определенные преимущества и недостатки. Большинство из этих методов не находит широкого применения из-за сложности, использования высоких температур и низкой воспроизводимости.

В данной работе используется метод spinning coating, который проводится при стандартных лабораторных условиях из водных растворов солей, использует преимущества центрифугирования для равномерного распределения покрытия по поверхности, характеризуется низкой материалоемкостью, позволяет формировать тонкие нанокристаллические слои с заданной толщиной. Полиэтиленгликоль (ПЭГ) используется для улучшения распыления капель раствора по всей поверхности пленки $CuBi_2O_4$, что позволяет осаждать плотные однородные пленки. Полученные тонкие пленки $CuBi_2O_4$ хорошо подходят для фундаментальных исследований фотоэлектрохимических свойств.

Для нанесения пленок использовали электроды, представляющие собой предварительно очищенные оптически прозрачные стеклянные пластины, покрытые слоем фторированного оксида олова (FTO). Положение электрода в горизонтальной плоскости при осаждении обеспечивал специальный держатель, конструкция которого позволила избежать смещения подложки при вращении и исключить влияние положения на равномерность нанесения пленки. Вращение осуществлялось при частоте 500 оборотов в минуту в течение 90 секунд.

Приготовление раствора для нанесения пленок $CuBi_2O_4$ происходило в несколько этапов, включающих смешивание азотных солей меди и висмута с подкислением концентрированной (65%) азотной кислотой, выпаривание и снижение температуры раствора до комнатной. Для экспериментов по осаждению пленок из растворов с содержанием полиэтиленгликоля (ПЭГ), в раствор добавляли 0,25 гр ПЭГ-2000 на каждые 5 мл раствора. Для эффективного перемешивания использовали ультразвуковую ванну. Результаты экспериментов показали, что оптимальный срок использования приготовленного раствора не более суток после приготовления.

В последнюю очередь осуществлялся отжиг пленок в муфельной печи в течение 2 часов при температуре 600 ˚С.

Результаты физико-химических исследований выявили значительные отличия в образцах, изготовленных из электролитов с различным содержанием ПЭГ.

Данные сканирующей электронной и атомно-силовой микроскопии демонстрируют упорядочивание роста частиц $CuBi_2O_4$ (размер ≈200 нм) и снижение в 1,5 раза шероховатостей рельефа при добавлении в раствор полиэтиленгликоля. На микрофотографиях виден рост равноразмерных округлых кристаллитов.

При сравнительном анализе XRD diagram образцов, наблюдается увеличение количества и интенсивности пиков, соответствующих кристаллической фазе Kusachiite ($CuBi_2O_4$) при введении ПЭГ в исходный раствор.

На основании результатов фотоэлектрохимических измерений установлено, что добавление в электролит полиэтиленгликоля способствует увеличению фотоактивности образцов в 2 раза.

Таким образом, разработанная методика осаждения сложнооксидной системы медь-висмут $CuBi_2O_4$ позволяет получать поликристаллические пленки p-типа проводимости с высокой фоточувствительностью, перспективные для использования в фотоэлектрохимических преобразователях.

Ключевые слова: материалы для солнечной энергии, spin coating, $CuBi_2O_4$, полиэтиленгликоль.

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