Development of technology for plasma-enhanced chemical vapor deposition of boron phosphide at low temperatures

© A.A. Maksimova[1,2], A.V. Uvarov[1], E.A. Vyacheslavova[1], A.I. Baranov[1], A.S. Gudovskikh[1,2]

[1] Alferov Federal State Budgetary Institution of Higher Education
and Science Saint Petersburg National Research Academic University
of the Russian Academy of Sciences,
St. Petersburg, Russia
[2] St. Petersburg State Electrotechnical University „LETI"
St. Petersburg, Russia

E-mail: maksimova_alina@spbau.ru

Received May 19, 2023
Revised July 17, 2023
Accepted October 30, 2023

In this work, boron phosphide was deposited on silicon substrates using plasma-chemical deposition at a low temperature (350°C) for the first time. The following precursors were used: a gas mixture of diborane (B_2H_6/H_2) and pure phosphine (PH_3). The Raman spectra of the original samples showed broadened peaks at 450 cm^{-1} and $\approx$ 700 cm^{-1} corresponding to amorphous boron phosphide. Annealing of the samples affected the structure of the layers and led to partial crystallization; a peak of crystalline boron phosphide was detected at 823 cm^{-1}.

Keywords: boron phosphide, PECVD, scanning electron microscopy, Raman spectroscopy.

DOI: 10.61011/PSS.2023.12.57678.5207k

1. Introduction

Boron phosphide (BP) is a new material for use in photovoltaics that has a number of attractive characteristics. BP is chemically inert, resistant to oxidation at high temperatures, has high thermal conductivity and mechanical stability [1]. It was also theoretically shown that BP is one of the most promising materials for creating transparent conductive coatings of *p*-type, since it is an indirect band gap semiconductor with a band gap of 2.1 eV, while the band gap for direct junction is 4 eV, which implies low optical losses [2]. Due to this, the use of boron phosphide to create heterostructural solar cells (SCs) can help to increase the short-circuit current compared to the use of amorphous hydrogenated silicon (*a*-Si:H). On the other hand, the negative (-0.3 ± 0.1 eV) break of the valence band (ΔE_V) for the BP/Si interface [3] provides the necessary selectivity, which makes boron phosphide an excellent candidate for *p*-type selective contact without requiring an additional indium tin oxide (ITO) layer. The efficiency of the *p*-BP/*n*- Si/*n*-GaP structure calculated using the AFORS-HET program can reach values of up to 28% [4].

The growth of boron phosphide on Si substrate can be carried out by various methods: halide vapor phase epitaxy (HVPE) at a temperature of 1030°C [5], chemical vapor deposition (CVD) at 800–900°C [6], by metal-organic chemical vapor deposition (MOCVD) at 850°C [7]. Also sometimes the method of high-frequency (HF) reactive magnetron sputtering at 450°C is used [8].

For most photovoltaic devices, including solar cells, low layer deposition temperatures are preferred to reduce overall production costs. In this paper, it is proposed to use the plasma enhanced chemical vapor deposition (PECVD) method. This is a reliable industrial method that allows the growth of electronic quality films at low temperatures (250–400°C) over large areas.

In this paper the boron phosphide layers were grown in Oxford PlasmaLab 100 PECVD unit (13.56 MHz) on crystalline silicon (100) substrates at a low substrate temperature (350°C). The following were used as precursors: a gas mixture of diborane (B_2H_6/H_2-2%) and pure phosphine (PH_3), which were subsequently diluted with hydrogen (H_2) in the ratio 2/1/10. Deposition was carried out at different plasma powers (20, 100, 200 W) at a constant pressure of 1000 mTorr. The deposition process parameters are given in the Table. The thickness of the layers was estimated using Horiba PZ2000 laser ellipsometer with 632.8 nm He-Ne source. Using scanning electron microscopy (SEM) in Zeiss Supra 25 unit, the structural properties and surface morphology of boron phosphide layers deposited on silicon substrate were studied. SEM images of the sample at high power 200 W (Figure 1) showed that the layer surface has an uneven structure, which may be due to the effusion of hydrogen that diffused into the Si substrate at high deposition power, so in subsequent processes the power was reduced to 100 and 20 W. A decrease in power led to an improvement in the morphological properties of boron phosphide films.

