Thermochromism of the semiconductor film system Pb-Se

A G Razina
Department of Applied Physics and Nanotechnology, The Chuvash State University, Cheboksary 428015, Russia
E-mail: razina_ag@mail.ru

Abstract. Semiconductor film systems of Pb-Se were obtained by solid-state synthesis. The results of the study of reflection spectra at the temperatures of 300 K and 373 K showed that heating leads to an increase in the reflection coefficient in the visible region of the spectrum. It is suggested that this change in the optical properties is due to a change in the electronic conductivity of the Pb-O phase.

1. Introduction
Lead selenide has a wide variety of physical properties. Due to its unique optical and photoelectric characteristics, PbSe is widely used in opto- and microelectronics [1-3].

It is known that lead selenide films are synthesis by various methods [2, 3], and the physical properties of films strongly depend on the method of their preparation [4]. The method of solid-phase synthesis is more optimal for studying the electrophysical properties of Pb-Se films investigated by us earlier [5-7]. In these studies, an abnormal change in electrical conductivity was found near the temperature of the T=343 K phase transition, which was further investigated in [7] and identified as a semiconductor-metal phase transition. In particular, X-ray diffraction studies show the presence in the Pb-Se system of two phases of PbSe and PbSeO$_3$ on the surface, which, in all probability, leads to the transition of a thin semiconductor film to the metallic state.

Typically, phase transitions are accompanied by changes not only the structure and conductivity of the material, but also magnetic, thermoelectric, optical properties. [8]. For example, the change in optical properties in vanadium dioxide, accompanied by a semiconductor-metal phase transition, causes the existence of such a phenomenon as thermochromism. Thermochromism is the property of a substance to change color reversibly when heated or cooled [9]. Thus, the spectral behavior of the optical reflectivity of the Pb-Se film system should also vary with the temperature near the phase transition.

This work is devoted to the study of the effect of temperature on the reflection spectrum of Pb-Se films.

2. Methodology
Two-layer film systems of Pb-Se with a thickness of 300-400 nm was obtained using a vacuum device UVR-3M. Ion purification of the substrate with argon was preliminarily carried out, then Pb and Se films were successively deposited by thermal evaporation on the substrate. The obtained samples were thermally annealed in a nitrogen atmosphere in a vacuum furnace MIMP-VM at a temperature of 523 K for 45 minutes.
The reflection spectra of films in the semiconductor (300 K) and metal phases (363 K) in the wavelength range of 250-1000 nm were obtained using a spectral ellipsometer and a heating element. The minimum scanning step is 0.5 nm. The procedure for determining the reflection coefficient for the samples was reduced to the following. At first, the reflection spectrum of the standard (aluminum mirror) was taken, reflecting the spectral behavior of the instrument function and the reflection coefficient of which was close to 100% in the red and near IR region of the spectrum. After that, the reflection spectrum of the studied film was taken at a temperature of 300 K, then at 373 K. Further, these spectra were divided into an instrumental function, which gave the spectra of the absolute reflectivity of the film.

3. Results and discussion

Figure 1 shows the spectral curves of the reflectivity of the Pb-Se film system at temperatures of 300 and 373 K. It was found that increasing temperature the reflection coefficient increases in the ultraviolet and visible regions of the spectrum. In this regard, when the film is heated, the color of the film changes in the reflected light, from dark gray to gray-blue with a metallic sheen. This transition is reversible.

![Figure 1. The reflection spectra of the Pb-Se film system at temperatures of 300 and 373 K.](image)

Earlier, when studying the Raman spectrum at temperatures of 300 and 373 K [7], it was shown that when the film is heated to 373 K, changes in spectral parameters (frequency, width, position) occur, which can be associated with changes in both the structural and dynamic characteristics of the films, as well as features of electron-vibrational interactions. These changes were clearly expressed in the low frequency region (94.6, 113, 132.7 and 275 cm⁻¹) related to the Pb-O phase. First, the bands 94.6, 113 and 275 cm⁻¹, almost disappear, while the intensity of the line at 139 cm⁻¹ increases on the contrary. Secondly, there is a shift of oscillatory modes 132 to 7 cm⁻¹ and 790 to 5 cm⁻¹ in the direction of high frequencies. In addition to the frequency shift of 790 cm⁻¹, related to the oscillations of the SeO₂ bond, no other changes were noted [7].

Perhaps the change in the reflection spectrum after heating the Pb-Se film to 373 K is accompanied by a change in the nature of the electronic conductivity of the Pb-O phase. The results of X-ray studies [7] do not exclude the presence of nuclei of the metallic phase of Pb-O in the Pb-Se semiconductor system.
Thus, the nature of changes in optical properties at varying temperatures also indicates the presence of a semiconductor-metal phase transition in the Pb-Se film system.

4. Conclusion
The reflection spectra of semiconductor film systems Pb-Se obtained by solid-state synthesis at temperatures of 300 and 373 K were studied. It is shown that the appearance of characteristic anomalies of optical properties near the transition temperature may be accompanied by a change in the nature of the electronic conductivity of the Pb-O phase. Thus, an independent confirmation was obtained that T=343 K is the phase transition temperature in a thin film Pb-Se.

References
[1] Abrikosov N Kh and Shelimova L Ye 1975 Poluprovodnikovye materialy na osnove soedineniy $ABV_3$ (Moscow: Nauka)
[2] Tomaev V V, Mazur A S and Grevtsev A S 2017 Glass Phys. Chem. vol 43 (Moscow: Nauka Press) pp 70-74
[3] Tretyakova N A, Markov V F, Maskaeva L N and Mukhamedzyanov Kh N 2005 Kondensirovannye sredy i mezhfaznye granitsy vol 7 (Voronezh: Voronezhskiy gosudarstvenny universitet Press) pp 189-194
[4] Ulman A 1991 Introduction on Ultrathin Films, from Langmuir-Blodgett to Self-Assembly (San Diego: Academic Press)
[5] Krasnova A G, Kokshina A V, Belova A V and Kochakov V D 2012 Vestnik Chuvashskogo Universiteta vol 3 (Cheboksary: Chuvash State University Press) pp 46-47
[6] Krasnova A G 2013 Proc. Int. Conf. Nanostrukturirovannye materialy i preobrazovatelnye ustroystva dlya solnechnoy energetiki 3-go pokoleniya (Cheboksary: Poligrafika Press) pp 76-77
[7] Razina A G, Kazakov V A, Ashmarin A A and Kochakov V D 2018 vol 20 Izvestiya vysshikh uchebnikh zavedeni. Problemy energetiki (Kazan: Kazanskiy gosudarstvenny energeticheskiy universitet Press) pp 132-142
[8] Bugaev A A, Zakharchenya B P and Chudnovskiy F A 1979 Fazovyy perekhod metall-poluprovodnik i ego primenenie (St. Petersburg: Nauka)
[9] Yarina Ye A and Menshikov V V 2015 Proc. Int. Conf. Vektory razvitiya nauki (Ufa: AETYeRNA Press.) pp 13-14