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Energy Conservation New and Renewable Energy Sources: Production of Fluorescent Coatings Containing PbS Quantum Dots for Single-Crystal Silicon Photovoltaic Converters

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Abstract: Economical method of sequential adsorption and reaction of ionic layers has been implemented to obtain the fluorescent coatings containing PbS quantum dots with adjustable dimensions and controllable optical properties. The PbS quantum dot manufacturing mode has been identified and it allows forming a photoluminescent coating with a stable face-centered cubic structure of galena, the minimized level of micro and macro-deformations on the surface of single-crystal silicon photovoltaic devices. It was shown that the resulting fluorescent coating is characterized by an intense absorption of light within the spectral range of 300-400 nm. It is experimentally proved that application of PbS quantum dots on the surface of industrial prototypes of single-crystal silicon photovoltaic devices made in China leads to an increase in their coefficient of performance by 0.3% by increasing the short circuit current density by 1 mA $cm^{-2,}$ which is caused by the expansion of the spectral photosensitivity range to shorter wavelengths end up to 300 nm.

Key words: Photovoltaic devices based on single-crystal silicon, photo luminescent coatings from quantum galena dots, optical properties, coefficient of performance, Moscow

INTRODUCTION

Analysis of the literature (Svetlichnyi *et al*., 2013; Huang *et al*., 2013; Shcherbatyuk *et al*., 2010; Gordillo *et al*., 2012) showed that the absorption spectrum of single-and polycrystalline Silicon widely used in Photovoltaic Converters (Si-PVC) is shifted to longer wavelengths compared to the maximum radiation in sunlight ground conditions. Therefore, ultraviolet and blue-green regions of the solar spectrum are underutilized for photovoltaic conversion. The task of expanding the spectral range of Si-PVC photosensitivity is solved by spectrum shift of solar radiation due to the use of light correction reemitting coatings that absorb short wavelengths of the solar spectrum and re-emit it in the long-wave region (Nair *et al*., 2008). Usually, reemitters are polymer plates doped with fluorescent additives, such as fluorescent nanoparticles, or semiconductor Quantum Dots (QDs). The QDs have unique spectral frequency adjustment properties whereby the absorption and emission characteristics of quantum dots are controlled by changing their size.

According to literature data (Gordillo *et al*., 2012; Rowan *et al*., 2008), the most effective fluorescent material with quantum dots in light correction reemitting coatings for Si-PVC is lead sulfide (PbS) due to the fact that the quantum dots of lead sulfide have broad absorption spectra with high absorption coefficients and are characterized by peaks of emission in near infrared region. Upon that, the forbidden bandwidth of PbS is very sensitive to the quantum size effect which manifests itself in ultra-high growth of optical energy absorbtion by PbS QDs in comparison with the massive sulfur sulphide (Semonin *et al*., 2010). Development of economically efficient, Hi-tech methods of chemical production of lead sulfide quantum dots is an essential task for the efficient use of commercially available fluorescent coatings in the construction of silicon photovoltaic converters.

MATERIALS AND METHODS

Experimental technique: We have implemented economically efficient Successive Ionic Layer Adsorption and Reaction Method (SILAR Method) to obtain quantum

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dots (Demchenko *et al*., 2013; Karabulut *et al*., 2014). The main controlled parameters of SILAR deposition method are concentration and composition of the precursor solution, reaction time and bath temperature. Synthesis of thin films by SILAR Method consists of four stages. The first step consists in substrate immersing in a cationic precursor which is a methanol solution of Pb $(NO_3)_2$ (Rajashree *et al*., 2014; Gulen, 2014; Li *et al*., 2013) (Fig. 1a). The second step is to remove from the substrate surface of nonadsorbed cations by washing it with methanol in an ultrasonic bath (Fig. 1b).

