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Interaction of PbCsBr_3 with solutions of the dimethyl sulfoxide – ethyl acetate system

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The process of chemical-dynamic polishing of the surface of metal-halide perovskite PbCsBr_3 by etchants based on solutions of the dimethyl sulfoxide – ethyl acetate (DMSO-EA) system has been studied. The dependences of the perovskite dissolution rates on the content of ethyl acetate in the etchant solution were investigated. The qualitative characteristics of the surface, obtained as a result of etching, were analyzed by optical microscopy. It has been established that the process of dissolution of PbCsBr_3 in the DMSO-EA etching solution is carried out by the diffusion mechanism. On the basis of the obtained results, the compositions of etching solutions and technological modes of chemical-dynamic polishing of PbCsBr_3 single crystals were optimized. The ethyl acetate-modified etching solutions are promising for use in the technology of perovskite materials when the main goal is to slowly remove the surface layer of the semiconductor and obtain a high-quality, structurally perfect surface.

Keywords: perovskite, surface, etching rate, chemical-dynamic polishing, dimethyl sulfoxide, ethyl acetate, solution.

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Introduction

The results of scientific research in the field of optoelectronics show that perovskite materials are characterized by many properties necessary for this field: high thermal stability, good photovoltaic properties, and low cost [1-3]. Perovskites of various chemical designs (inorganic, hybrid (organic-inorganic)) are widely used in optoelectronic devices such as solar cells, light-emitting devices, radiation and photodetectors, etc. [4, 5].

It is noted that inorganic metal-halide perovskites (MHPs) exhibit higher chemical resistance compared to hybrid organic-inorganic perovskites. This can obviously be explained by the strengthening of chemical bonds between the particles of the MHPs crystal structure compared to the weaker chemical interaction of organic components in hybrid perovskites. Nevertheless, many recent studies have shown that the issue of chemical stability of MHPs is still quite relevant at present. Despite their promise, inorganic MHPs are subject to degradation under the influence of external conditions (temperature, moisture, light), which significantly affects the

performance of devices made from them [6-8]. This can be caused by both internal and surface defects in the crystal structure of perovskite.

Degradation processes primarily occur on the surface of the material, so studying the methods of perovskite surface treatment, reducing its chemical activity, and analyzing the surface states of MHPs will help to obtain a high-quality material with stable characteristics. It is the quality and stability of MHPs that will play a crucial role in the creation of high-performance perovskite (optoelectronic) devices that will be sufficiently durable in real operating conditions.

Like other MHPs, single-crystal CsPbBr_3 is characterized by quite pronounced optoelectronic properties. High mobility of charge carriers, long diffusion length, high photoabsorption coefficient, high average atomic number (Pb-82, Cs-55, Br-35) and large band gap of cesium plumbum bromide make it possible to use it in various devices, including radiation detectors of various origins (including gamma and X-rays), solar cells, light emitting devices, and others [9-12].

As in the case of other perovskite materials, the

reliable and trouble-free operation of devices based on CsPbBr_3 largely depends on the condition of its surface. Therefore, the purpose of our study was to develop technological conditions for the preparation of the surface of CsPbBr_3 perovskite, to select substances suitable for all stages of processing such material, and to determine the composition of solutions that can be used to obtain a high-quality surface of MHPs CsPbBr_3 .

I. Materials and methods

The samples for the study were cut from a CsPbBr_3 ingot in the form of round plates. The plates were mechanically polished using oil suspensions of abrasive materials. Organic solvents (methanol (CH_3OH), acetone ($\text{C}_3\text{H}_6\text{O}$), n-hexane (C_6H_{14}), toluene ($\text{C}_6\text{H}_5\text{CH}_3$)) were used for interoperative cleaning. The polished plates were cut into smaller samples. After that, the samples were glued to quartz substrates with the wrong side using wax.

The chemical treatment was carried out on a chemical-dynamic polishing device, which provides stable, reproducible hydrodynamic conditions for the surface treatment of samples. The quartz substrates were fixed in the disc-shaped Teflon holder of the device. The rotation speed of the Teflon holder (disc) in the etchant was 90 rpm. When determining the limiting stage of the dissolution process, this speed was varied from 30 to 130 rpm.

The etching rate (v_{etch}) was determined by the decrease in sample thickness (thickness of the removed layer). For this purpose, the thickness of the sample was measured before and after etching using a clock indicator ICh 10.

