UDC 620.3
IRSTI 29.19.22

https://doi.org/10.55452/1998-6688-2024-21-1-123-129

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THE EFFECT OF PLASMA SURFACE TREATMENT ON THE STRUCTURE OF THE LEAD SULFIDE FILM

Abstract

In this work, the effect of the substrate surface on the formation of structured lead sulfide films is studied. For this purpose, the surface of single-crystalline silicon (100) was subjected to plasma treatment in a glow discharge in an argon atmosphere, at a working pressure of 1 Pa and a potential difference across the electrodes of 2 kV. Lead sulfide films were obtained on treated and untreated single-crystalline silicon surfaces by chemical deposition from an aqueous solution of lead nitrate, thiourea and sodium hydroxide at a temperature of 70°C for 30 minutes. The surface morphology, elemental composition, and crystal structure were studied by scanning electron microscopy, energy dispersive analysis, and X-ray diffraction, respectively. As a result, the films deposited on pretreated substrates have a distinctly different surface structure compared to films deposited on untreated substrates. Under the same synthesis conditions, the growth of crystals on the treated surface occurred predominantly along certain lines and were grouped into individual particles, while on the untreated surface a continuous film was formed. Thus, through plasma treatment, crystal growth can be controlled to create nanostructures.

Key words: Lead sulfide films, plasma treatment, chemical bath deposition, morphology, elemental composition, structure.

Introduction

PbS thin films are widely used in optoelectronics and sensors as materials for IR detectors, optical switches, efficient solar radiation conversion devices, chemical sensors, temperature sensors, photodetectors that operate in the infrared wavelength range and photoresistors, temperature-sensitive sensors, detectors in the infrared range of the spectrum [1–6]. Lead sulfide, a narrow-band semiconductor, which is the basic thermoelectric materials in the temperature range of 300-950 K and this material is also a promising material in semiconductor optoelectronics for the creation of injection lasers [7–10]. In this group, lead sulfide (PbS), which is a narrow-band semiconductor (≈ 0.41 eV at room temperature), is widely used in many fields, such as Pb^{2+} ion-selective sensors, in micro and optoelectronics, nanotechnology [11–12], in photometric switches [13]. Unlike all other semiconductors, the temperature band gap coefficient in PbS is positive [14]. Of all the currently used methods for producing PbS, the method of chemical precipitation from solutions is of the greatest interest [15]. This method makes it possible to obtain thin films of metal chalcogenides, which provides great opportunities for the synthesis of new compounds. The study of the properties of the obtained films is the main task, since this is the main criterion of the material. Lead sulfide is one of the most promising materials for use in the infrared field. Therefore, the synthesis of semiconductor PbS films from aqueous solutions is of great interest [16–18].

Plasma treatment is a method of modifying the surface of a substrate that uses plasma to affect the structure of vegetation on this substrate. Plasma is an ionized gas consisting of charged particles (ions and electrons) [19]. Plasma treatment can affect the structure of lead sulfide in several ways, for example, by changing the surface of the substrate, the morphology can be changed. Plasma can change the shape and size of lead sulfide particles. This can lead to an increase in the surface area of the material, which can improve its characteristics [20]. Plasma surface treatment can lead to defects in the structure of lead sulfide. These defects can affect its electrical and optical properties [21–22].

Materials and methods

The substrate of monocrystalline silicon (100) was subjected to plasma treatment in a glow discharge in an argon atmosphere for t = 5 minutes at a discharge voltage U = 2 kV and a current strength equal to I = 0.5 mA.

Thin films of lead sulfide were produced by precipitation from an aqueous solution in a chemical bath on silicon substrates purified in alcohol. During the experiment, deionized water was used in solutions. First: Pb $(NO_3)_2$ (lead nitrate) 25 ml 0.18 M (1.525 g), NaOH (sodium hydroxide) 75 ml 0.38 M (1.162 g), the solutions were mixed with a magnetic mixer for 120 minutes in a 150 ml glass. CH_4N_2S (thiourea) 50 ml of 0.11 M (0.398 g) was added to this solution [23]. The formula for the chemical reaction will be as follows:

$$Pb(NO_3)_2 + 2NaOH + CH_4N_2S \longrightarrow H_2O + PbS + CH_4N_2O + 2NaNO_3 \quad (1)$$

Then the silicon substrates cleaned by ultrasound were immersed in a glass in a vertical direction. The temperature of the bath was maintained at 70°C. At the end, the resulting structures were washed with deionized water. The substrate was placed in the solution for 30 minutes, resulting in homogeneous thin films of gray color.

The morphology and elemental composition were studied by electron microscopy and energy dispersive analysis using an FEI Quanta 200i installation.

