Influence of carbon in the sp\(^1\) hybridized state on the structure of PbSe thin films

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Abstract. The optical reflection spectra of PbSe films and PbSe films coated with a layer of linear chain carbon were studied by IR Fourier spectroscopy in the wavelength range of 1-16 μm. In all IR spectra of the samples, two minima were observed, related to plasma fluctuations of free charge carriers and related to the PbSe and PbSeO\(_3\) phases. It was found that the PbSe film coated with a layer of linear chain carbon is less oxidized. This conclusion is confirmed by the results of x-ray structural studies of the samples. The results showed a decrease in the percentage of oxygen-containing phase PbSeO\(_3\) by 2-4 times.

1. Introduction
Lead selenide is a promising material in a field of micro-and nanotechnology. Due to their good photoelectric properties, PbSe films are used as IR photodetectors and for manufacturing photoresistors [1-3].

In our previous work [4], it was shown the possibility of using PbSe films in which the effect of an abnormal change in resistance is observed near the temperature \(T_P = 343\) K to create thermostressive elements. However, a big problem in the practical use of PbSe films is the instability of properties associated with oxidation over time, which leads to a deterioration in their semiconductor characteristics. The solution to this problem should be found in phase stabilization, for which a protective coating can be used. As a protective layer a film of linear chain carbon (LCC, carbon in the sp\(^1\) hybridized state) can be selected. In [5] it was found that the nature of the temperature dependence of the resistance of PbSe films coated with a layer of LCC does not change. Basic information about the film of LCC presented in [6].

The aim of this work is to study the effect of linear-chain carbon film on the structure of PbSe films.

2. Methodology
In this work PbSe films with a thickness of 300-400 nm with a coating of LCC film and without a coating of LCC film were studied. PbSe film systems were obtained on a UVR-3M vacuum system.
Pb and Se films were applied by thermal evaporation by sequentially deposition. Subsequently, the obtained samples were subjected to thermal annealing in a nitrogen atmosphere in a MIMP-VM vacuum furnace at a temperature of 250 °C for 45 minutes to diffuse the layers. A carbon film with a thickness of 150 nm was synthesized on top of one of the PbSe films by the ion-plasma method using the modernized industrial equipment "URM.3.279.070 Almaz". The temperature dependences of the film's resistance were studied on these samples, i.e. one heating-cooling cycle was reproduced before the structural characteristics were studied.

The reflection spectra were measured on a VERTEX 80 Fourier spectrometer in the wavelength range of 1–16 μm at room temperature.

The phase composition and structural features of the samples were determined on a PANalytical Empyrean X-ray diffractometer in copper β-filtered radiation with a wavelength of $\lambda_{Kα}=1.54184$ Å. Radiographs were processed using HighScore Plus and the ICDD PDF-4 2015 database.

3. Experimental results
The reflection spectra $R(\lambda)$ of PbSe and PbSe-LCC films shown in Fig.1. As can be seen from the figure, there are no significant changes in the form of spectral dependencies of PbSe films, both carbon-coated and uncoated. According to [7], in this range of wavelengths, the refractive index of the LCC film does not depend on the wavelength. Therefore, the shape of the reflection spectrum after applying the LCC layer should not change.

![Figure 1. IR-spectra of the reflection of PbSe and PbSe-LCC films](image)

The optical properties of semiconductor materials in the infrared region of the spectrum are largely determined by the behavior of free charge carriers [8]. In the $R(\lambda)$ spectra two reflection minima are observed, the position and depth of which are different for the studied films. The observed minima of the reflection coefficient are due to the plasma resonance of free charge carriers.

According to [3], the spectral region of 7.5-11 μm of the studied films (Fig.1) can be attributed to an abnormal dispersion of the crystal phase of lead selenide (PbSe), 11-12.3 μm – an abnormal dispersion of the crystal phase of lead selenite (PbSeO₃), 12.3-16 microns – fluctuations of the selenite ion $\text{SeO}_2^-$, which is part of the PbSeO₃ phase. The concentration of charge carriers in PbSeO₃ is much lower than in PbSe, so the plasma minimum of lead selenite, in contrast to lead selenide, should be in the longer-wave region of the spectrum [3] since
$$\omega_p = \sqrt{\frac{ne^2}{m^*\varepsilon_\infty\varepsilon_0}},$$

where $\omega_p$ - plasma frequency, $e$ - electron charge, $\varepsilon_\infty$ - high-frequency dielectric constant, $\varepsilon_0$ - electric constant, $n$ and $m^*$ - concentration and effective mass of free charge carriers.

In the R ($\lambda$) spectrum (Fig. 1) of the PbSe film in the wavelength range of 7.5–9.5 μm, a region with abnormal dispersion and a characteristic maximum at the wavelength of 8.1 (8.5 - [3]) μm is observed, and also with the corresponding plasma minimum at a wavelength of 8.9 (depending on the oxidation time 9.45, 9.0, 8.5, 8.3 - [3]) μm. In the PbSe-LCC sample, this plasma minimum is shifted to the long-wavelength region and has a value of 9.22 μm. In [3], it was noted that as the oxidation time increases, the region of abnormal dispersion related to the PbSe crystal phase decreases, and in proportion to it, the corresponding region of abnormal dispersion related to the PbSeO$_3$ phase increases. Thus, as the oxidation time increases, the mass of PbSe in the film decreases, and the mass of PbSeO$_3$ increases, which affects the size of the regions of abnormal dispersion [3]. From this, it can be concluded that the PbSe film coated with a layer of LCC is less oxidized.

In the second region of wavelengths of 11–12.3 μm, the plasma absorption peaks for lead selenite in both studied samples coincide and have a value of 12.3 μm.

X-ray phase analysis (XRD) of the samples was carried out to confirm the data obtained by the method of IR Fourier spectroscopy. The diffractograms of the films (Fig. 2) contain maxima corresponding to the cubic structure of the NaCl (B1) type, characteristic of lead selenide crystals (PbSe), and the monoclinic structure related to the lead selenite phase (PbSeO$_3$). The halo, which is more intense in the PbSe sample due to the smaller film thickness, with a center of gravity of $\sim 220$ by 2θ is caused by the glass substrate. The composition and structural features of the phases of the PbSe films according to the XRD data are shown in table 1. The concentrations of the phases present in the films were calculated by the corundum number method [9]. The phase of the selenide of lead in both films is predominant. In addition, table 1 shows that the percentage of the oxygen-containing phase of PbSeO$_3$ in PbSe-LCC films is much lower, which coincides with the data of IR Fourier spectroscopy.

### Table 1. The composition and structural features of the phases of the samples

| Sample    | Phase   | Stoichiometric formula | Title       | Syngony | Structure | Marking | Mass content, % |
|-----------|---------|------------------------|-------------|---------|-----------|---------|-----------------|
| PbSe-LCC  | PbSe    | Clausthalite           | Cubic       | Fm-3m   | □         |         | 90              |
|           | PbSeO$_3$ | Molybdenite           | Monoclinic  | P21/m   | ▲         |         | 10              |
| PbSe      | PbSe    | Clausthalite           | Cubic       | Fm-3m   | □         |         | 52              |
|           | PbSeO$_3$ | Molybdenite           | Monoclinic  | P21/m   | ▲         |         | 48              |
4. Conclusion
A comparison of the data of IR-Fourier spectroscopy and XRD shows that the sample with LCC film is less oxidized comparing to the sample without LCC film. Therefore, LCC films can be used as a protective coating against further oxidation of PbSe samples.

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