Before etching, the samples were rinsed with anhydrous methanol for 2 minutes. Dimethyl sulphoxide ($\text{C}_2\text{H}_6\text{OS}$), dimethylformamide ($\text{C}_3\text{H}_7\text{ON}$), and ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$) were used to etch the samples. After etching, the samples were rinsed with n-hexane. All reagents were of p.a. grade. The etched and washed samples were dried with a stream of compressed dry air.

The surface of the single crystals after treatment was photographed using a Leitz/Wetzlar Germany microscope with a built-in MD-CP 250 video camera with a magnification of $8\times$ to $16\times$.

II. Results and discussion

A high-quality polished surface of a solid crystalline substance can be obtained when the process of removing the surface layers of the material is carried out at a low rate. This condition is one of the main ones when selecting solution compositions for polishing semiconductor materials. It should be noted that the removal of the surface layer of a solid can occur both during its dissolution and in the process of chemical interaction of the semiconductor with the components of the etchant. Accordingly, the issue of selecting the composition of etching agents and determining the etching rate is one of the key issues in the technology of semiconductor materials.

It is known that water is a universal solvent for many

solid inorganic substances. However, CsPbBr_3 and water undergo not only a dissolution process but also a chemical interaction. The products of this reaction are insoluble (poorly soluble) substances. These substances are deposited on the surface of crystals in the form of insoluble films and cannot be removed even after thorough cleaning. This makes it impossible to use water or aqueous solutions in the process of preparing a high-quality polished CsPbBr_3 surface. Therefore, the main components of mixtures for surface treatment of perovskite materials are mainly organic substances. It is known that dimethyl sulfoxide and dimethylformamide are good solvents for CsPbBr_3 [13]. Therefore, at the first stage of our study, we determined the dissolution rate of CsPbBr_3 in dimethyl sulfoxide (DMSO) and dimethylformamide (DMFA). The dependence of the thickness of the removed perovskite layer (l) on the time of exposure of the samples to the organic solvent is shown in Figure 1.

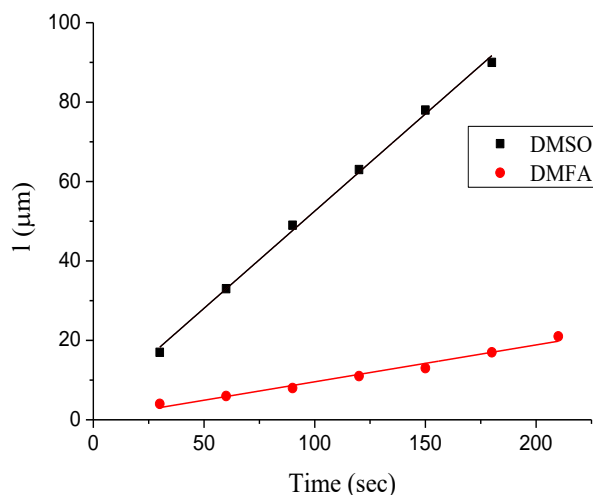


Fig. 1. Dependence of the thickness of the removed surface layer of CsPbBr_3 on the etching time in DMSO and DMFA ($T = 298\text{K}$).

The diagram shows that the thickness of the layer removed from the perovskite surface depends on the processing time in both organic solvents in a linear fashion. From this dependence the average value of the etching rate of the samples was calculated. In the DMSO solution, the etching rate of CsPbBr_3 was $29 \mu\text{m}/\text{min}$, and in the DMFA solution – $6 \mu\text{m}/\text{min}$. The low value of the etching rate of samples in DMFA is a positive characteristic in terms of the possibility of its use for polishing etching of CsPbBr_3 . However, the results of the study showed that the surface quality of the samples after treatment with dimethylformamide deteriorated significantly, while the treatment with dimethyl sulphoxide, although at a higher rate, gave a better result (Figure 2).

Since the treatment of the perovskite surface with dimethylformamide leads to a significant deterioration in its quality, dimethyl sulfoxide was used for our further studies.

