Conference materials
UDC 538.958
DOI: https://doi.org/10.18721/JPM.163.239

Optical anisotropy of black phosphorus characterized by FTIR spectroscopy methods

S.A. Khakhulin✉, O.E. Lakuntsova, D.D. Firsov, O.S. Komkov

St. Petersburg Electrotechnical University "LETI", St. Petersburg, Russia

✉ khsmn@ya.ru

Abstract. The present study employs the FTIR spectroscopy methods, such as polarized transmittance measurements and the reflectance anisotropy spectroscopy technique, to characterize the optical properties of black phosphorus - a layered semiconductor with a narrow band gap. Our results reveal a notable crystal absorption anisotropy within the 0.26-0.42 eV range with strong linear dichroism, wherein a polarization-dependent feature is observed in the reflectance anisotropy spectra with a maximum near 0.33 eV. This feature is believed to be related to a direct interband transition E_0, which is permitted for linearly polarized incident radiation along the AC crystal direction and forbidden for the ZZ direction.

Keywords: Black phosphorous, reflectance anisotropy spectroscopy, in-plane anisotropy, FTIR spectroscopy

Funding: The study was supported by the Russian Science Foundation, grant 22-29-20141 and the St. Petersburg Science Foundation (grant under agreement 18/2022 dated April 14, 2022).

Citation: Khakhulin S.A., Lakuntsova O.E., Firsov D.D., Komkov O.S., Optical anisotropy of black phosphorus characterized by FTIR spectroscopy methods, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.2) (2023) 228–232. DOI: https://doi.org/10.18721/JPM.163.239

Материалы конференции
УДК 538.958
DOI: https://doi.org/10.18721/JPM.163.239

Характеризация анизотропии оптических свойств черного фосфора методами ИК фурье-спектроскопии

С.А. Хахулин✉, О.Е. Лакунцова, Д.Д. Фирсов, О.С. Комков

Санкт-Петербургский государственный электротехнический университет «ЛЭТИ», Санкт-Петербург, Россия

✉ khsmn@ya.ru

Аннотация. Методами ИК фурье-спектроскопии, такими как поляризованное пропускание и анизотропное отражение, охарактеризован кристалл черного фосфора – узкозонного слоистого полупроводника. Получены результаты существенной анизотропии вблизи края поглощения материала, а также поляризационно-зависимый сигнал при энергии, соответствующей прямому межзонному переходу.

Ключевые слова: черный фосфор, спектроскопия анизотропного отражения, ИК фурье-спектроскопия, узкозонные полупроводники, слоистые полупроводники

Финансирование: Работа выполнена при поддержке Российского научного фонда (грант № 22-29-20141) и Санкт-Петербургского научного фонда (грант по договору № 18/2022 от 14 апреля 2022 г.).

Ссылка при цитировании: Хахулин С.А., Лакунцова О.Е., Фирсов Д.Д., Комков О.С. Характеризация анизотропии оптических свойств черного фосфора методами ИК фурье-спектроскопии // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 3.2 № .16. С. 228–232. DOI: https://doi.org/10.18721/JPM.163.239

Introduction

Black phosphorus is a direct-gap layered semiconductor crystal with an interband transition energy of approximately 0.3 eV [1], which corresponds to the mid-IR range. The crystal consists of atomic layers connected to each other by weak van der Waals forces, enabling the production of single semiconductor layers via exfoliation. As the number of layers in the structure decreases, the material's band gap increases, with a monolayer having a value of approximately 2 eV. This property makes it possible to create photonic devices with a broad optical range from mid-IR to visible using black phosphorus layers [2, 3].

In the plane of layer, the black phosphorus crystal has two orthogonal nonequivalent crystallographic directions known as 'zigzag' (ZZ) and 'armchair' (AC). Differences in chemical bond lengths and atomic arrangement [4] result in significant anisotropy of optical properties. According to literature data, when the incident radiation is polarized along the AC direction, the absorption of optical radiation is orders of magnitude more intense [1]. This feature is crucial for creating polarization-sensitive emitters, detectors and modulators of optical radiation based on the material under consideration [5].