The third step comprises immersing the substrate in an anionic precursor in the capacity of which we used alkaline solution (with addition of KOH) of commercially available, cheap and chemically stable chemical reagent of Thiourea (TU) (Gulen, 2014; Li *et al*., 2013). The fourth or last step is re-rinsing the substrate in distilled water using an ultrasonic bath to remove non-adsorbed material from the surface. These four stages are one deposition cycle of SILAR Method. We have used seven SILAR cycles to manufacture each of the nano-sized lead sulfide films. Temperature of a cationic precursor in all experiments was 25°C. Substrate immersion time in each of the precursors was 30 sec. Washing with distilled water was carried out with stirring for 3 sec. Custom samples were dried in a stream of warm air. Table 1 shows the typical modes of obtaining photoluminescent coating on the surface of industrial prototypes of single-crystal Si-PVCs made in China.

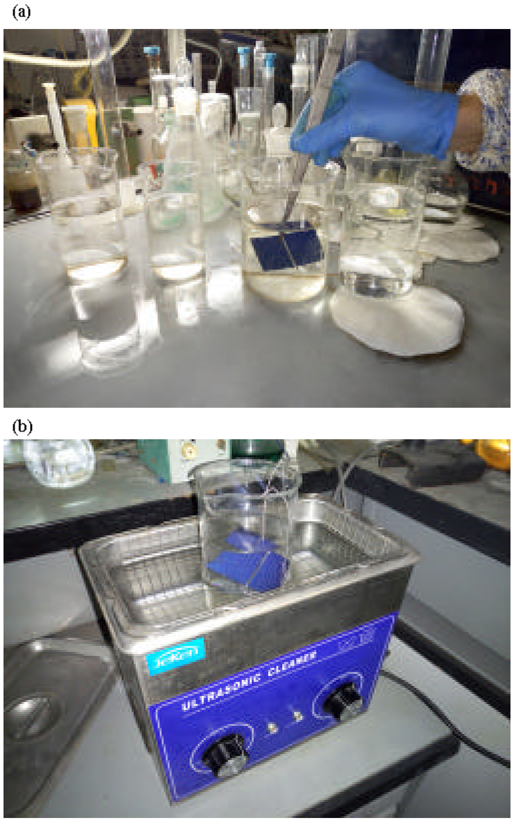

Fig. 1: Synthesis of tin sulfide films using SILAR method

The Si-PVC used have coefficient of performance equal to 18% what corresponds to the average values for the device structures on the market. Modes for manufacturing the lead sulfide films differs by cationic precursor concentration Pb $(NO_3)_2$, concentration of thiourea and KOH concentration in the anion precursor. Coatings were applied on glass substrates K8F to obtain test specimens in the same conditions.

Micro-sized PbS films were also obtained to study the phase composition and crystalline structure of quantum dots in the same solutions on glass substrates by SILAR method. Measurement of X-ray diffractograms of such films was carried out by X-ray device DRON-4M with automatic recording of diffraction spectrum with continuous 2θ-scanning within the range of angles 2θ from 20-75° with Bragg-Brentano focusing (θ-2θ) inside the radiation of the cobalt anode. Goniometer rotation speed was $0.5° \min^{-1}$. Initial processing of the profile of the diffraction peak during X-ray diffractometry analysis included smoothing of the diffraction profile, background discrimination and separation of $K_{\alpha 1}$-component of K_α-doublet.

Determination of the microstrain level (ϵ) and the size of coherent scattering regions (L) was carried out by the physical broadening of the diffraction lines in X-ray diffractograms. In this case, a Cauchy function was used as an approximating function for diffraction peaks.

