

PHYSICAL ELECTRONICS

Conference materials

UDC 621.315.592

DOI: <https://doi.org/10.18721/JPM.153.323>

Plasma deposited indium phosphide and its electrophysical properties

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Abstract. In this article, indium phosphide (InP) layers were grown using the method of plasma-chemical atomic layer deposition on crystalline silicon substrates for the first time. Trimethylindium (TMI) was used as a source of indium, and phosphine (PH₃) was used as a source of phosphorus. Properties of InP layers were evaluated, such as structural properties, electrical conductivity, type of conductivity and carrier concentration to integrate them into a c-Si-based solar cell. Root-Mean-Square (RMS) roughness measurements showed that the use of intermediate annealing in Ar plasma after the stage of deposition of a phosphorus monolayer leads to a significant decrease in roughness to the level of fractions of nanometers. The composition of the InP layers according to the energy dispersive X-ray spectroscopy (EDX) was close to stoichiometric. The measurements of dark IV characteristics showed that the InP layer has a donor type of conductivity. I–V characteristics of InP/p-Si structure under solar spectrum illumination, show open circuit voltage of $V_{oc} = 0.48$ V. Van der Pauw measurements demonstrate high concentration of carriers and their high mobility. Thus, the possibility of using InP-based layers for solar cells was shown.

Keywords: silicon, solar cells, indium phosphide, plasma enhanced chemical vapor deposition, atomic layer deposition

Funding: This study was funded by Ministry of Science and Higher Education of the Russian Federation (research project 0791-2020-0004).

Citation: Maksimova A. A., Uvarov A. V., Kirilenko D. A., Baranov A. I., Vyacheslavova E. A., Gudovskikh A. S., Plasma deposited indium phosphide and its electrophysical properties. St. Petersburg State Polytechnical University Journal. Physics and Mathematics, 15 (3.3) (2022) 123–127. DOI: <https://doi.org/10.18721/JPM.153.323>

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Материалы конференции

УДК 621.315.592

DOI: <https://doi.org/10.18721/JPM.153.323>

Плазменно-осажденный фосфид индия и его электрофизические свойства

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Аннотация. Впервые методом плазмохимического атомно-слоевого осаждения были выращены слои фосфида индия (InP). В качестве источника индия выступал триметиллиндий (ТМИ), а в качестве источника фосфора – фосфин (PH₃). Были оценены структурные свойства слоев InP, а также электропроводность, тип проводимости и концентрация носителей. Состав слоев InP по данным энергодисперсионной рентгеновской спектроскопии (EDX) близок к стехиометрическому. Выращенные слои имеют донорный тип проводимости, световые ВАХ продемонстрировали напряжение холостого хода Voc=0.48 В. Таким образом, была оценена возможность использования слоев на основе InP для создания солнечных элементов.

Ключевые слова: кремний, солнечные элементы, фосфид индия, плазмохимическое осаждение, атомно-слоевое осаждение

Финансирование: Работа выполнена в рамках Госзадания № 0791-2020-0004 «Исследования по разработке новых физико-технологических подходов формирования фотоэлектрических преобразователей солнечной энергии на основе кремния».

Ссылка при цитировании: Максимова А. А., Уваров А. В., Кириленко Д. А., Баранов А. И., Вячеславова Е. А., Гудовских А. С., Плазменно-осажденный фосфид индия и его электрофизические свойства // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2022. Т. 15. № 3.3. С. 123–127. DOI: <https://doi.org/10.18721/JPM.153.323>

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Introduction

Indium phosphide (InP) is a promising material for applications in various areas of electronics due to its distinctive properties such as high electron mobility (higher than that of silicon, germanium and gallium arsenide) and high band gap value (1.3 eV). In this regard, InP has found application in power and high-frequency electronics. InP-based solid solutions are widely used to create light emitting diodes (LEDs), laser diodes, and avalanche photodiodes. InP has good optical and electronic properties, it is also a direct-gap semiconductor, due to which it has found application in the creation of photonic integrated circuits. The above properties also make indium phosphide an attractive material in solar cells (SCs) fabrication. According to [1], the efficiency of SCs based on InP under standard conditions reaches 21.9%.

