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Quantum size effect in cadmium sulphide films after plasma treatment

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Abstract. In this work, the optical properties of nanocrystalline CdS films in the initial state and after ion-plasma treatment have been studied. The chemical bath deposition technique was used to prepare CdS films with thickness 80–115 nm on glass substrates. The ion-plasma treatment was carried out in argon plasma in a high-density low-pressure radio frequency inductively coupled plasma reactor at an argon ion energy of 25 eV for 30–50 s. It has been established that ion-plasma treatment leads to a decrease in film thickness by 10–15% of the initial one and the formation of new nanostructures on its surface. The results showed that the sizes of coherent scattering regions during plasma treatment decreased for a series of studied samples from 8.2–10.0 nm to 6.3–7.7 nm. This led to an increase in the band gap energy of the for nanocrystalline CdS films from 2.53–2.78 eV to 2.95–3.11 eV.

Keywords: cadmium sulphide, thin films, chemical bath deposition, plasma treatment, transmission spectra, band gap energy

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Квантовый размерный эффект в пленках сульфида кадмия после плазменной обработки

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Аннотация. В данной работе исследовано влияние плазменной обработки на оптические свойства нанокристаллических пленок CdS толщиной 80–115 нм, полученных на стеклянных подложках методом осаждения из химической ванны. Результаты показали, что плазменная обработка пленок CdS при 25 эВ в течение 30–50 с приводит к увеличению оптической ширины запрещенной зоны с 2,53–2,78 эВ до 2,95–3,11 эВ. Такое увеличение значений ширины запрещенной зоны пленок связано с уменьшением размеров областей когерентного рассеяния (размера кристаллитов) с 8,2–10,0 нм до 6,3–7,7 нм.

Ключевые слова: сульфид кадмия, тонкие пленки, химическое осаждение в ванне, плазменная обработка, спектры пропускания, энергия запрещенной зоны

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Introduction

Cadmium sulphide (CdS) is an important semiconductor of II-VI group with a band gap of 2.42 eV for the hexagonal modification, which has potential application in nanoelectronic and optoelectronic systems, in particular thin-film solar cells and photocathodes. Today, improving the efficiency of thin-film solar cells and photocathodes is a current research problem.

In solar cells, films of CdS are used as a buffer layer between the transparent conductive oxide (ZnO) and the light-absorbing layer to improve their interface. The buffer layer should have minimal absorption losses, low surface recombination, and minimal electrical resistance during the transport of photogenerated carriers. The CdS films is the most preferred among the known materials, but it has optical absorption losses, especially in the shortwave range. As noted in the literature, the photogeneration of charge carriers can be maximized using buffer materials with minimal recombination losses by a wider extension of the space charge region in the absorbing layer [1]. Therefore, the development of methods for controlling surface properties is of absolute relevance. And, an actual direction of CdS research in recent years is the formation and study of nanostructured materials with controllable properties. One of the effective methods of nanostructuring is the method of ion-plasma treatment [2]. Its effect is generally due to both the introduction of impurity atoms and various processes associated with the action of an ion beam (ion etching, ion-stimulated diffusion, the formation of disordered regions due to the accumulation of point defects, etc.). For example in [3], it was shown that oxygen plasma treatment of CdS allows to reduce parasitic absorption of the device and leads to an increase in the short-circuit current density of $Sb_2(S,Se)_3$ solar cells. It was found that Ar-plasma treatment of thermally evaporated In_2S_3 thin films, which are also used as a buffer layer in solar cells, leads to the formation of an array of metallic indium nanostructures on their surface and an increase in optical absorption, but the band gap width decreases by 0.21 eV [4]. Such metallic nanostructures on the semiconductor surface can form a Schottky barrier, which acts as an electron trap and, accordingly, can effectively prevent the recombination of photo-generated electron-hole pairs [4]. In [5] showed that the electrochemically deposited CdS films after cold plasma-surface modification change their surface from hydrophobic to hydrophilic, and have a