In order to reduce the etching rate of the surface of semiconductor materials, an additional component that does not chemically interact with the material is often

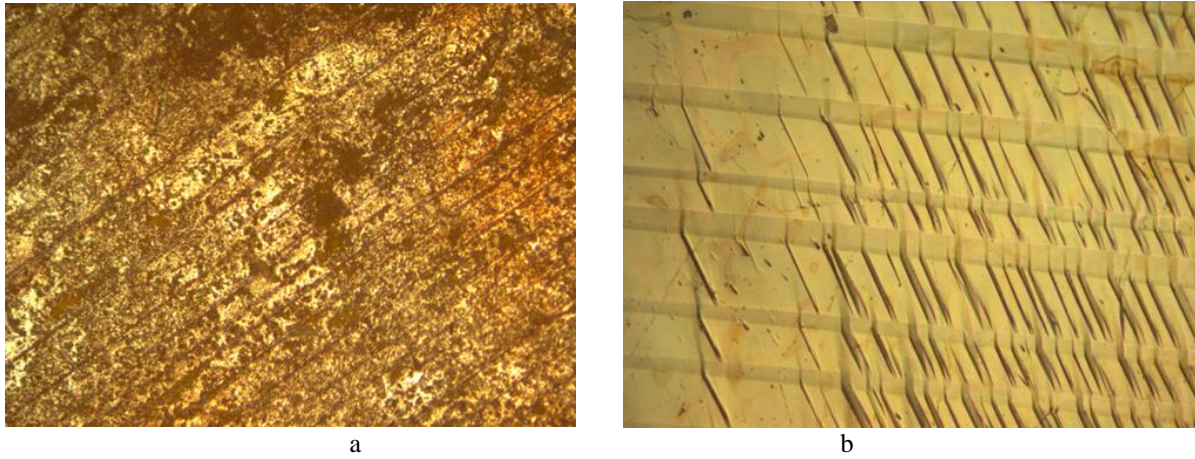


Fig. 2. CsPbBr₃ surface treated with DMFA (a) and DMSO (b). The etching time was 60 sec (T = 298 K).

introduced into the etchant composition. In our study, ethyl acetate (EA) was used as such component. The content of ethyl acetate in the solutions of the DMSO-EA system was increased from 0 to 80 vol. % (Table 1).

Table 1.

Composition of solutions of DMSO – EA system		
	Volume ratio	Composition vol. %
DMSO : EA	4 : 1	20 % solution EA in DMSO
DMSO : EA	3 : 2	40 % solution EA in DMSO
DMSO : EA	2 : 3	60 % solution EA in DMSO
DMSO : EA	1 : 4	80 % solution EA in DMSO

The dependence of the thickness of the removed perovskite layer on the time of chemical treatment for the various compositions (Table 1) is shown in Figure 3.

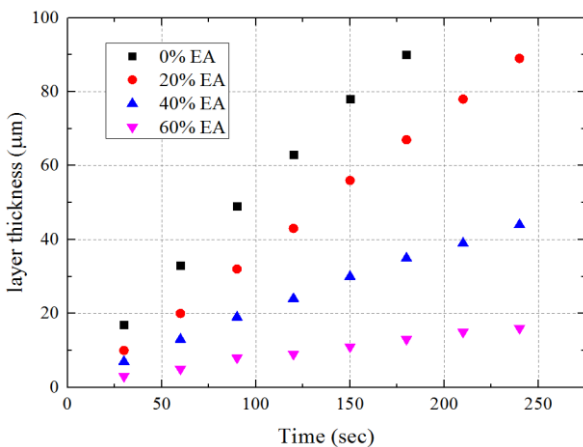


Fig. 3. Dependence of the thickness of the removed surface layer of CsPbBr₃ on the etching time in solutions of the DMSO-EA system (T = 298 K).

As with dimethyl sulfoxide (Fig.1), the corresponding dependence is linear. Increasing the ethyl acetate content in the solutions significantly reduces the perovskite dissolution rate from 23 µm/min in a solution of 80 vol. % DMSO - 20 vol. % EA to 4 µm/min in a solution of 40 vol.

% DMSO - 60 vol. % EA. In a solution containing 80 % ethyl acetate, etching of perovskite does not occur and the dissolution rate decreases to almost zero. The surface of the samples after treatment with this solution loses its lustre and is covered with a white film that cannot be removed by rinsing.

In the solution, containing 60 vol. % EA, slow etching occurs, but a white film of lower intensity also appears on the surface of the samples. For this reason, a solution of this composition cannot be considered suitable for polishing etching of the perovskite surface.

The addition of 40 vol. % ethyl acetate to dimethyl sulphoxide reduces the etching rate of the samples by almost three times compared to pure DMSO. At the same time, the quality of the surface obtained is not inferior to the surface quality of samples treated with DMSO alone. Therefore, it can be assumed that solutions of the DMSO-EA system, in which the content of EA does not exceed 40 vol. %, can be used for polishing etching of CsPbBr₃.

To determine the limiting stage of the CsPbBr₃ dissolution process in solutions of the DMSO-EA system, the dependence of the samples etching rate on the disc rotation speed (γ) was investigated. The results of the obtained dependence plotted in the coordinates $v^{-1} - \gamma^{-1/2}$ are shown in Fig. 4.