Parameters of the deposition process of boron phosphide layers

Power, W	20	100	200
Depositing time, min	30	20	20
Growth rate, nm/min	6.9	9.75	18.9
Thickness, nm	208	195	378

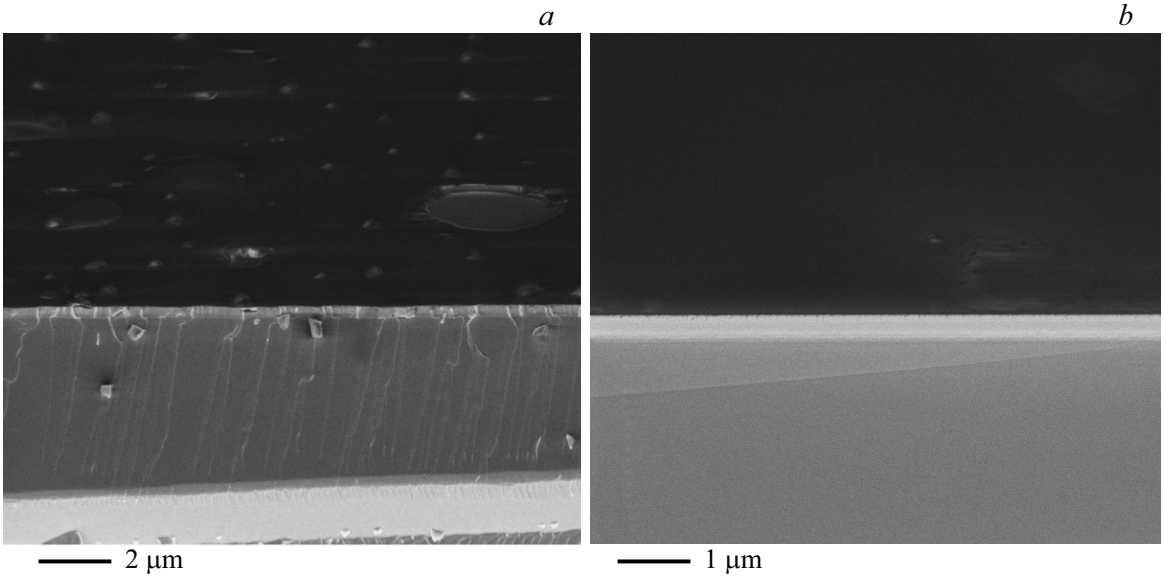

Figure 1. Scanning electron microscopy images of boron phosphide layers on silicon substrate: *a* — 200, *b* — 20 W.

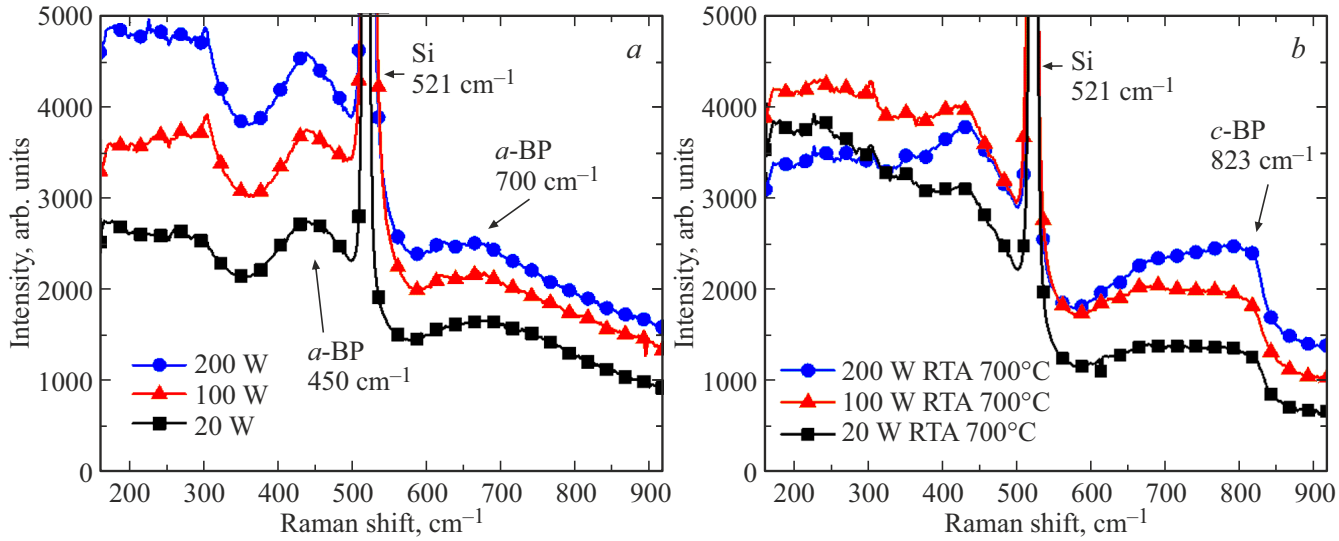

Figure 2. Raman scattering spectra of boron phosphide layers on silicon substrate: *a* — initial, *b* — after high-temperature annealing at 700°C.