long average lifetime with a rapid reduction time constant, indicating a high quality films with low trap density. In [6], in order to improve the photovoltaic characteristics of Sb_2Se_3 films for application as photocathodes for H_2 generation via solar-driven water splitting, an approach to plasma treatment of N_2 and ambient air was developed. After plasma treatment, the surface of Sb_2Se_3 films also changed from hydrophobic to hydrophilic, which provided a significant increase in photocurrent density by 3-fold compared to the untreated film and improved H_2 generation via light-driven water splitting. Thus, plasma treatment can be an effective way to form an intrinsic nanostructure for chalcogenide materials.

The aim of this work was to study the effect of ion plasma treatment on the optical characteristics of CdS films obtained by chemical bath deposition for further modification of the physical properties of various devices based on this material.

Materials and Methods

In our experiments the chemical bath deposition (CBD) technique was used to prepare CdS thin films (80–115 nm). The resulting solution in the bath used for CdS preparation, composed of 90 ml deionized water, 30 ml NH_4OH (wt 25%), 40 ml 0.0096M $CdSO_4$ as a source of cadmium and 40 ml 0.8M $CS(NH_2)_2$ as a source of sulphide [7]. The deposition is performed at a bath temperature of 50–70 °C for 5–20 min onto pre-cleaned glass substrates. The ion-plasma treatment was carried out in Ar plasma in a high-density low-pressure radio frequency inductively coupled plasma reactor at an Ar ion energy of 25 eV for 30–50 s [8]. The elemental composition was obtained using energy-dispersive X-ray spectroscopy (EDS) on AZtecLive Advanced with Ultim Max 40 (Oxford Instruments). The structural properties of films were studied by using Ultima IV X-ray diffractometer (Rigaku) in grazing incidence X-ray diffraction geometry at 1 degree with CuK_α radiation source (λ = 1.5418 Å). Morphological of films was analyzed using an H-800 scanning electron micro-scope (SEM, Hitachi) with a resolution of 0.2 nm. The transmission and reflection spectra of the films were obtained using Photon RT (Essent Optics) spectrophotometer with spectral resolution better than 4 nm using unpolarized light at room temperature.

Results and Discussion

The elemental composition of the deposited CdS films on glass substrate is sulphur 42.5–50.0 at.% and cadmium 50.0–57.5 at.%. It did not change after ion-plasma treatment.

Figure 1 shows typical the X-ray diffraction patterns of the synthesized CdS films in initial state and after plasma treatment. The three peaks observed in the XRD pattern of the deposited CdS films: a strong reflection at (111) and two minor peaks at (220) and (311), correspond to a cubic structure of the space group $F\bar{4}3m$ according to the Powder Diffraction File for CdS (PDF no. 75-1546). The cubic crystal structure of the synthesized CdS films is retained after plasma treatment no matter of its duration (30–50 s) at an ion energy of 25 eV. Moreover, for the plasma-treated films, no additional diffraction peaks concerning the formation of secondary phases or the hexagonal phase of CdS have been identified. It is known that the most common phase of the bulk CdS crystal is the hexagonal structure, while the cubic phase of CdS is metastable and appears in low-dimensional structures [9]. This indicates the nanocrystalline nature of the CdS

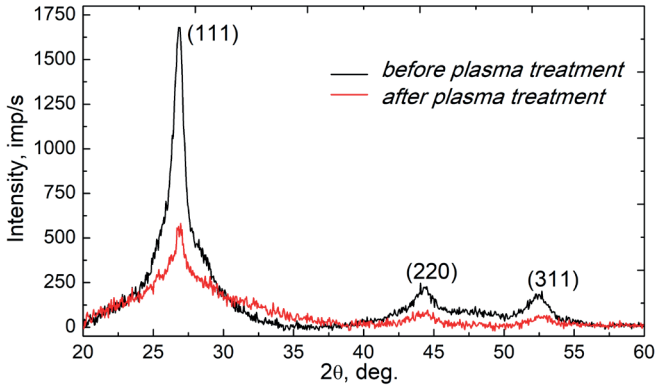

Fig. 1. Typical X-ray diffraction patterns of the CdS film before and after plasma treatment

thin films in the initial state and after ion bombardment. The presence of a broad diffraction peaks is probably due to small grain size and/or a thin layer of CdS presenting a broad noisy background [9].

