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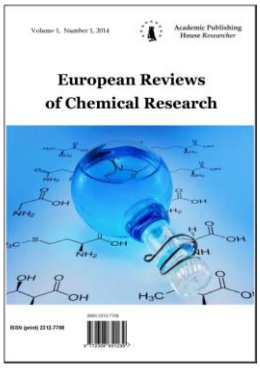

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Thermal Activation of Iodine-Containing PbSe thin Films

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Abstract

Influence of iodine addition on elemental composition, structure and surface morphology on lead selenide thin films prepared by chemical bath deposition method was studied by methods of X-ray diffraction analysis and scanning electron microscopy with elemental energy-dispersive analysis. Content of iodine in thin films raised to 4.25 at.% with increasing concentration of ammonium iodide in bath solution. Influence of anneal on structure and crystallite size of lead selenide thin films was found.

Keywords: chemical bath deposition, thin films, lead selenide, iodine doping, annealing, thermal activation, X-ray diffraction, scanning electron microscopy, doping, semiconductors

Introduction

Thin films based on lead chalcogenide are one of the most promising semiconductor material. Lead chalcogenides have high photovoltaic properties in spectral range from 2.0 to 5.0 micrometer, due to they have been found wide applications in photodetector [1].

Both physical and chemical methods of deposition have been used for prepare lead chalcogenide. Thermal evaporation technique [1-4] and chemical bath deposition [1, 5-7] are the most popular method which permit to obtain polycrystalline materials providing a different structure and physical properties. The chemical bath deposition method is low-cost processes and the films are of comparable quality to those obtained by more complicated and expensive physical deposition processes. It can be used for preparation of high-quality lead chalcogenide films with control of the deposition parameters such as stirring period, reaction time, bath temperature, solution pH, and added impurities.

As-deposited thin films also don't have photosensitivity because they are subject to high-temperature annealing in an oxygen atmosphere. Changing the conditions of thermal activation, it can also affect the photovoltaic properties of materials [8]. Alloy addition may occur both during the synthesis of the films and during annealing. Iodine-containing additions use in the chemical deposition of thin films because the iodine provides with high sensitive to IR radiation [2, 3, 5, 6].

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It was found that iodine stimulates physical-chemical processes conductive improvement of photosensitivity.

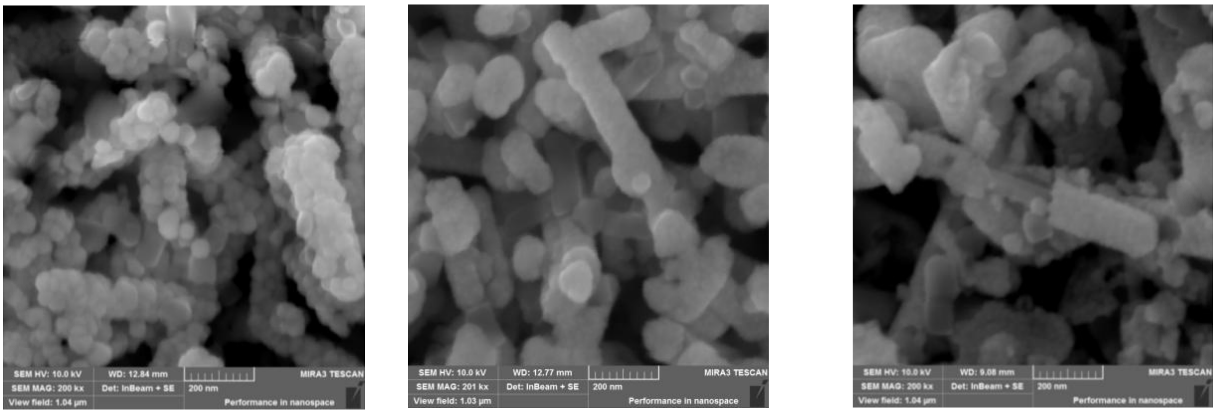
In the present study we investigated thermal activation of iodine-containing PbSe thin films on composition, morphology and structure.

Materials and methods

PeSe thin films were prepared by means of chemical bath deposition technique. The glassceramics substrate were previously cleaned. Bath solution contained lead acetate $Pb(CH_3COO)_2$, selenourea $CSe(NH_2)_2$, ammonium hydroxide NH_4OH, and ammonium iodine NH_4I as s dopant. The reaction temperature was fixed 353 K. The films were annealed at 513-548 K. The film thickness was measured by means of interference microscopy on microinterferometer Linnika MII-4M. The surface morphology and elemental composition of films were characterized by scanning electron microscopy with elemental energy-dispersive analysis (EDX) using SEM JEOL JSM–5900LV. The structure of the films was analyzed by X-ray diffraction using DRON-UM1 using Cu Kα radiation. X-ray diffraction patterns were recorded in the range 2θ from 20 to 75°.

