

OPTICAL PROPERTIES OF PrSb₂ THIN FILMS OF DARK BLUE COLORING**Z.U. Jabua, I.L. Kupreishvili, A.V. Gigineishvili***Department of Physics, Georgian Technical University (Tbilisi)
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A process has been developed for the growth of thin crystalline PrSb₂ films of different coloring by thermal evaporation using Pr and Sb separate sources. The room-temperature optical spectra (reflectivity, absorption coefficient, loss function, real and imaginary parts of dielectric permittivity, optical conductivity) of PrSb₂ films of dark blue coloring have been studied at photon energy from 0.05 to 5.5 eV. The behavior and energy position of features in the spectra have been analyzed.

Keywords: film, substrates, intermediate valence, absorption, refraction, loss function, optical conductivity.

ОПТИЧЕСКИЕ СВОЙСТВА ТОНКИХ ПЛЕНОК PrSb₂ ТЕМНО-СИНЕЙ ОКРАСКИ**З.У. Джабуа, И.Л. Купреишвили, А.В. Гигинеишвили**

Разработана технология приготовления тонких плёнок PrSb₂ различной окраски методом вакуумно-термического испарения из двух независимых источников Pr и Sb. При комнатной температуре измерены оптические спектры (отражение, поглощение, функция потерь, действительные и мнимые части диэлектрической проницаемости, оптическая проводимость) тонких плёнок PrSb₂ тёмно-синей окраски, в области энергии фотонов 0.05 – 5.5 эВ. Проанализированы спектральные зависимости экспериментально полученных результатов.

Ключевые слова: плёнка, подложка, переменная валентность, поглощение, отражение, функция потерь, оптическая проводимость.

ОПТИЧНІ ВЛАСТИВОСТІ ТОНКИХ ПЛІВОК PrSb₂ ТЕМНО-СИНЬОГО ЗАБАРВЛЕННЯ**З.У. Джабуа, І.Л. Купреїшвілі, А.В. Гігінєшвілі**

Розроблено технологію приготування тонких плівок PrSb₂ різного забарвлення методом вакуумно-термічного випаровування із двох незалежних джерел Pr і Sb. При кімнатній температурі виміряні оптичні спектри (відбиття, поглинання, функція втрат, дійсна та мінна частини діелектричної проникності, оптична провідність) тонких плівок PrSb₂ темно-синє забарвлення, в області енергії фотонів 0.05 – 5.5 еВ. Проаналізовані спектральні залежності експериментально отриманих результатів.

Ключові слова: плівка, підкладина, змінна валентність, поглинання, відбиття, функція втрат, оптична провідність.

INTRODUCTION

Rare-earth antimonides continue to receive a great deal of attention owing to their interesting properties, which have not yet been studied in sufficient detail and are the subject of controversy [1 – 11]. The effect of the oxidation state of rare-earth ions in antimonides on their physical properties is high current interest because the rare-earth ions are not always in their typical oxidation state and this materials involves the so-called phenomenon of intermediate valence [10, 11]. Thus using X-ray L_{III} – edge absorption spectroscopy was shown that oxidation state of the Yb ion in YbSb₂ thin films of blue coloring is +2.2 and + 2.5 in films of brown coloring.

In this work are presented results of investigation of optical properties of PrSb₂ thin films of dark blue coloring.

EXPERIMENTAL

Crystalline PrSb₂ films 0.4 – 1.8 μm thickness, were grown by evaporation from Pr and Sb sources. The source materials used were 99.9% PrM-1 praseodymium and 99.9999% antimony. As substrates, we used glass-ceramic, fused silica, alpha-alumina, and (111) – oriented single crystal Si plates.