Researches of a preferred orientation of the films was carried out by the analytical processing of the diffraction peaks by value of a texture coefficient C_i:

Table 1: Modes for manufacturing PbS quantum dots by SILAR method and the forbidden bandwidth E_g for PbS QDs layers

		Solution concentration (M)			
		Anionic precursor			
Sample	Cationic precursor Pb $(NO_3)_2$	TU	KOH	Anionic precursor temperature TU (°C)	E_g (eV)
PbS1(mode 1)	0.26	0.44	0.89	100	3.5
PbS2 (mode 2)	0.14	0.44	0.42	70	3.5
PbS3 (mode 3)	0.10	1.01	0.42	40	4.0

$$C_i = \frac{(I_i / I_{oi} N)}{(\sum_{1}^{N} I_i / I_{oi})} \qquad (1)$$

Where:

I_i = Intensity of the ith-pea

I_{oi} = Intensity of the ith-peak as shown in Table 1 ASTM

N = No. of the diffraction peaks which were determined by phase analysis (reflections which match multiple indices are not taken into account)

Parameter G was calculated proceeding from comparison of the samples by their degree of texture:

$$G = \sqrt{N^{-1}} \sum_{1}^{N} (C_i - 1)^2 \qquad (2)$$

Precise determination of the lattice period was carried out using the extrapolation function $(\cos^2\theta/\sin\theta)+(\cos^2\theta/\theta)$.

Optical properties of PbS films were investigated by spectrophotometer SF-2000 and a reflective add-on unit SFD-2000 by measuring the dependencies for spectral transmittance and diffuse and mirror reflection of layers formed on glass substrates. Forbidden optical bandwidth of the lead sulfide films under study were calculated by the analytical processing of spectral curves.

Study of spectral dependencies of the quantum efficiency coefficients Q (λ) Si-PVC was conducted by the analytical processing of experimental short-circuit current dependencies measured with a smooth change of the incident radiation wavelength with double monochromator DMP-4.

Determination of the short-circuit current density (J_{SC}), open-circuit voltage (U_{xx}), Filling Factor of light CVC (FF) and Coefficient of Performance (COP) of Si-PVCs was carried out by the analytical processing of light current-voltage characteristics measured using a laboratory bench under irradiation of device structures by a solar radiation simulator in ground conditions with the light output of 100 mW cm^{-2}. A halogen 50W lamp connected to a stabilised power supply was used in the capacity of a simulating solar radiation source. Measurement of light CVCs was carried out by applying a potential difference to contact systems with the subsequent registration of the induced current. The applied voltage varied from -0.6 V to 1.0 V in steps of 0.01 V. As a result, the dependence of measuring system output current on applied voltage was formed.

RESULTS AND DISCUSSION

Study of crystalline structure and optical properties of PbS luminescent coatings: Optical properties of nanosized layers formed on glass substrates in different modes (Table 1) were investigated to optimize the physical and technological modes for producing lead sulfide films with SILAR method. Analysis of the optical transmission spectra T (θ) of nanosized PbS films (Fig. 2a) showed that the fluorescent layers which are most transparent in the visible and near-infrared spectrum regions, consist of quantum dots of lead sulfide have been obtained with the implementation of mode 3 which in comparison with other characteristic modes 1 and 2 differ by lowering the cationic precursor concentration to 0.10 M, increasing in thiourea concentration to 1.01 M and lowering the anion precursor temperature to 40°C (Table 1). As shown in the absorption spectra D (λ) = -Lg (T (X), these films had a noticeable light absorption within the spectral range of 300-400 nm (sample PbS3 in Fig. 2b. For layers obtained in modes 1 and 2, there was observed an increase in light absorption in the visible and near-infrared spectral regions (samples PbS1, PbS2 in Fig. 2b) what reduces the photon flux entering Si-PVC if such film coatings are formed on the surface of the specified device structures.