Discussion

The SEM images of as-deposited PbSe thin films prepared by chemical bath deposition are shown in Fig. 1.



a *b* *c*

Fig. 1. SEM images of as-deposited undoped PbSe thin films (a) and doped PbSe(I) prepared from solution containing NH_4I mol/L: 0.05 (b); 0.20 (c).

As shown in Fig. 1 PbSe thin films are not compact. Their crystallite are randomly arranged on the surface. The crystallite size of undoped films (Fig. 1a) is about 1 mkm in length and it consists of nanoparticles with average size 42 nm. The structure of films is disordered. The crystalline particles of films prepared from solution with concentration of NH_4I 0.05 mol/l (Fig. 1b) are degraded and decreased to 0.5 mkm. The polygonized crystal of films is almost destroyed by addition on bath 0.20 mol/l of NH_4I (Fig. 1c). The average size of nanoparticles decreases to 23 nm. The crystallite size decreases due to spontaneous formation a large number of nucleation center [5]. Therefore synthesis in the early stages of grow represents bulk crystallization. Iodine is sorbed on crystal face and blocks crystal grow. Injection of ammonium iodine in bath solution changes not only morphology thin films but also thickness of forming layer.

Dependence of thickness of lead selenide thin films from concentration of ammonium iodide is shown in Fig. 2. Thickness of PbSe films decreases twice with increasing of content of NH_4I to 0.20 mol/l by comparison with undoped samples. This could be due to decreasing of content of lead in reacting system by formation of complex with I-ions and PbOHI slightly soluble subsalt [3].

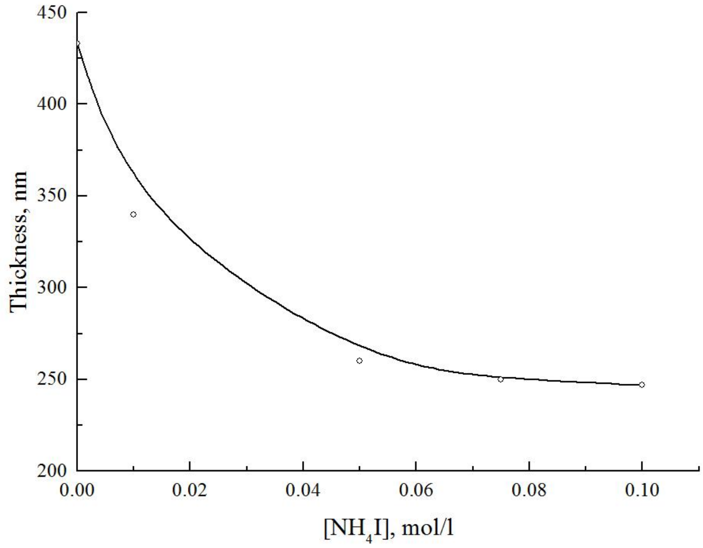
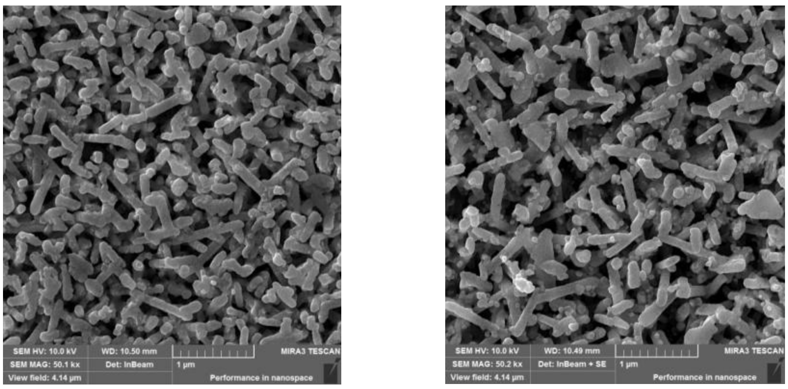


Fig. 2. Dependence of thickness of PbSe thin films from content ammonium iodide at 353 K.

Stoichiometry of undoped and doped PbSe films was found by elemental energy-dispersive analysis. The ratio of lead and selenium is 1:1 at undoped films. Content of iodine in films monotonic increases to 4.25 at % with increasing of ammonium iodine in bath solution to 0.20 mol/l and content of selenium decreases. This occurs because iodine enters into the composition as insoluble PbI_2.

The annealing of lead selenide thin films was carried out in quasi-closed volume air. Preliminary experiments have shown that we have obtained samples do not withstand temperatures above 573 K. Therefore, thermal sensitization films of lead selenide were carried out in a temperature range of 503-548 K.

Fig. 3 demonstrates the SEM images of annealing films of PbSe. The surface of PbSe was transformed in more defect structure. Increase annealing temperature result in more damage surface. The film, which was synthesized from a less concentrated on the dopant in solution, is more uniform and evenly distributed over substrate. The crystallite length of annealing films decreases to 0.5 mkm (Fig. 3c) and 0.7 mkm (Fig. 3d).