During the growth processes, the vacuum in the deposition chamber was – 10⁻⁵ Pa. Pr was deposited by electron-beam evaporation at 910 K, and Sb by thermal evaporation between 910 and

960 K. In all the growth runs, the substrate temperature was maintained at 1020 K. The source substrate separation was 35 mm for Pr and 25 mm for Sb. The axis of the Pr and Sb evaporation made angle of -20° and -25° , respectively, with the normal to the substrate surface. The deposition rate of the films was varied from 45 to 70 Å/s. The phase composition and structural perfection of the films were determined by X-ray diffraction (XRD) and electron diffraction. The surface morphology of the films was imaged using characteristic X-rays (Camebax Microbeam system). The elemental composition of the films was determined by electron probe microanalysis. Auger electron spectroscopy was used to obtain composition-depth profiles. The films deposited at a fixed praseodymium source temperature (1910 K) and fixed substrate temperature (1020 K), but at different antimony source temperatures in the range 910–960 K varied in color from goldish (~ 910 – 925 K) to black (~ 925 – 940 K) and to dark blue (~ 940 – 960 K). The reproducibility of results was ~ 75 – 80% . The reflection and transmission spectra, in the photon energy range 0.05–5.5 eV at room temperature, of the PrS films of goldish and black we studied elsewhere [12, 13]. In this work we studied the reflection and transmission spectra of the dark blue coloring films, in the photon energy range 0.05–5.5 eV at room temperature on an IKS-21 spectrometer. Spectra of optical constants were obtained by processing reflectivity data using the Kramers-Kronig relations.

We also measured the electro resistivity, Hall coefficient, Hall mobility, and Seebeck coefficient of the films at 300 K.

RESULTS AND DISCUSSION

Analysis of the XRD and electron diffraction data led us to conclude that the films were single phase and had an orthorhombic structure (LaSb₂ type) with lattice parameters $a = 6.24$ Å, $b = 6.06$ Å, and $c = 17.91$ Å, in good agreement with those of bulk PrSb₂ crystals [14].

According to X-ray microanalysis data, the composition of the PrSb₂ films was 33.1% Pr + 66.9% Sb. X-ray maps of the film surface showed that the films were rather uniform in composition. As shown by Auger depth profiling, the films were homogeneous in the depth direction. At a substrate temperature of 1050 K or above, the films contained additional phases, which was probably caused

by Sb revaporization. The substrate material had an insignificant effect on the crystallinity, phase composition, and color of the films.

The room temperature electrical properties of the films are typical of the many mixed valence compounds [11]: resistivity, $2 \cdot 10^5$ Ω·cm, Hall coefficient, 10^{-4} to 10^{-3} cm²/C, Hall mobility, 12 cm²/(V·s), and Seebeck coefficient 1.5 μV/K.

The data in the tabl. 1 and fig. 1–5 illustrate the optical properties of the PrSb₂ films of dark blue coloring.

Table 1

Data on position of features in spectra of PrSb₂. Note: E^I and E^{II} are the energy of the zero crossing in the spectrum of the real part of permittivity, $\epsilon_1(\omega) = 0$ with negative and positive slope, respectively; E_0^I and E_0^I , E_0 are the energy positions of the minima in parameters; and $E_1 - E_5$ are the energy positions of the maxima (eV)

Parameter	E^I	E_2	E_0^I	E^{II}	E_4	E_5
R	–	–	0.48	–	1.45	–
α , 10^5 , cm ⁻¹	–	0.13	0.58	–	–	4.35
σ , Ω ⁻¹ , cm ⁻¹	–	–	0.61	–	–	2.89
ϵ_2	–	–	0.59	–	1.79	–
ϵ_1	0.057	0.12	–	0.35	–	–
$\text{Im}\epsilon^{-1}$	–	–	–	0.39	–	–

Everyone spectral dependence can be divided into two sites – area where, the contribution of plazmon ($\hbar\omega < 0.5$ eV), it is obviously essential, and the area, which spectral dependences should will be defined by electronic transitions. Existence of one, wide strip of reflection (fig. 1), covering a