Recently, research has been actively conducted on the creation of solar cells based on the integration of third group elements A₃B₅ compounds with silicon (Si) in order to reduce the cost and increase the efficiency of solar cells. Thus, it is possible to create solar cells based on the InP/Si heterojunction.

Materials and Methods

In this work, we propose to use the method of plasma-chemical vapor deposition (PECVD) for the growth of InP films. It is a reliable industrial method, which allows the growth of electronic quality films at low temperatures over large areas. Plasma-chemical deposition methods make it possible to form layers several nanometers thick, which play the role of both passivating and highly doped layers at relatively low temperatures on an industrial scale. A low-temperature (250–380 °C) plasma-chemical technology for the synthesis of thin GaP layers on Si [2] and the possibility of their donor doping [3] have recently been developed.

Phosphide layers were grown by atomic layer deposition (ALD) using an Oxford Plasmalab 100 PECVD setup. The InP films were deposited on p- and n-type silicon substrates at a temperature of 380 °C. Trimethylindium (TMI) was used as a source of indium and phosphine (PH₃) was used as a source of phosphorus. The decomposition of TMI was due to temperature, and the decomposition of phosphine was due to RF plasma with a power of 200 W (Fig. 1). Annealing in argon plasma was performed at the end of each cycle. The growth rate was 0.17 nm/cycle, which corresponds to the growth of 0.7 monolayers per cycle.

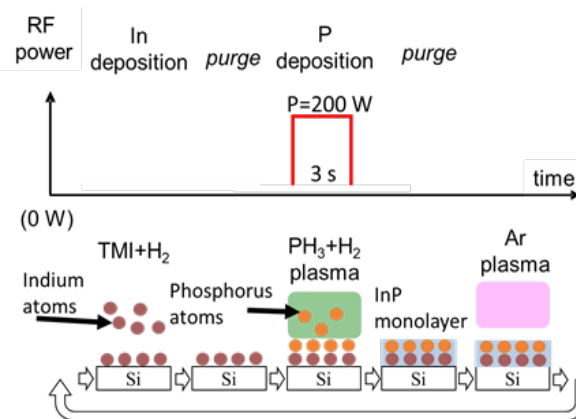


Fig. 1. Scheme of the deposition process

Results and Discussion

InP layers have a fairly rough surface with a root mean square (RMS) roughness of 3–5 nm, which is due to their microcrystalline structure. The use of intermediate annealing in Ar plasma after the stage of deposition of a phosphorus monolayer immediately before deposition of indium leads to a significant decrease in the roughness to the level of fractions of nanometers. The use of additional annealing in the Ar plasma does not lead to an increase in the growth rate. The composition of the InP layers according to energy dispersive X-ray diffraction (EDX) data was close to stoichiometric within the measurement errors.

The Raman spectra distinguish the LO peak at 341.9 cm^{-1} , which is characteristic of crystalline InP. Another L– peak characteristic of InP at 303.7 cm^{-1} merges with the response from the Si substrate at 303.44 cm^{-1} , which greatly complicates its identification [4].

Transmission electron microscopy (TEM) measurements (Fig. 2) showed that the InP film has thickness about 50 nm. A preferred orientation of the film grains is observed, consistent with the structure of the substrate. High angle annular dark-field scanning transmission microscopy (HAADF STEM) image is presented on Fig. 2, *c*), the sample position is on the left and on the right is the sample holding carbon glue. The EDX maps show high In and P content in deposited layer, which indicates successful InP layer growth. In addition, a layer at the interface with a small amount of O and C was detected, which can be connected with the insufficient treatment of the Si substrate before deposition process.