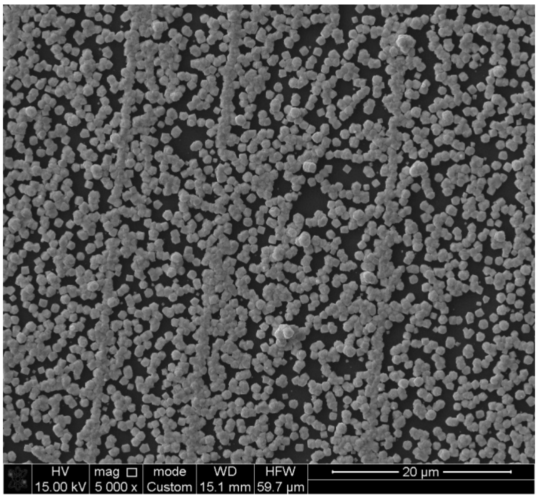
The structure of the resulting films was studied by X-ray diffraction (XRD) using a Rigaku MiniFlex installation. The wavelength corresponds to the excitation of the copper atom on the line. The scanning speed was deg/min, the angles varied in the range of 10° - 90°.

Main provision

It was revealed that preliminary plasma treatment of the substrate surface affects the growth of PbS crystals, that is, it allows preserving the individuality of the particles.

Results and discussion

Figure 1 shows the images of a scanning electron microscope and the elemental composition of the films obtained, 1 (a) – the morphology of the film obtained on the treated surface 1 (b) – the morphology of the film obtained on the untreated surface. 1 (c) and 1 (d) are the corresponding elemental composition of the obtained films



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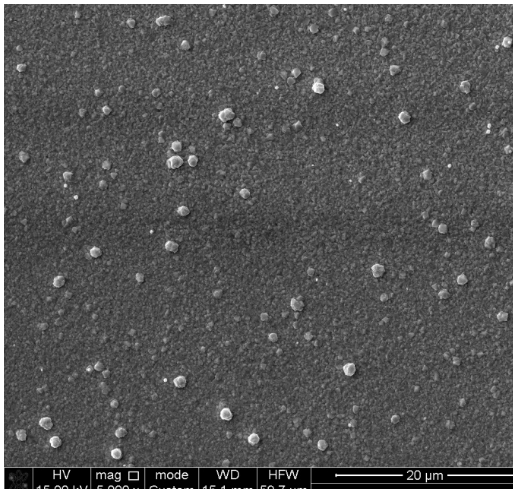

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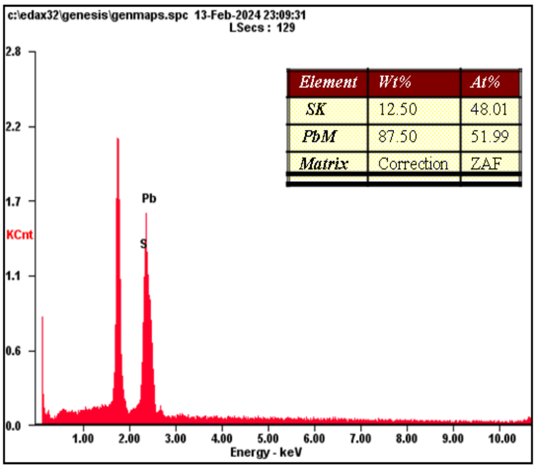

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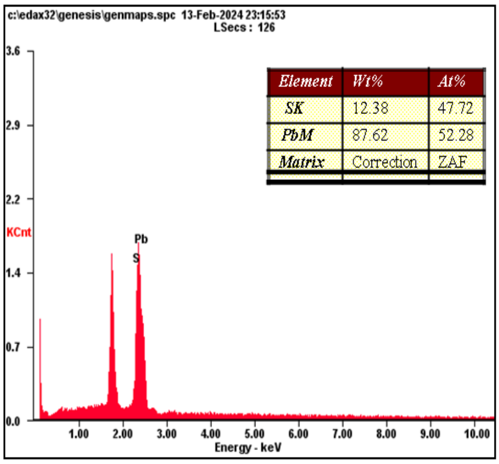

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Figure 1– (a) – morphology structure and (c) – energy-dispersion analysis of PbS obtained on a treated substrate, (b) – morphology structure and (d) – energy-dispersion analysis of PbS obtained on an untreated substrate