Despite the extensive research on the optical properties of black phosphorous, recent studies [6, 7] using photoluminescence have yielded varying bandgap energy values. The application of transmittance and reflectance spectroscopies [1, 8] in the corresponding studies has been limited due to the smooth nature of the spectra, making it challenging to obtain precise information about optical transition values.

As a result, we present an investigation of the optical properties of black phosphorus near its absorption edge using various Fourier-transform infrared (FTIR) spectroscopy methods with linearly polarized probe light. Additionally, to improve the accuracy of measurements and obtain more detailed information we use a novel modulation method of FTIR reflectance anisotropy spectroscopy (RAS).

Materials and Methods

In this work, a synthetic black phosphorus crystal bulk manufactured by HQGraphene was studied. To study the practically significant band structure characteristics of semiconductor black phosphorus, we employ polarization-sensitive optical spectroscopy techniques. Specifically, we utilize transmittance and reflectance spectroscopy while varying the direction of incident radiation polarization along the AC and ZZ crystallographic directions. By utilizing these methods, we are able to determine the absorption edge of black phosphorus and analyze its dependence on the polarization direction of the incident radiation.

To obtain detailed information regarding the in-plane anisotropy of black phosphorus optical properties, we employ a novel method of modulation FTIR reflectance anisotropy spectroscopy [9]. This method involves modulating the direction of probe radiation linear polarization within the sample plane along two orthogonal directions, namely x and y. Consequently, the measured value in this technique is the normalized difference in reflectance coefficients, expressed as $\Delta R/R = 2(R_x - R_y)/(R_x + R_y)$. In the case of black phosphorus, the two orthogonal directions are AC and ZZ.

All measurements were carried out using the Vertex 80 FTIR spectrometer. An InSb photodetector with the effective spectral range of 0.23–1.55 eV (0.8–5.4 um) was employed. ZnSe wire grid polarizers, operating within the spectral range of 0.062–0.827 eV (1.5–20 um), were utilized. Modulation of linear polarization was achieved with a ZnSe photoelastic modulator PEM-100 manufactured by Hinds Instruments.

Results and Discussion

The obtained transmittance spectra of black phosphorus are presented in Fig. 1. There are two different absorption edges for different polarization directions of the incident radiation. A sharp absorption edge was observed within the range of 0.26–0.3 eV with the position of linear polarization along the AC direction (Fig. 1, dash-dotted line). In the case of the ZZ direction, a uniform decrease was obtained within the range of 0.32–0.44 eV (Fig. 1, dotted line).

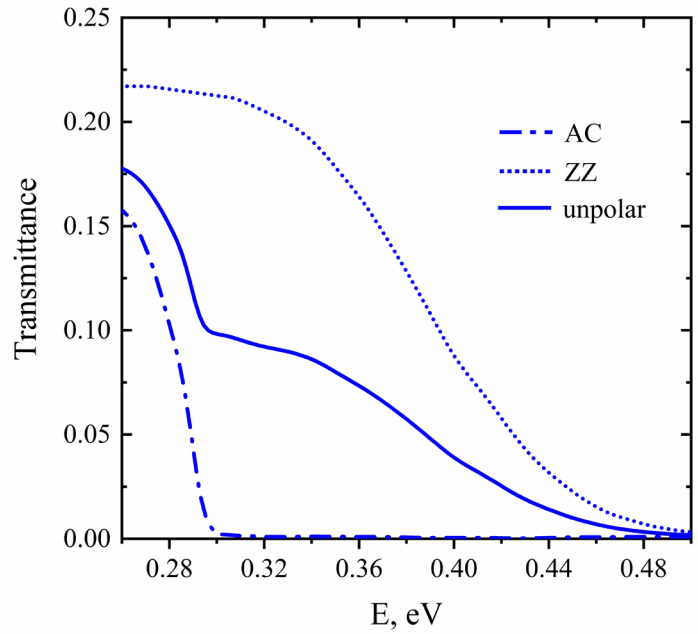

Fig. 1. Transmittance spectra of black phosphorous crystal. Spectrum obtained with direction of polarization along AC is dot-dashed, along ZZ is dotted. Spectrum with unpolarized probe radiation is solid

