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Alexander S. Gudovskikh, Alexander V. Uvarov, Ivan A. Morozov, Artem I. Baranov, Dmitry A. Kudryashov, Ekaterina V. Nikitina, and Jean-Paul Kleider*

Significant progress in photovoltaic conversion of solar energy can be achieved by new technological approaches that will improve the efficiency of solar cells and make them appropriate for mass production. A new technological approach for the growth of III-V compounds on Si substrates using low temperature plasma-enhanced atomic layer deposition (PE-ALD) is explored in the paper. This technique, which consists of alternatively changing the phosphorus and gallium atom source flows providing the growth of one monolayer by cycle, was developed for the growth of GaP films on Si substrates in a standard PECVD setup at 380 °C using PH_3 and TMG (Trimethylgallium) as sources of III and V atoms. First (n)GaP/(p)c-Si anisotype heterojunction solar cell structures fabricated by PE-ALD exhibit open circuit voltage values similar to that obtained for (n)a-Si:H/(p)c-Si heterojunctions fabricated using the same (p)c-Si substrates. However (n) GaP/(p)c-Si solar cells demonstrates a potential to extend a high quantum efficiency in the short wavelength region due to lower absorption losses in the GaP emitter layer.

1. Introduction

Photovoltaic development requires to increase the efficiency of solar cells as well as to reduce their cost. One of the most successful ways to improve solar cell performance is the usage of heterostructures. There are various types of solar cells based on heterostructures which use different materials like silicon, III-V compounds, oxides etc. However there are basic requirements for the photovoltaic materials such as using abundant and environmental friendly elements as well as non expensive and energy-saving technologies. From this point of view, silicon can be considered as an ideal photovoltaic material since it is one of the most abundant elements on earth, and its production, purification and treatment have reached high level technology at relatively low cost. However, the traditional silicon solar cell manufacturing process at temperatures of 750–900 °C is quite energy-intensive. Thus a-Si:H/c-Si heterojunction solar cells, which fabrication process does not require high temperatures, are of great interest. The current state of the art demonstrates that this type of solar cells has a leading position in the conversion efficiency for terrestrial non-concentrated photovoltaic.[1] An efficiency of 25.1% has been achieved for this type of both-side contacted solar cell,[2] which is close to the theoretical limit for silicon single junction solar cells (28%). Limitations come from the a-Si:H top emitter that strongly absorbs photons above the bandgap around 1.7 eV, leading to the absorption of high energy photons, while the created photocarriers mostly recombine in the highly defective doped a-Si:H layer. Further increase of efficiency was achieved by turning to heterojunction interdigitated back contact cells (with the record efficiency of silicon cells of 26.3%[3]) but it could also be achieved in double-side contacted silicon-based heterostructures with a wider band gap emitter, which also provides a low density of surface states.

Thus, a heterostructure with a thin layer of gallium phosphide (GaP) on top of the Si absorber is of great interest. The lattice constant of GaP is very close to that of silicon, and the addition of small amounts of nitrogen can achieve full matching of the lattice parameters. Therefore a growth of lattice matched GaP layers on silicon, in theory, could provide formation of an interface with a minimum defect density. On the other hand GaP has a band gap of 2.26 eV and the use of thin layers (50–100 nm), almost completely eliminates the absorption in the visible region of the spectrum in these layers.

Conventional methods of synthesis of perfect III-V crystalline semiconductor layers, such as MOVPE and MBE normally use stationary processes with continuous sources of atoms flow. The process must take place at relatively high temperatures to provide effective migration of atoms on the surface and in some cases decomposition of the precursors. Decrease in temperature leads to a reduction of the structural quality of the formed layers. An additional high temperature step prior to the growth is also