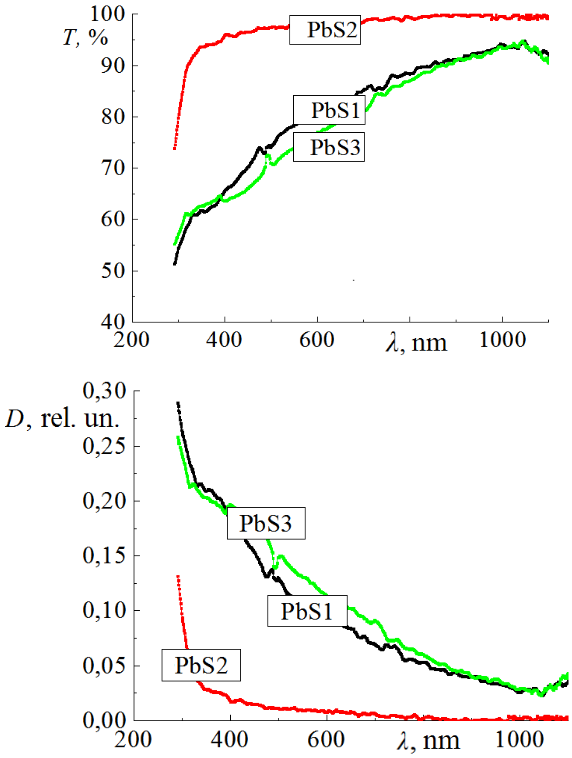

Fig. 2: Optical transmittance spectra T (λ): a) and optical absorption spectra D (λ) = -lg (T (λ)); b) of nanosized fluorescent coatings containing PbS quantum dots

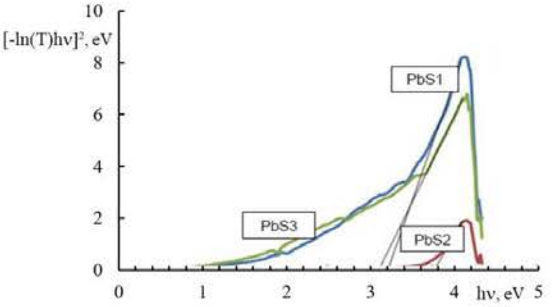

Fig. 3: Determination of the forbidden bandwidth of luminescent coatings containing PbS quantum dots

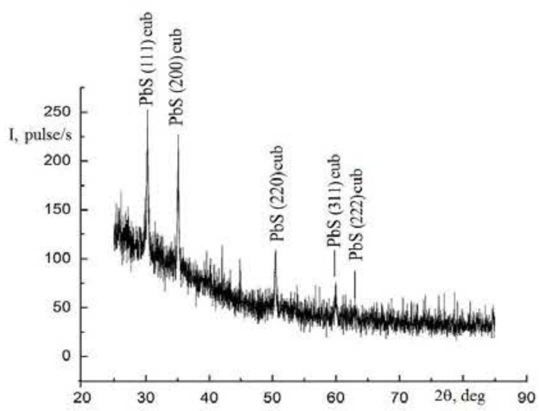

Fig. 4: The typical X-ray diffractogram of micro films PbS manufactured with SILAR method

The analysis of the optical spectra in coordinates (-ln (T) hν)^2 as a function of photon energy hν has shown (Fig. 3) that lead sulfide nano-sized films exhibit optical properties characteristic for direct-gap semiconductors.

It was found that the forbidden bandwidth E_g of nanosized PbS layers depending on the mode of manufacturing varies from 3.5-4.0 eV (Fig. 4, Table 1). The dependence of the forbidden bandwidth of PbS quantum dots on the composition of the cationic and anionic precursor and the temperature of the anionic precursor as well as high values of E_g are evidences of the quantum size effect. Thus, the developed recipe of PbS quantum dots manufacturing by SILAR Method allows control for their size and, consequently, their optical properties.

Micro-sized PbS film with a thickness of 0.3 μ were obtained for the study of the phase composition and crystalline structure of fluorescent coatings on the basis of lead sulfide in the same solutions with SILAR method on glass substrates. A typical X-ray diffractogram of a PbS film obtained in mode 3 is shown in Fig. 5.