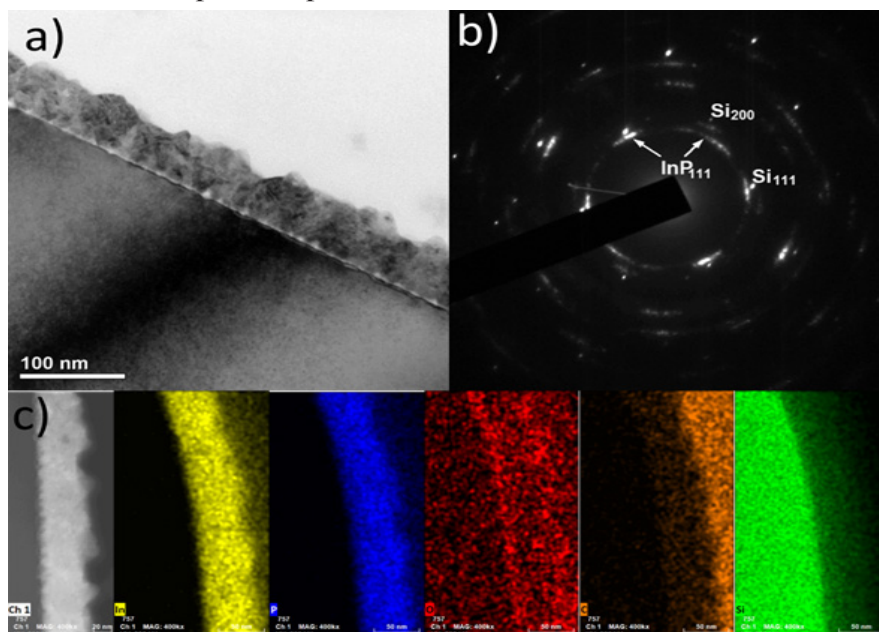


Fig. 2. TEM film images (a); electron diffraction pattern image (b); HAADF STEM image and distribution maps of the main elements (c)

To study the electrical properties of the resulting InP/Si heterojunctions to InP layers and silicon substrates, metal contacts were formed and the current-voltage characteristics (I-V) of the obtained structures were measured. An ohmic back contact to n-Si (10^{15} cm^{-3}) was formed by successive deposition of a highly doped n-GaP layer 5 nm thick and indium, while on p-Si (10^{16} cm^{-3}) indium was directly deposited without additional layers. Indium dot contacts were deposited on the front side of the InP layers.

As a result, the I-V characteristic across the InP/n-Si heterojunction has a ohmic linear form (Fig. 3), characteristic of a low resistance value, and not of a diode: this means that the resulting InP layer has a donor type of conductivity with a high concentration of free electrons. On the contrary, the dark I-V curves of InP/p-Si structure has an asymmetrical behavior: a low reverse bias current and an exponential increase in current at forward bias, which proves the presence of a p-n junction and confirms the donor type of InP layer conductivity. Further, the I-V characteristics of InP/p-Si structure under solar radiation spectrum illumination were measured, as a result of which open circuit voltage of $V_{oc} = 0.48 \text{ V}$ was obtained, which confirms the possibility of using InP-based layers for solar cells fabrication.

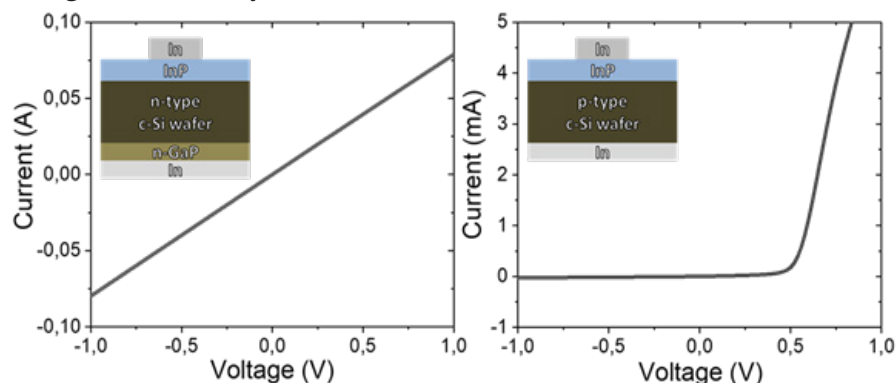


Fig. 3. Dark current-voltage characteristics for InP on n-type Si structure (a); InP on p-type Si structure (b)