After plasma treatment of CdS films, the intensity of all peaks on the X-ray pattern is significantly reduced, while the predominant orientation still remains in the direction of the (111) plane (Fig. 1). The Full Width at Half Maximum values of the main diffraction peak for the deposited films are about 1.9, which increases to ~5.4 after plasma treatment. At the same time, a shift of the main diffraction peak towards higher diffraction angle values (0.19°) compared to that of the untreated films and a slightly decrease in the interplanar spacing from 0.334 to 0.331 nm according to the Bragg's equation ($2d_{hkl} \sin\theta = \lambda$) are observed. The calculated value of the interplanar spacing for the deposited films is less than the theoretical value (d = 0.33601 nm, PDF no. 75-1546), indicating the appearance of compressive strain in the crystal lattice, which increases after ion bombardment of films. It is the explanation for the decrease in intensity, broadening and shift of the diffraction peaks in the X-ray pattern for the plasma-treated films. An average size of coherent scattering regions (crystallite sizes), calculated using the Scherrer equation, decreased from 8.2–10.0 nm to 6.3–7.7 nm during plasma treatment for a series of studied CdS films.

It was found that ion-plasma treatment leads to modification of morphology of nanocrystalline CdS films (Fig. 2).

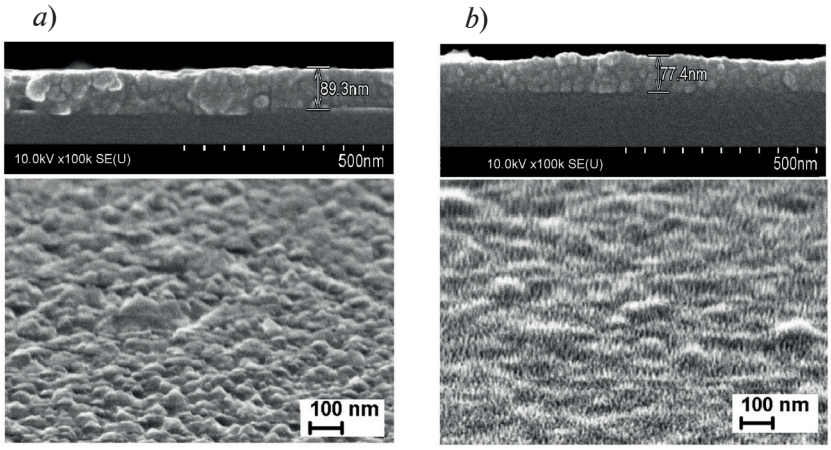

Fig. 2. Typical SEM top view and cross-sectional image of CdS thin film before (*a*) and after plasma treatment (*b*)

In the process of ion sputtering, a decrease in the film thickness by 10–15% of the initial one and the appearance of new nanostructures on their surface are observed. It is the result of the etching in plasma. As an example, the cross-section SEM images of CdS films shown in Fig. 2 demonstrate the reduction in film thickness after plasma treatment, and it is also seen that the cadmium sulphide layer becomes denser with smaller crystals. The surface of the initial deposited films is a collection of spherical CdS nanoparticles with sizes ranging from 30 to 100 nm (Fig. 2, *a*). Whereas ion-plasma treatment leads to nanostructuring of the surface in the form of formation of a homogeneous ensemble of vertical nanorods up to 20–30 nm high with lateral dimensions at the base of less than 15 nm (Fig. 2, *b*), the surface density of which is about $2 \cdot 10^{11}$ cm^{-2}.