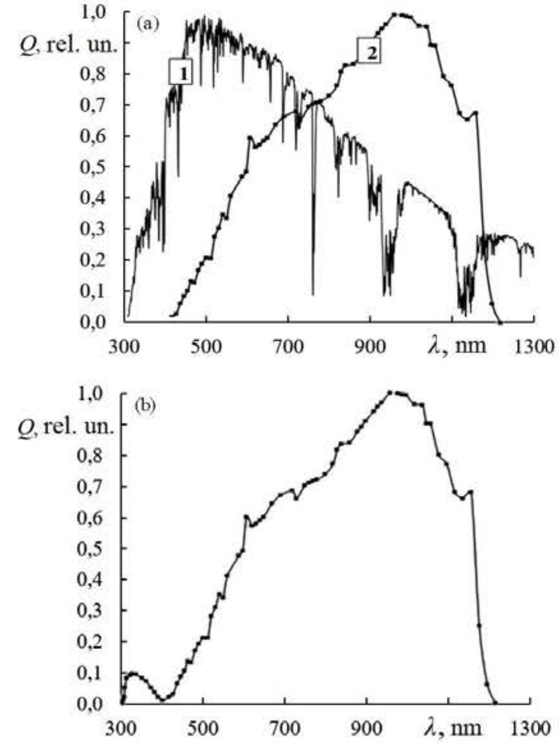

Fig. 5: Effect of a luminescent coating comprising PbS quantum dots on Si-PVC photosensitivity: a) Dependence of the quantum efficiency Q and the wavelength for Si-photovoltaic converters (2) and the spectral distribution of solar radiation in the AM mode 1.5 (1); b) Dependence of the quantum efficiency Q on a wavelength for Si-PVC after application on its surface of the luminescent coatings comprising PbS quantum dots

Phase analysis of lead sulfide films was conducted by position of the diffraction peaks and their intensity. X-ray diffractometry phase analysis showed that the film obtained under the modes described in Table 1 are single phase and have a face-centered cubic galena (PbS) structure (JCPDS, No. 5-0592). It was shown that the films deposited at a temperature of anionic precursor 100°C are oriented in the direction [200] (Table 2).

Upon transition from mode 1 and 2, the preferred orientation direction is not changed and the degree of preferred orientation decreases from G = 2.4-2.0. Upon transition to the mode 3 change in the direction of preferential orientation from the direction [200] to the direction [111] is observed (Table 2).

Research of influence of manufacturing modes on the parameters of the cadmium sulfide films crystalline structure showed that transition from mode 1 to mode 2 and then to mode 3 leads to a monotonic decrease in the

Table 2: The results of X-ray diffractometry analysis of micro-sized PbS films

Modes of obtaining	Preferential orientation direction	Relative units (G)	α (nm)	L (nm)	Relative units (ε)
1	200	2.4	0.59396	140	3.8×10^{-4}
2	200	2.0	0.59396	60	2.2×10^{-4}
3	111	1.4	0.59394	40	1.4×10^{-4}

size of coherent scattering region from L = 140-60 nm. Upon that, a monotonic decrease in the level of microstrains from $3.8\text{-}1.4\times10^{-4}$ is observed. It has been found that the value of the lattice period of films at the transition from mode 1 and 2 is not changed and the transition to mode 3 leads to decrease in the lattice period from 0.59396-0.59394 nm (Table 2). Since, the reference value of the lattice period is 0.59395 nm, this means that tensile macrostresses change to compressive ones upon decrease in anionic precursor temperature.

The comparison of carried out structural researches of micro-sized layers of lead sulfide and optical properties of PbS nanosized films obtained under the same conditions and differ only in the number of cycles of dipping a substrate, allowed mode 3 to select as an optimum. This is because nano-sized films obtained in this mode have a maximum coefficient of transparency in the visible and near infrared range (Fig. 2a, PbS sample, 3). Upon that, micro-sized films of lead sulfide obtained in mode 3 have a preferred orientation optimum [111]. This direction corresponds to the most close packed plane (111) that produces an intense photoluminescence. Availability of photoluminescence indirectly confirmed a noticeable absorption of light in the spectral range of 300-400 nm by nanosized films PbS3. It is necessary also to note insignificant level of PbS3 micro film macrodeformation evaluated by deviation of the experimental values of lattice constant from the table values and promoting film adhesion to the substrate what is a significant technological advantage. PbS3 micro films are also characterized by a minimum level of microstrain what indicates the low concentration of structural defects in the films that reduce the efficiency of photoluminescence.