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required to remove oxide and provide surface reconstruction. Requirement to use high temperatures makes it difficult to fabricate GaP/Si heterojunctions with high quality interfaces suitable for the use in photovoltaic structures. Interdiffusion processes of III-V compounds and group IV elements lead to a strong mutual doping. A formation of defective layer in Si near the surface was demonstrated after the molecular beam epitaxy of GaP,[4] as well as a significant drop of the minority charge carrier lifetime in the bulk of Si substrate was observed after GaP growth by MOVPE.[5]

Here a novel technological approach namely low-temperature plasma enhanced atomic layer deposition (PE-ALD) for the formation of GaP/Si heterojunctions is proposed. This technology allows one to fabricate solar cells at temperatures below 400 °C and enables easy process scaling for high throughput industrial equipment. The ALD technique is rather new and the list of materials, which could be deposited, expands every year. Significant progress has been achieved in the application of ALD for antireflection and passivation through Al_2O_3 coating on the silicon surface. The basic idea of the ALD technique is the sequential alternation of monolayer deposition cycles. This method has become widely used for oxides growth (ZnO, MoO_2, Ga_2O_3).[6] The first reports on the GaN semiconductor growth using PE-ALD have also appeared recently.[7] However, PE-ALD for growth of GaP layers was not yet applied.

2. Results and Discussions

2.1. GaP Deposition Technology

The basic idea of the method is to use a time modulation of the growth process, i.e. time separated stages of decomposition of precursors in glow discharge plasma, their transport to the growing surface, migration over the surface and the crystal lattice relaxation. The time interval between each stage is an addition degree of freedom that allows one to control the growth process. In case of GaP growth one monolayer of Ga atoms will alternate with the growth of one monolayer of P atoms. Based on the requirements to ensure potential large-scale production the sources of atoms that pass in the growth chamber are in gaseous form. Trimethylgallium (TMG) and phosphine (PH_3) can be used as precursors of Ga and P atoms, respectively. The schematic time diagram of the growth process is presented in **Figure 1**. In a first step the decomposition of hydrides or TMG in glow discharge plasma occurs, a monolayer of atoms is adsorbed on the surface. The next stage is a stimulation of the surface migration of adsorbed atoms by a glow discharge power with a simultaneous gas mixture change during the purge step. The time of the purge step should be enough to reduce the precursor concentration to a negligible level in order to avoid P and Ga deposition at the same time. The evacuation step could provide the fastest gas mixture change but it means a plasma interruption, while plasma ignition for TMG diluted in hydrogen atmosphere is difficult and can not be reliably realized for each cycle. Thus a continuous plasma process was performed using constant working gas flow. An addition of Si atoms deposition step from diluted silane (SiH_4) could provide an n-type doping of GaP.

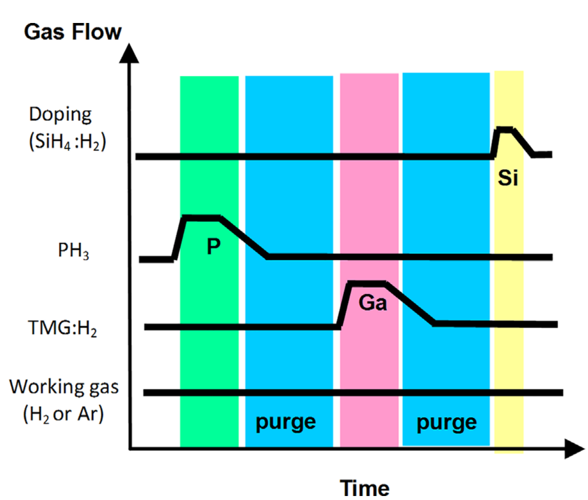

Figure 1. The time diagram of the growth process.

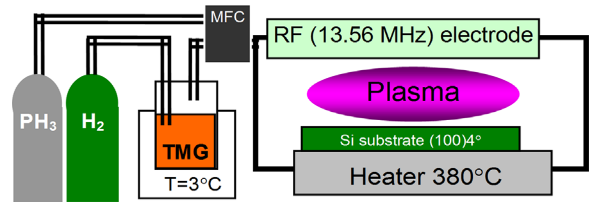

Figure 2. The schematic view of the PECVD setup.