The dissimilarity in the transmittance curves' behavior is attributed to the variance in previously discussed oscillator strength, leading to intense absorption in the AC direction. Similarly, the polarized reflectance curves exhibit analogous behavior when the polarization of the incident radiation aligns with the corresponding crystallographic directions. As a result of such strong linear dichroism, transmittance spectrum with unpolarized incident radiation has a complicated form (Fig. 1, solid line). It should be noted that the spectrometer radiation is partially polarized, and the corresponding transmittance spectrum has a slightly reduced amplitude compared to the average of the spectra obtained for the AC and ZZ polarizations.

The presented transmittance spectra exhibit weak spectral features near an energy of 0.29 eV, which is attributed to the absorption of carbon dioxide CO_2 in the atmosphere. The state of the surface of industrially obtained black phosphorus crystals poses a significant challenge in the registration and interpretation of ordinary reflectance spectra, as well as the specifics of the mid-IR range in which studies are conducted. For this reason, reflectance spectra with linearly polarized probe light exhibit low signal-to-noise ratio wherein demonstrate the same spectral behavior with strong linear dichroism as transmittance spectra.

The use of a FTIR reflectance anisotropy spectroscopy modulation technique significantly enhances the signal-to-noise ratio and enables the detection of relatively small changes in the reflectance coefficient. This is made possible by modulating the direction of linear polarization along two in-pane orthogonal crystallographic axes described earlier in the *Materials and Methods* section.

The reflectance anisotropy (RA) spectrum obtained by the FTIR RAS method has a broad negative peak in the range of 0.26–0.42 eV (Fig. 2). This signal is associated with a significant anisotropy of the reflectance coefficients of black phosphorus in two orthogonal directions, ZZ and AC. This result correlates with polarized transmittance and reflectance measurements discussed earlier.

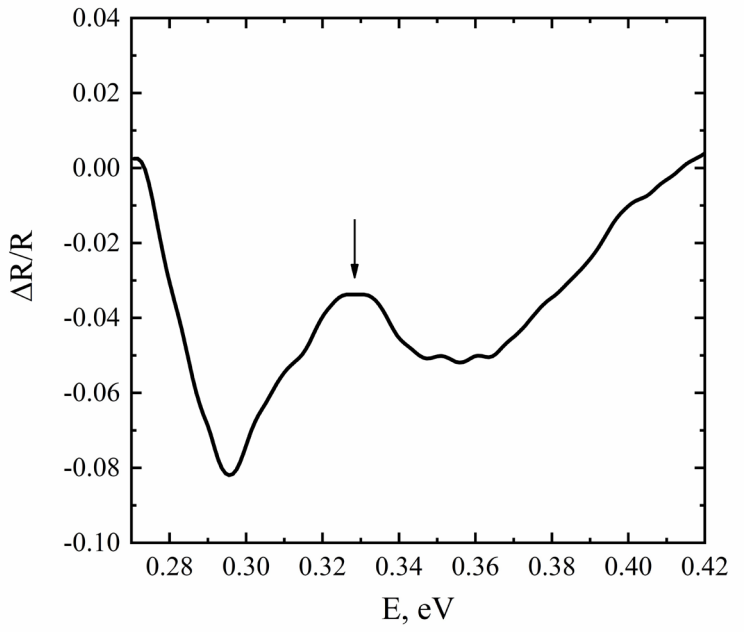

Fig. 2. Reflectance anisotropy spectrum of black phosphorous crystal. The peak associated with the main direct interband optical transition E_0 is marked by arrow

A relatively narrow peak of a different sign stands out against the background of a broad spectral line in the RA spectrum. An extremum of that peak is at an energy of 0.33 eV. Such a feature with an amplitude about several percent can be associated with a direct interband transition, which is allowed when the polarization of the incident light is along the AC direction and forbidden in the case of ZZ. In the study by Chen et al. (2019) [6], the energy of this transition was determined via photoluminescence and found to be 0.334 eV, while Zhang et al. (2020) [7] reported it to be 0.343 eV.