Changing the structural parameters and morphology of the CdS films leads to a change in their optical properties, which is shown on the example of one of the samples in Fig. 3. The presented optical spectra show that plasma treatment of the films results in a slight increase in transmission and, accordingly, a decrease in reflection (Fig. 3, *a*). All CdS films before and after plasma treatment were characterized by a sloping fundamental absorption edge, which shifts to high energies (smallest wavelength) as a result of ion bombardment.

Based on the analysis of the transmission and reflection spectra, the values of the band gap energy (E_g) were determined (Fig. 3, *b*). The obtained value of E_g = 2.53–2.78 eV for deposited CdS films differs from the reported values for the hexagonal (2.42 eV) and cubic (2.34–2.58 eV)

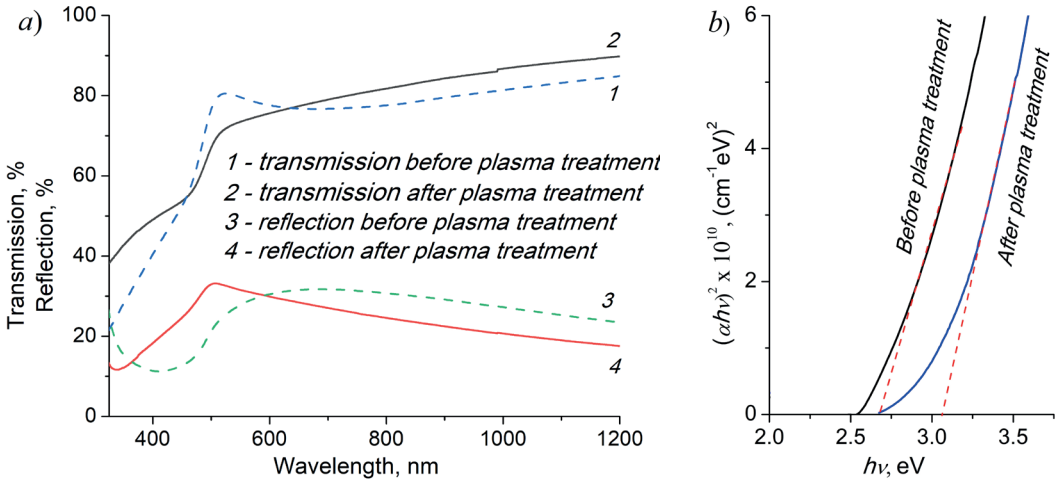

Fig. 3. Reflection and transmission spectra for CdS film before and after plasma treatment (*a*). Tauc plots and band gap values evaluation for as prepared and after plasma treatment CdS (*b*)

phases of CdS [7,9]. An increase in the E_g from 2.53–2.78 to 2.95–3.11 eV was observed for all samples after ion-plasma treatment. An increase in E_g as a result of plasma treatment is due to the manifestation of the quantum-size effect (the quantum confinement of carriers inside the grains) [10, 11]. For example, Cortes et al. report a clear increase in the band gap with decreasing grain size in CdS films, which is associated with quantum confinement and confirm by calculations of an inverse square dependence of the shifting band gap energy with grain sizes [9]. In our case, as noted above, during the ion bombardment of the CdS films, the grain sizes decrease and new nanostructures are formed on the surface of films in the form of ensembles of nanorods, smaller in size compared to the nanocrystals before plasma treatment. For example, such an increase in the optical band gap of the CdS films is useful for thin-films solar cells, where it is used as a buffer layer. An increasing the band gap energy of CdS minimizes optical absorption losses in the buffer layer, especially in the shortwave range. This will lead to increased current generation at lower wavelengths and, accordingly, can improve the efficiency of solar cells [12].

Conclusion

The results of this work showed that ion-plasma treatment of nanocrystalline films of cadmium sulphide with 80–115 nm thickness promotes the formation of nanostructures of smaller sizes, which provides an increase in the band gap energy due to the realization of quantum size effects. The report compares the obtained data with literature data and analyzes the physical reasons for the changes in the structural parameters of films during ion-plasma treatment.

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