The GaP layers were grown on p-type Si substrates by PE-ALD at 380 °C with PH_3 and TMG as sources of III and V atoms using the Oxford Plasmalab 100 PECVD (13.56 MHz) setup. The schematic view of the PECVD setup with capacitance coupled plasma is presented in **Figure 2**. Hydrogen was used as a gas carrier for TMG. Two different deposition modes were used: i) continuous PECVD mode; ii) PE-ALD mode with continuous plasma discharge due to Ar or H_2 flow addition during the purge step. For deposition of n-type doped layers 1% SiH_4 diluted in hydrogen was used as a source of Si doping atoms. The main deposition parameters are presented in **Table 1**. The minimal purge step time of 10 s was required for the used setup, being a main growth rate limiting parameter.

Scanning and transmission electron microscopy (TEM) demonstrate that the GaP films grown by the PE-ALD mode have homogeneous structure, smooth surface and a sharp GaP/Si interface (**Figure 3**a) while GaP films fabricated using the continuous PECVD mode exhibit inhomogeneous structure with voids (Figure 3b).

Table 1. Deposition conditions.

Parameter	PECVD	PE-ALD
RF power, W	5–100	5–20
Presure, mTorr	250–350	250–350
Deposition step time, s	–	2–10
Total gas flow, sccm	100–200	100

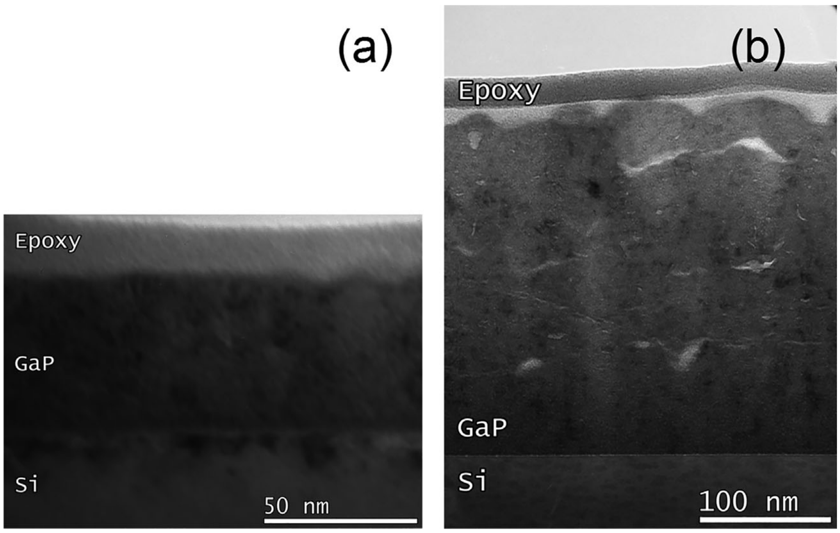

Figure 3. The TEM image of GaP/Si cross section deposited by PE-ALD (a) and PECVD (b) at 350 mTorr.

Photoluminescence (PL) measurements were used for the characterization of the passivation properties. PL is known to be a powerful tool to determine the interface properties in Si based heterojunctions.[8,9] The radiative recombination of excess carriers in the volume depends on the effective lifetime, which is affected by surface recombination. The signal of the PL from Si (at $\lambda = 1150\,nm$) decreases with increasing recombination rate at the GaP/Si interface. The PL spectra for GaP/Si samples deposited at different conditions are presented in **Figure 4**. The GaP/Si structures obtained in the PE-ALD mode exhibit higher PL intensity compared to that conventionally grown by continuous PECVD. However GaP/Si structures grown with hydrogen plasma demonstrate better passivation properties compared to that obtained with an Ar plasma. Indeed, a usage of Ar plasma leads to a decrease of effective lifetime in the Si substrate due to radiation defects, which are created in Si. A low bulk lifetime of Si (100) 4° off cut substrates (10 µs), which are used for GaP deposition, does not allow us to deduce the surface recombination velocity ($s_{GaP/Si}$) at the GaP/Si interface. The upper limit of $s_{GaP/Si} < 1000\,cm\,s^{-1}$ could be estimated only.