Conclusion

Thus, we have experimentally characterized the optical properties of black phosphorus that are related to the anisotropy of optical transitions in this material by methods of FTIR spectroscopy including the FTIR-RAS method. Within the 0.26–0.42 eV range, there exists a pronounced linear dichroism, accompanied by a polarization-dependent characteristic at 0.33 eV associated with the direct interband transition. The information obtained is in great demand for the development of polarization-sensitive photodetectors and light emitters in the mid-IR range based on black phosphorus.

REFERENCES

1. **Wang X., Lan S.,** Optical properties of black phosphorus, Advances in Optics and photonics. 8 (4) (2016) 618–655.

2. **Xia F., Wang H., Hwang J.C., Neto A.C., Yang L.,** Black phosphorus and its isoelectronic materials, Nature Reviews Physics. 1 (2019) 306–317.

3. **Huang L., Dong B., Guo X., Chang Y., Chen N., Huang X., Liao W., Zhu C., Wang H., Lee C., Ang K-W.,** Waveguide-Integrated Black Phosphorus Photodetector for Mid-Infrared Applications, ACS Nano 13 **(913 (2019) (1**–921.

4. **Akahama Y., Endo S., Narita S.,** Electrical properties of black phosphorus single crystals, Journal of the Physical Society of Japan. 52 (6) (1983) 2148–2155.

5. **Deng B., Frisenda R., Li C., Chen X., Castellanos-Gomez A., Xia F.,** Progress on black phosphorus photonics, Advanced Optical Materials. 6 (19) (2018) 1800365.

6. **Chen C., Chen F., Chen X., Deng B., Eng B., Jung D., Guo Q., Yuan S., Watanabe K., Taniguchi T., Lee M. L, Xia F.,** Bright Mid-Infrared Photoluminescence in Thin-Film Black Phosphorus. 19 (3) (2019) 1488–1493.

7. **Zhang Y., Wang S., Chen S., Zhang Q., Wang X., Zhu X., Zhang X., Xu X., Yang T., He M., Yang X., Li Z., Chen X., Wu M., Lu Y., Ma R., Lu W., Pan A.,** Wavelength-Tunable Mid-Infrared Lasing from Black Phosphorus Nanosheets. 32 (17) (2020) 1808319.

8. **Xin W., Jiang H.B., Sun T.Q., Gao X.G., Chen S.N., Zhao B., Yang J.L., Liu Z.B., Guo C.L.**, Optical anisotropy of black phosphorus by total internal reflection, Nano Materials Science. 1 (4) (2019) 304–309.

9. **Firsov D.D., Khakhulin S.A., Komkov O.S.,** Fourier-Transform Infrared Reflection Anisotropy Spectroscopy of Semiconductor Crystals and Structures: Development and Application in the Mid-Infrared, Applied Spectroscopy. 77 (5) (2023) 470–481.

THE AUTHORS

KHAKHULIN Semyon A.
khsmn@ya.ru
ORCID: 0000-0002-1780-2013

FIRSOV Dmitrii D.
ddfirsov@gmail.com
ORCID: 0000-0001-7608-9580

LAKUNTSOVA Olga E.
olya-lakuncova@mail.ru
ORCID: 0000-0000-0000-0000

KOMKOV Oleg S.
okomkov@yahoo.com
ORCID: 0000-0002-8999-1175

Received 05.07.2023. Approved after reviewing 09.08.2023. Accepted 09.08.2023.