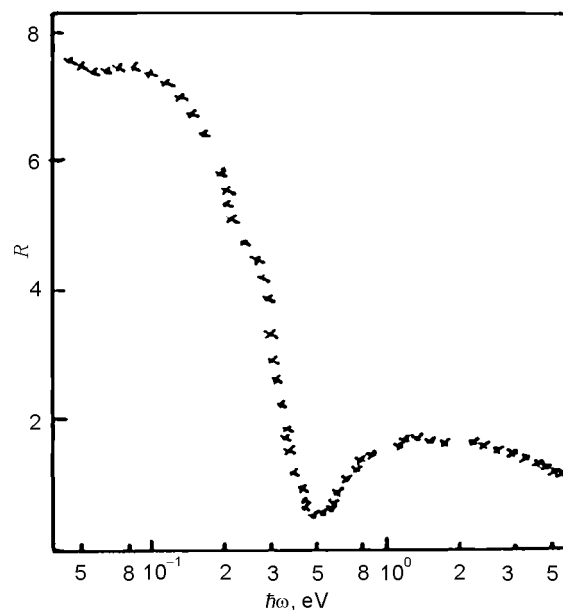


Fig. 1. Reflection spectra.

power interval 0.5 – 5 eV, indicates very powerful contribution transitions of fundamental character (at high value of force of an oscillation of transitions) which absorbs more and more thin features of a structure of power zones. It proves to be true regional nature of spectral dependence of factor of absorption, since 0.58 eV value α changes from $9 \cdot 10^3 \text{ cm}^{-1}$ to $3 \cdot 10^5 \text{ cm}^{-1}$. This last size α forms an absorption maximum at 4.35 eV (fig. 2).

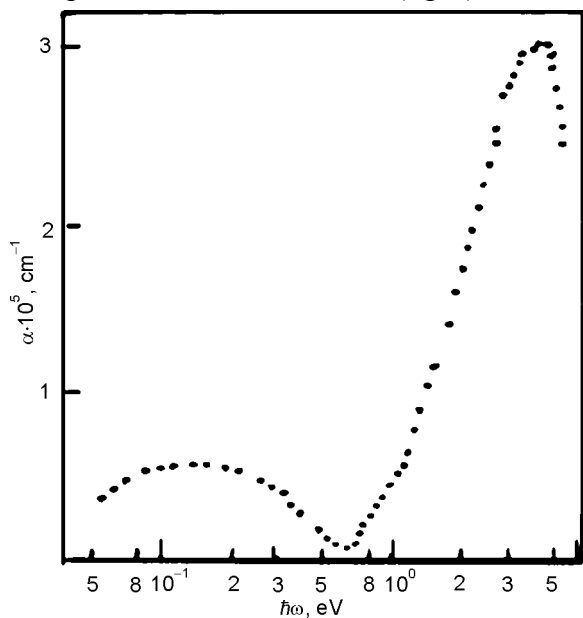


Fig. 2. Absorption spectra.

The absolute minimum and all other parameters describing processes of absorption (k , ϵ_1 , σ) is observed also at 0.60 eV (fig. 3 – 5). However, power provisions of their short-wave maxima differ

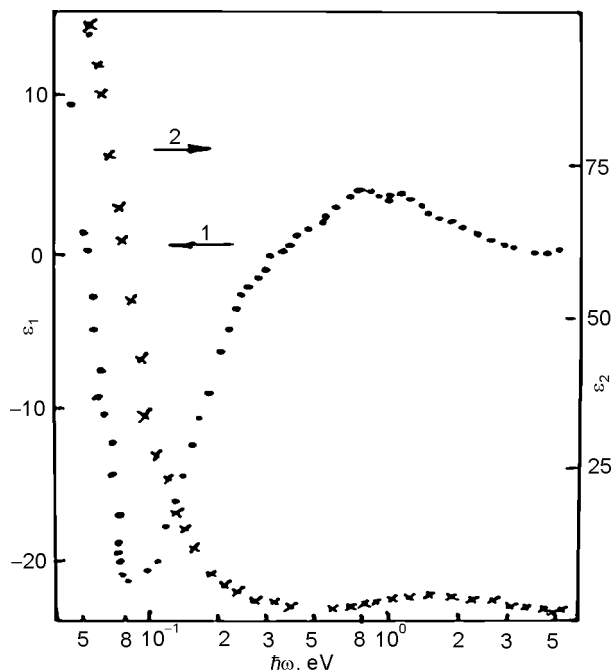


Fig. 3. Spectra of the real (ϵ_1) and imaginary part (ϵ_2) of permittivity.