The compositional properties of the layers were studied using Raman scattering spectroscopy. The measurements were carried out using ENSPECTR R532 Raman spectrometer with a 532 nm laser source, with an optimal integration time of 3000 msec and averaging by 100 times.

Figure 2 shows the Raman scattering spectra of the initial samples and after rapid thermal annealing of the structures for 1 min at high temperature of 700°C in inert nitrogen (N_2) atmosphere in the Jipelec JetFirst 100 unit.

The Raman scattering spectra of all samples showed broadened peaks at 450 cm^{-1} and $\approx$ 700 cm^{-1} (Figure 2, *a*), corresponding to amorphous boron phosphide [9]. Also in all spectra there is a high-intensity response from the silicon substrate at 521 cm^{-1}. Annealing of the samples affected the structure of the layers and led to partial crystallization; a broadened peak of crystalline boron phosphide was detected at 823 cm^{-1} (Figure 2, *b*) [10].

Figure 3 shows the characteristic electron energy loss spectrum (EELS) of boron phosphide layer deposited at power of 20W on the silicon substrate. Using this method, the stoichiometric ratio of elements was estimated: the proportion of boron is about 40% and phosphorus is about 60%. The image obtained using Jeol JEM-2100F transmission microscope shows the smooth and uniform structure of the boron phosphide layer.

Thus, in this paper, boron phosphide was successfully deposited onto silicon substrates at low temperatures using the plasma chemical deposition method. Scanning electron mi-

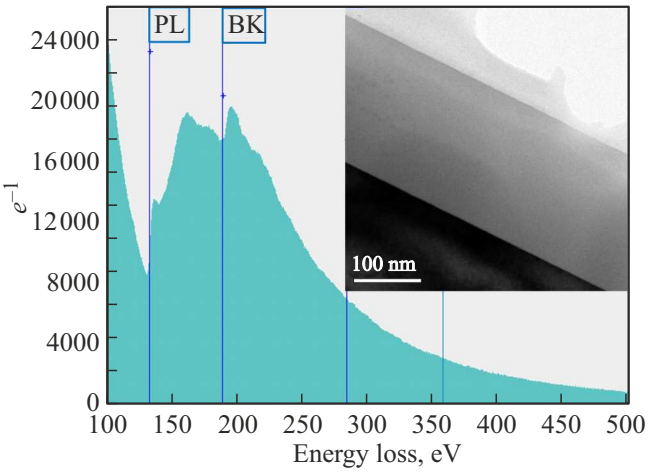

Figure 3. Characteristic electron energy loss spectrum (EELS) of boron phosphide layer (20 W) and transmission microscopy image of the layer.

croscopy showed that the surface of the layer grown at high plasma power has homogeneous structure, but decrease in power leads to improved homogeneity. Measurements of Raman scattering spectra showed that the initial layers are amorphous, but rapid high-temperature annealing at a temperature of 700°C led to partial crystallization of the layers.

Funding

The study was carried out as part of project of the Russian Science Foundation No. 21-79-10413 https://rscf.ru/

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M. Neuberger. III–V Semiconducting Compounds. Springer, Boston (1971).
[2] J.B. Varley, A. Miglio, V.-A. Ha, M.J. van Setten, G.-M. Rignanese, G.Hautier. Chem. Mater. **29**, *6*, 2568 (2017).
[3] S.W. King, M. French, M. Jaehnig, M. Kuhn, G. Xu. ECS J. Solid State Sci. Technol. **1**, *5*, P250 (2012).
[4] A.S. Gudovskikh, D.A. Kudryashov, A.I. Baranov, A.V. Uvarov, I.A. Morozov. Pisma v ZhTF **47**, *2*, 49 (2021). (in Russian).
[5] S. Nishimura, H. Hanamoto, K. Terashima, S. Matsumoto. Mater. Sci. Eng. B **93**, *1–3*, 135 (2002).
[6] J.K.C. Abbott, J.D. Brasfield, P.D. Rack, G.J. Duscher, C.S. Feigerle. MRS Proceed. **1432**, 65 (2012).
[7] M. Odawara, T. Udagawa, G. Shimaoka. Appl. Surf. Sci. **244**, *1–4*, 289 (2005).
[8] Z.C. Jia, J.Q. Zhu, C.Z. Jiang, W.X. Shen, J.C. Han, R.R. Chen. Appl. Surf. Sci. **258**, 356 (2011).
[9] V.-A. Ha, B. Karasulu, R. Maezono, G. Brunin, J.B. Varley, G.-M. Rignanese, B. Monserrat, G. Hautier. Phys. Rev. Mater. **4**, 065401 (2020).
[10] V.L. Solozhenko, O.O. Kurakevych, Y. Le Godec, A.V. Kurnosov, A.R. Oganov, J. Appl. Phys. **116**, *3*, 033501 (2014).

Translated by I.Mazurov