Research of the influence of fluorescent coatings containing PbS quantum dots on the spectral photosensitivity and efficiency of single-crystal silicon photovoltaic converters: Researches of spectral dependence of the quantum efficiency factor for industrial prototypes of single-crystal silicon photovoltaic converters made in China have showed that the spectral range of their photosensitivity is in the range from 420-1200 nm (Fig. 5a). Comparison of the spectral range of photosensitivity for Si-photovoltaic converters and the spectral distribution of solar radiation intensity in the ground conditions (mode AM 1.5) shows that a substantial part of the solar spectrum is concentrated within the spectral range of 300-400 nm that is not converted by the photovoltaic converter (Fig. 5a).

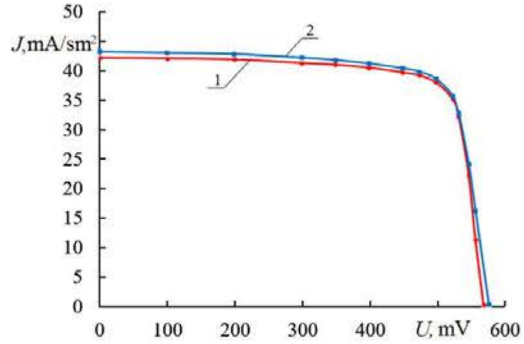

Fig. 6: Current-voltage characteristic of Si-PVC with AM 1.5 mode lighting before (1) and after (2) applying to its surface of luminescent coatings comprising PbS quantum dots

It has been experimentally shown that application of a luminescent coating on a photovoltaic converter surface in mode 3 leads to appearance of photosensitivity within the range of 300-400 nm (Fig. 5b) that corresponds to the additional absorption region of a lead sulfide nanosized film formed on a glass substrate (Fig. 2b, sample PbS3) without reducing photosensitivity in the spectral range [420-1200] nm.

Researches of spectral photosensitivity were supplemented by experimental studies of light CVC of PVC before and after application of a luminescent coating in mode 2 (Fig. 6).

Analytical processing of light VAC data showed that applying a luminescent coating increases the coefficient of performance from 18.4-18.7% what is primarily caused by an increase in short circuit current density of $J_{sec} = 42\text{-}43$ mA cm^{-2}. At the same time, the open circuit voltage was increased slightly from $U_{xx} = 572\text{-}580$ mV and the fill factor of the light CVC did not change and amounted to FF = 0.76.

CONCLUSION

The economic method of sequential ion layer adsorption and reaction has been implemented (SILAR Method) using inexpensive, available and chemically stable components for obtaining PbS quantum dots with adjustable size and optical properties on the surface of single-crystal silicon photovoltaic converters.

By comparison of structural studies data of micro-sized lead sulfide layers and the optical properties of the nanosized PbS films obtained under the same conditions on the glass substrates and differing only in the number of substrate dipping cycles, we have shown that the optimum concentration of the cationic Precursor $(PbNO_3)_2$ makes 0.10 M, the concentration of thiourea makes 1.01 M and KOH concentration is 0.42 M and the anionic precursor temperature is 40°C

It was found that the application in this mode of nanosized luminescent coatings containing quantum dots of lead sulfide on the surface of industrial prototypes of single-crystal silicon photovoltaic converters made in China shifts the short-wave boundary of their photosensitivity from 420-300 nm what can increase coefficient of performance by 0.3% due to increasing in the short circuit current density by 1 mA cm^{-2}.

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