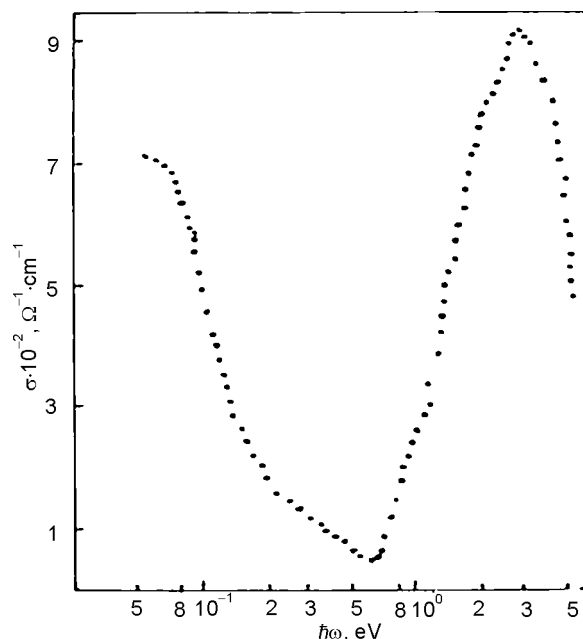


Fig. 4. Spectra of optical conductivity.

– 1.75 eV for ϵ_1 , 2.83 eV for σ . Thus specified maxima of optical conductivity and factor of absorption are dominant in their ranges. Absorption in low-energy area is shown in the form of monotonously increased k , ϵ_2 , σ and in a range of factor of absorption the strip with the center of gravity is formed at 0.16 eV, value in which 10 times less, than in a short-wave maximum. Zero crossing by dependence $\epsilon_1(\omega)$ takes place (fig. 3) at 0.057 eV (with a negative inclination) and 0.35 eV (with positive).

The maximum of function of losses also settles down near this energy (0.38 eV, fig. 5). Well created negative and positive extreme of the valid part of dielectric permeability it is observed, respectively, at 0.12 eV and 0.78 eV.

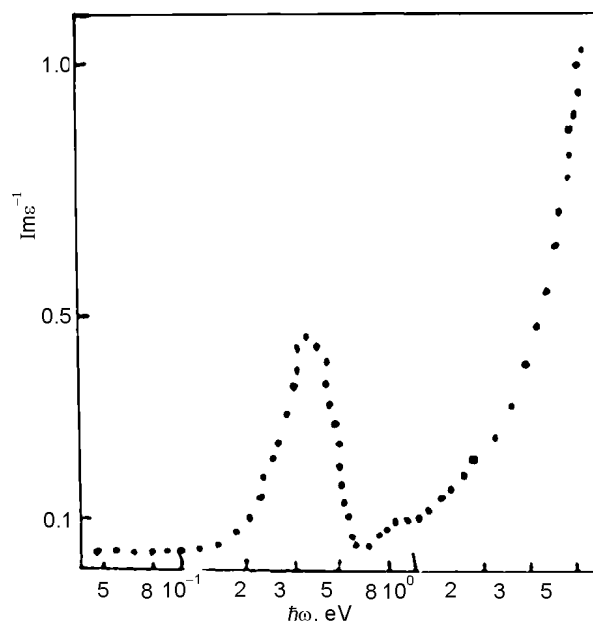


Fig. 5. Loss function spectra.

Data on position of features in spectra are summarized in the tabl. 1.

CONCLUSION

The first process has been developed for the growth of thin crystalline PrSb₂ films of different coloring (orthorhombic symmetry, LaSb₂ structure, lattice parameters $a = 6.24 \text{ \AA}$, $b = 6.06 \text{ \AA}$, and $c = 17.91 \text{ \AA}$).