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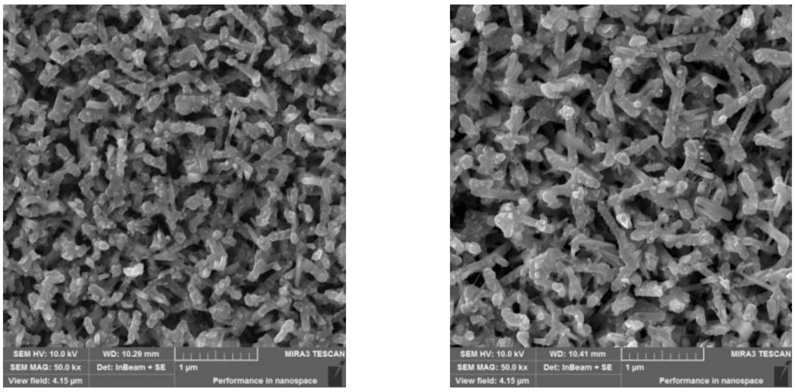
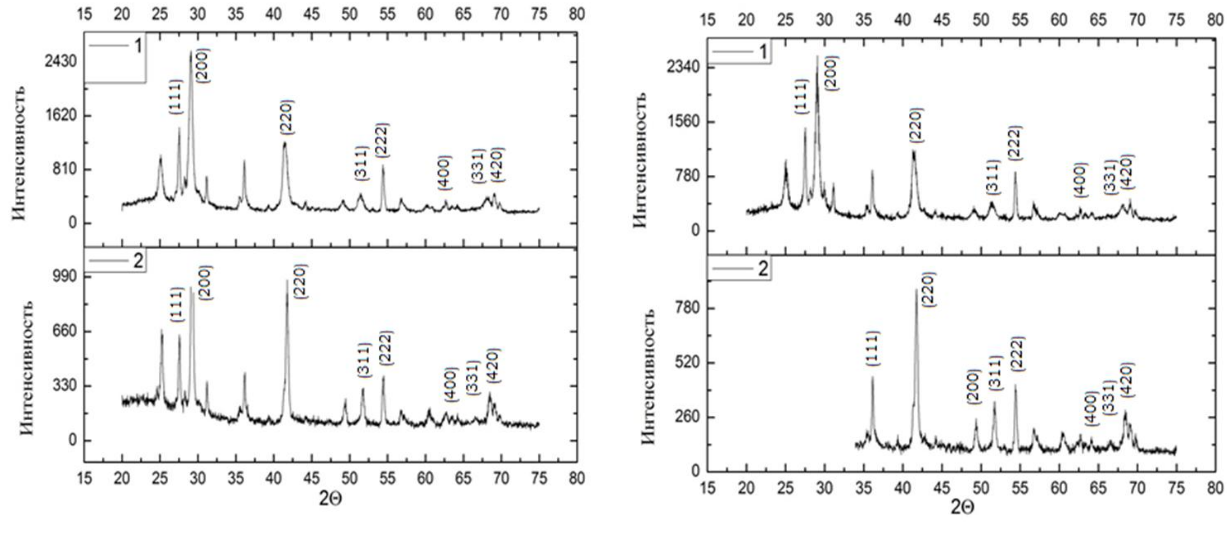


c *d*

Fig. 3. SEM images of annealing PbSe thin films prepared from solution containing NH_4I mol/L: 0.05 (a, b); 0.20 (c, d). Temperature of thermoactivation: 513 K (a, c) and 538 K (b, d).

The XRD patterns of as-deposited and annealing PbSe thin films are shown in Fig. 4. The reflection peaks of PbSe phase were observed for all samples that is to say all films are one-phase. The peaks of XRD patterns of PbSe correspond to cubic lattice NaCl (B1, Fm-3m) in accordance with the standard card PDF Card No. 03-065-0133. The peaks of glassceramics substrate were observed (PDF Card No. 01-071-4513). Another phase are not observed. Annealing samples are more crystalline then as-deposited films.

The introduction of iodine in the film does not lead to a drastic change in the preferred orientation of micro-crystallites PbSe. Growth of crystallites along [200] direction is predominant iodine-doped films. At the same time the preferred growth orientation in the iodine-doped PbSe films changed to [220] with increasing of content of iodine. Change of texture is concerned with saturation of PbSe film by iodine prevented the growth along [200] direction, and the maximum concentration of ammonium iodine leads to destruction of polygonized crystal.



a *b*

Fig. 4. XRD pattern of annealing PbSe thin films at 513 K (1) and as-deposited films (2). Content of NH_4I in reactor mixture is: 0.05 M (a) and 0.2 M (b).

Conclusion

We have successfully deposited PbSe thin films by using the CBD method. Addition of ammonium iodide in bath solution for chemical bath deposition of PbSe thin films influence deeply on their thickness and microstructure. Thermal sensitization of lead selenide films was carried out at 503-548 K. Annealing films have more uniform surface then as-deposited. Increase of concentration of ammonium iodide in bath solution to 0.20 mol/L lead to gradual variation preferred orientation of PbSe from [200] to [220].

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