Using a scanning electron microscope (SEM), a sample of lead sulfide (PbS) was magnified 5000 times. The accelerating voltage of the electron beam was 15 kV, the beam current was 10 nA, the working distance, i.e. the distance between the electron gun and the sample was 15.1 mm. From the results obtained using a scanning electron microscope, it follows that the plasma-treated surface promotes crystal growth while maintaining the individuality of the particles and mainly along certain lines, while a continuous film is formed on the untreated surface. Figure 1(a) shows the results of a scanning electron microscope (SEM) study of the morphology of lead sulfide (PbS) produced on a plasma-treated surface. The purpose of the study was to study the effect of plasma treatment on the structure and properties of PbS films. It was found that plasma treatment leads to a change in the morphology of PbS films. On a plasma-treated substrate, the PbS film is more uniform and has a smoother surface. The sizes of the resulting particles are approximately uniform and average 500 nm, and also had the shape of cubic crystallites. This texture was found in all studied samples. The texture and morphology of films grown on a silicon surface depends on the time and deposition rate, on the pH level, temperature, but also, as it turns out, on the substrate surface. Preliminary plasma treatment of the substrate apparently leads to an uneven charge distribution on the silicon surface, associated with the crystalline structure of the surface. This helps preserve the individuality of the particles.

To determine the elemental composition of PbS material samples, the energy dispersive spectroscopy (EDS) method with an energy of 20 keV was used. The results of determining the chemical composition and atomic content of the elements Pb and S in the film are presented in the figure. 1(c) and 1(d). The figure clearly shows the presence of Pb and S peaks in the energy dispersive spectroscopy of the samples. Energy dispersive analysis shows that the sample is composed of lead (Pb) and sulfur (S). The Pb/S ratio is 1:1, which corresponds to the stoichiometric composition of lead sulfide (PbS). Based on the data obtained, it can be concluded that the material under study is lead sulfide (PbS). Peaks in the energy-dispersive spectrum correspond to the energy that is emitted by atoms when electrons transition to lower energy levels.

When conducting energy dispersive analysis, it was found that as a result of plasma treatment, the peak corresponding to lead sulfide (PbS) was lower than the peak of the silicon (Si) substrate. At the same time, in the substrate untreated with plasma, the PbS peak was higher than the Si peak. This corresponds to the fact that after treatment the silicon surface had a larger area. In addition, after treatment, a decrease in the atomic fraction of lead by 1 at.% was revealed.

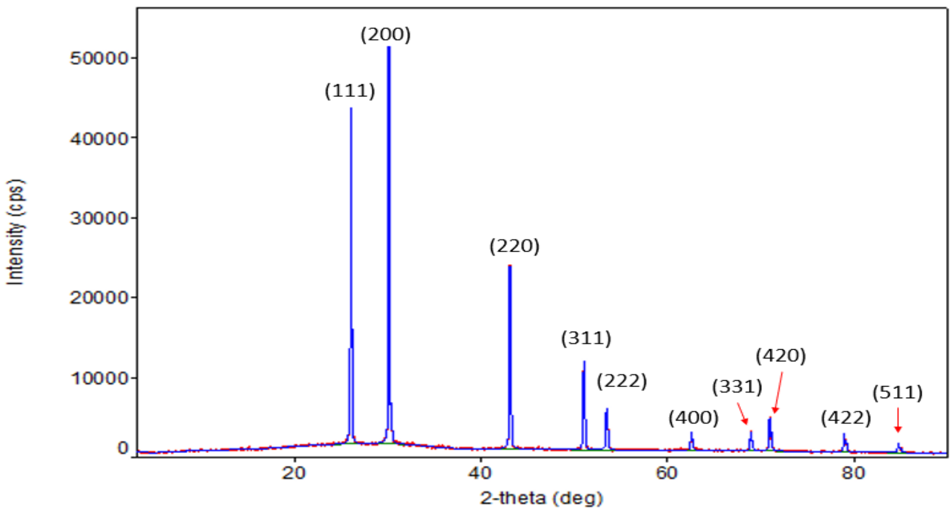

Figure 2 – X-ray diffraction of the PbS film

From X-ray diffraction analysis, peaks corresponding to the plane indices (111), (200), (220), (311), (222), (400), (331), (420), (422) and (511) were identified at angles 2θ 26.10°, 43.22°, 51.20° and 53.62°, respectively. It follows from the diffract gram that the film has a face-centered cubic structure and corresponds to the Fm-3m spatial group. The determination of the lattice parameters is carried out by fulfilling the Bragg's law [24].

$$2d_{hkl}\sin 2\theta = m\lambda \tag{2}$$

Where, d_{hkl} – interplant distance, θ – sliding angle, that is, the angle between the reflecting plane and the incident beam, λ – the wavelength of the X-ray radiation ($\lambda(Cu_{K\alpha})$ = $1{,}5418\ \mathring{A}$) and m – the order of reflection and has a positive integer, for cubic symmetry is determined by:

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \tag{3}$$

Where, a – the lattice constant, h,k,l – plane indexes. The lattice constant was calculated, and it is 5.93 A. The results of X-ray diffraction analysis correspond to world literature data.