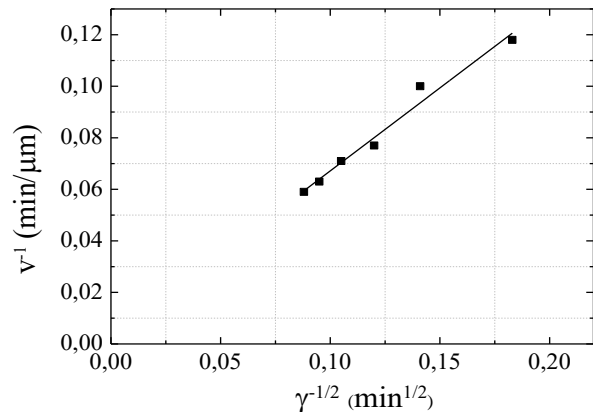


Fig. 4. Dependence of the CsPbBr₃ etching rate on the disc rotation speed in solutions of the DMSO-EA system (T = 298 K).

By analyzing the obtained dependences of the etching rate on the disc rotation speed and taking into account the general principles of determining the stages, limiting the rate of chemical interaction, it can be stated that the etching process of CsPbBr_3 by solutions of the DMSO–EA system occurs by the diffusion mechanism. Such conclusion can be made taking into account that the acceleration of the disc rotation speed in the etchant solution leads to an increase in the rate of samples dissolution in general, and the corresponding lines are extrapolated to the coordinate's origin.

The diffusion mechanism is one of the main criteria in the selection of etchant compositions that exhibit polishing properties on the semiconductor surface. Therefore, taking this fact into account, we can assert that some compositions of solutions of the dimethyl sulfoxide–ethyl acetate system are promising for obtaining a high-quality, contamination-free, polished surface of CsPbBr_3 .

Conclusions

Reliable and trouble-free operation of electronic devices based on CsPbBr_3 MHPs depends not only on the bulk properties of the material but also on the state of its surface. In view of this, the preparation of the CsPbBr_3 surface is one of the critical stages of the technology of perovskite semiconductor materials. The surface of CsPbBr_3 cannot be treated with water or aqueous solutions, as this would result in chemical interaction, which would produce insoluble or poorly soluble products. In our study, anhydrous dimethyl sulfoxide was used for CsPbBr_3 chemical etching. Based on this organic solvent, a series of new polishing compositions of etching

solutions for chemical polishing of CsPbBr_3 was developed. It was found that the dissolution of perovskite in dimethyl sulfoxide occurs at a rate of 29 $\mu\text{m}/\text{min}$. The addition of 20 and 60 vol. % ethyl acetate to dimethyl sulfoxide leads to a decrease in the perovskite dissolution rate to 23 $\mu\text{m}/\text{min}$ and 4 $\mu\text{m}/\text{min}$, respectively. It has been shown that solutions with ethyl acetate content in dimethyl sulfoxide not exceeding 40 vol. % have polishing properties on the surface of CsPbBr_3 . The limiting stage of the process of CsPbBr_3 dissolving in solutions of the DMSO-EA system is diffusion. This indicates the prospect of using them for polishing etching of the CsPbBr_3 surface.

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Взаємодія PbCsBr₃ з розчинами системи диметилсульфоксид – етилацетат

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Вивчено процес хіміко-динамічного полірування поверхні метал-галогенідного перовскіту PbCsBr₃ травниками на основі розчинів системи диметилсульфоксид – етилацетат (ДМСО-ЕА). Досліджено залежності швидкостей розчинення перовскіту від вмісту етилацетату у складі розчину травника. Аналіз якісних характеристик одержаної в результаті травлення поверхні здійснено за допомогою метода оптичної мікроскопії. Встановлено, що процес розчинення PbCsBr₃ у травниках системи ДМСО-ЕА відбувається за дифузійним механізмом. На основі одержаних результатів оптимізовано склади травильних розчинів та технологічні режими проведення хіміко-динамічного полірування монокристалів PbCsBr₃. Модифіковані етилацетатом травники є перспективними для використання у технології перовскітних матеріалів у тому випадку, коли основною метою є повільне видалення поверхневого шару напівпровідника, а також одержання високоякісної, структурно-досконалої його поверхні.

Ключові слова: перовскіт, поверхня, швидкість травлення, хіміко-динамічне полірування, диметилсульфоксид, етилацетат, розчин.