We have studied the room-temperature optical spectra (reflectivity, absorption coefficient, loss function, real and imaginary parts of dielectric permittivity, optical conductivity) of PrSb₂ films of dark blue coloring at phonon energy from 0.05 to 5.5 eV. The main features, power position of the revealed structures in all ranges are considered.

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REFERENCES

1. Gasgnier M. Rare Earth Compounds (Oxides, Sulfides, ...) As Thin Films and Thin Crystals// Phys. Status Solidi A. – 1989. – Vol. 114, No. 11. – P. 11-71.
2. Gigineishvili, A.V., Jabua Z.U., Taktakishvili M.S. Preparation of SmS Thin Films and Influence of Sm Ion Valency on the Optical Properties//Material Science Days (Tbilisi). – 2009. – P. 37.
3. Vaitheesvaran G., Petit L., Svane A., et. al. Electronic Structure of Praseodymium Monopnictides and Monochalcogenides under Pressure//J. Phys.: Condens. Matter. – 2004. – Vol. 16. – P. 4429-4433.
4. Verna, A.S. Electronic and Optical Properties of Rare Earth Chalcogenides and Pnictides//Afr. Phys. Rev. – 2009. – Vol. 3. – P. 11-28.
5. Duan C., Sabirianov R.F., Mei W.N., Dowben P.A., Jaswal S.S., Tsumbal E.Y. Electronic, Magnetic and Transport Properties of Rare Earth Monopnictides//J. Phys.: Condens. Matter. – 2007. – Vol. 19. – P. 1-32.
6. Svane A., Strance P., Temerman W., Szotek Z., Winter H., Petiot L. Pressure induced valence transition in rare earth chalcogenides and pnictides//Phys. Status. Sol. – 2001. – Vol. 229. – P. 105- 116.
7. Long L. Zhao, Lausberg Stefan, Kim H., Ttannatar A., Brando Manuel, Prozorov R., Morosan E. Type I superconductivity in Y single crystals//Physical Review B. – 2012. – Vol. 85. – P. 6.
8. Shirakavia Naoki, Koiawi Sadayoshi, Uwatoko Yoshiya. Pressure effect on the superconductivity of YbS//High Pressure Conference of Japan. Program and Abstracts. – 2000. – Vol.41. – P. 211.
9. Singh S., Singh R.K., Gour A. High pressure transition and stability of CeSb, LaSb and LuSb with NaCl-type structure//International journal of modern physics. – 2010. – Vol.24, № 18. – P. 3543-3550.
10. Antonov V.N., Shpark A.P., Yarersko A.N. Electronic structure of mixed valent systems//Condensed matter physics. – 2004. – Vol. 7, № 2 (38). – P. 211- 246.
11. Glurjidge L.N., Dadiani T.O., Jabua Z.U., Plavinski T.L., Gigineishvili A.V., Sanadze V.V., Finkelshtein L.D., Efremova N.N. Intermediate valency of Yb in films//Sol. St.Phys. – 1988. – Vol. 30, № 4. – P. 1171-1175 (in Russian).
12. Jabua Z.U., Gigineishvili A.V., Iluridze G.N., Minashvili T.A., Kupreishvili I.L. Optical properties of PrSb₂ thin films of black coloring//Collection of articles of conference. (St –Peterburg, Russia). – 2011. – Vol.1. – P. 155-160 (in Russian).
13. Trapaidze I., Jabua Z., Kupreishvili I., Gigineishvili A., Iluridze G., Minashvili T., Davitadze K. The absorption spectra of PrSb₂ thin films of golden colour//76 Annual Conference of The DPG (Deutschen Physikalischen Gesellschaft) and DPG-fruhjahrstagung 2012 (Spring Meeting) of the Condensed Matter Section (SKM). Berlin. – 2012. – P. 224.
14. Abdusaliyeva M.N.. Antimonides and bismutides of rare earth elements. – Dissertation. Sverdlovsk, 1987. – 385 p. (in Russian).