Conclusion

In this study, the morphology and elemental composition of PbS films obtained on surfaces pretreated and untreated by plasma were studied using scanning electron microscope (SEM) and energy dispersive spectroscopy. Preliminary plasma treatment of the substrate surface leads to a change in the morphology of PbS films. The PbS film obtained on the treated substrate is more uniform in size and has an average size of 500 nm, as well as a shape in the form of cubic crystallites. Thus, we can conclude that treating the surface of single-crystalline silicon in a glow discharge plasma promotes the growth of crystals on this surface individually and predominantly along certain lines, while a continuous film is formed on the untreated surface. This indicates that crystal growth can be controlled using plasma treatment to create nanostructures.

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ПЛАЗМАЛЫҚ БЕТТІ ӨҢДЕУДІҢ ҚОРҒАСЫН СУЛЬФИДІНІҢ ПЛЕНКА ҚҰРЫЛЫМЫНА ӘСЕРІ

Аңдатпа

Бірегей қасиеттеріне байланысты қорғасын сульфиді (PbS) қазіргі уақытта әлемнің көптеген жетекші зертханаларында зерттелетін материал. Мұндай қасиеттерге құрылымдық модификация арқылы оптикалық және электронды қасиеттер жатады. Бұл жұмыста субстрат бетінің қорғасын сульфидінің құрылымдық пленкаларының түзілуіне әсері зерттеледі. Ол үшін монокристалды кремнийдің (100) беті аргон атмосферасында солғын разрядта, 1 Па жұмыс қысымында және 2 кВ электродтардағы потенциалдар айырмасында плазмалық өңдеуден өтті. Қорғасын сульфидінің пленкалары 30 минут ішінде 70°C температурада қорғасын нитраты, тиомочевина және натрий гидроксидінің сулы ерітіндісінен химиялық тұндыру әдісімен монокристалды кремнийдің өңделген және өңделмеген беттеріне алынды. Сәйкесінше сканерлейтін электронды микроскопия, энергия дисперсиялық талдау және рентгендік құрылымдық талдау әдістерімен беттік морфология, элементтік құрам және кристалдық құрылым зерттелді. Нәтижесінде, алдын-ала өңделген субстраттардағы алынған пленкалар өңделмеген субстраттарға тұндырылған пленкалармен салыстырғанда айқын беткі құрылымға ие. Бірдей синтез жағдайында өңделген беттегі кристалдардың өсуі, негізінен белгілі бір сызықтар бойымен жүрді және жеке бөлшектерге топтастырылды, ал өңделмеген бетте біртұтас пленка пайда болды. Осылайша, наноқұрылымдарды құру үшін плазмалық өңдеу арқылы кристалдардың өсуін бақылауға болады.

Тірек сөздер: қорғасын сульфидінің пленкалары, плазмалық өңдеу, химиялық ваннадағы сулы ерітіндіден тұндыру, морфология, элементтік құрамы, құрылымы.

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ВЛИЯНИЕ ПЛАЗМЕННОЙ ОБРАБОТКИ ПОВЕРХНОСТИ НА СТРУКТУРУ ПЛЕНКИ СУЛЬФИДА СВИНЦА

Аннотация

Благодаря своим уникальным свойствам сульфид свинца (PbS) является материалом, который в настоящее время изучается во многих ведущих лабораториях мира. К таким свойствам можно отнести оптические и электронные свойства за счет структурных модификаций. В данной работе изучается влияние поверхности подложки на формирование структурированных пленок сульфида свинца. Для этого поверхность монокристаллического кремния (100) подвергалась плазменной обработке в тлеющем разряде в атмосфере аргона, при рабочем давлении 1 Па и разности потенциалов на электродах 2 кВ. Пленки сульфида свинца были получены на обработанные и необработанные поверхности монокристаллического кремния методом химического осаждения из водного раствора нитрата свинца, тиомочевины и гидрооксида натрия при температуре 70 °С в течение 30 минут. Были изучены морфология поверхности, элементный состав и кристаллическая структура методами сканирующей электронной микроскопии, энергодисперсионного анализа и рентгеноструктурного анализа соответственно. В результате полученные пленки на предварительно обработанные подложки имеют явную отличительную поверхностную структуру по сравнению с пленками, осажденными на необработанные подложки. При одинаковых условиях синтеза рост кристаллов на обработанной поверхности происходил преимущественно вдоль определенных линий и сгруппированы в отдельные частицы, тогда как на необработанной поверхности формировалась сплошная пленка. Таким образом, путем плазменной обработки можно контролировать рост кристаллов для создания наноструктур.

Ключевые слова: пленки сульфида свинца, плазменная обработка, осаждения из водного раствора в химической ванне, морфология, элементный состав, структура.