Studies of electrical conductivity, type of conductivity and carrier concentration were carried out by the Van der Pauw 4-probe method at a temperature of 25°C [5]. To do this, the obtained structures were divided into square samples at the corners of which point ohmic contacts to the InP layer were formed. The measurements were carried out using a measuring bench based on a Keithley 2401 precision source-meter and NdFeB permanent magnets with a uniform magnetic field of 0.56 T. Results are presented in Table 1.

Table 1

Van der Pauw measurements

	Surface resistance of the layer, Ohm/sq	Surface concentration of carriers, cm^{-2}	Carrier concentration (for $d = 50 \text{ nm}$), cm^{-3}	Carrier mobility, $\text{cm}^2/(\text{V}\cdot\text{s})$
InP/p-Si	$8.82 \cdot 10^3$	$-5.25 \cdot 10^{12}$	$-1.04 \cdot 10^{18}$	136
InP/quartz	$1.66 \cdot 10^6$	$-8.55 \cdot 10^{11}$	$-1.71 \cdot 10^{17}$	3.7

The surface resistance of InP layers on silicon and quartz substrates was $8.82 \cdot 10^3 \text{ Ohm/sq}$ and $1.66 \cdot 10^6 \text{ Ohm/sq}$, respectively. Large values of conductivity on silicon substrates are due either to the better structural properties of the InP layer or to the presence of leakage currents through the silicon substrate. The surface concentration and mobility of carriers in the InP layer are: $-5.25 \cdot 10^{12} \text{ cm}^{-2}$ and $136 \text{ cm}^2/(\text{V}\cdot\text{s})$ on silicon substrates; $-8.55 \cdot 10^{11} \text{ cm}^{-2}$ and $3.7 \text{ cm}^2/(\text{V}\cdot\text{s})$ on quartz substrates.

InP layers both on p-Si and quartz substrates have predominantly electronic type of conductivity, which indicates the absence of leakage currents through the silicon substrate with p-type conductivity. The mobility of layers on different substrates differs significantly, which also indicates the best structural properties of InP on silicon substrates. It should be noted that the resistivity of InP ($8.3 \text{ } \Omega \text{ cm}$) on quartz substrates is much lower than the resistance of GaP on quartz substrates (more than $5 \cdot 10^3 \text{ } \Omega \text{ cm}$) obtained by the same method.



Conclusion

In this work, a technology was developed to deposit layers of indium phosphide (InP) by plasma-chemical atomic layer deposition using trimethylindium (TMI) and phosphine as precursors.

RMS measurements showed that the use of intermediate annealing in Ar plasma after the stage of deposition of a phosphorus monolayer leads to a significant decrease in roughness to the level of fractions of nanometers and does not lead to an increase in the growth rate. A preferred orientation of the film grains is observed, consistent with the structure of the substrate by TEM measurements.

The measurements of dark IV characteristics showed that the InP layer has a donor type of conductivity. I–V characteristics of InP/p-Si structure under solar radiation spectrum illumination were measured, as a result of which open circuit voltage of $V_{oc} = 0.48$ V was obtained. Comparative measurements of the conductivity of InP layers on quartz and silicon indicate better mobility on silicon substrates than on quartz, which indicates their best structural properties. Thus, it is possible to use InP-based layers to create solar cells.

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Received 01.08.2022. Approved after reviewing 05.08.2022. Accepted 05.08.2022.