In contrary, an effect of hydrogen passivation of boron atoms (acceptor impurity deactivation) can appear for hydrogen plasma surface treatment of boron doped p-Si substrate.[10] The *C–V* profiling measurements were performed for the GaP/Si heterostructures grown on p-Si substrates (doped with boron) using hydrogen plasma. The concentration profile, which is presented in **Figure 5**, demonstrates constant electrically active acceptor impurity concentration indicating the absence of acceptor impurity deactivation during the deposition process. Therefore, PE-ALD with continuous hydrogen plasma seems to be the optimal process for further technology development.

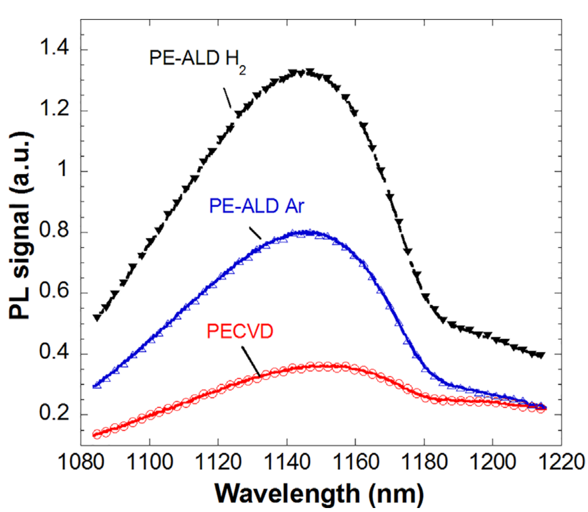

Figure 4. The PL spectra for GaP/Si samples fabricated by PECVD and PE-ALD using Ar and H_2 constant plasma (5W).

2.2. GaP/Si Solar Cells

Theoretical analysis demonstrated that for photovoltaic application the n-GaP/p-Si heterojunction has favorable band diagram compared to that of p-GaP/n-Si.[11] The GaP/Si interface has a significant valence band offset ($\Delta E_V = 0.8–0.95\,eV$) and relatively low conductance band offset ($\Delta E_C = 0.2–0.35\,eV$).[12,13] In case of the n-GaP/p-Si heterojunction (band diagram is shown in **Figure 6**) the transport of holes, which are generated in Si, is limited by the GaP/Si interface preventing surface recombination, while electrons can easily overpass through the spike

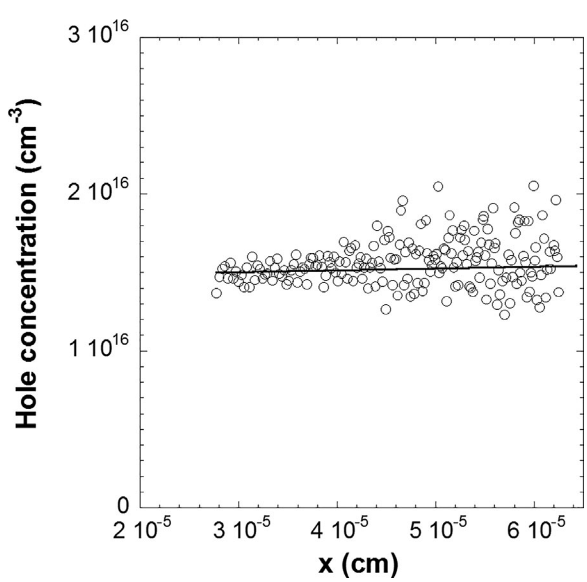

Figure 5. The concentration profile from *C–V* measurements for the n-GaP/p-Si heterostructures grown on p-Si boron doped substrates using hydrogen plasma (20 W).

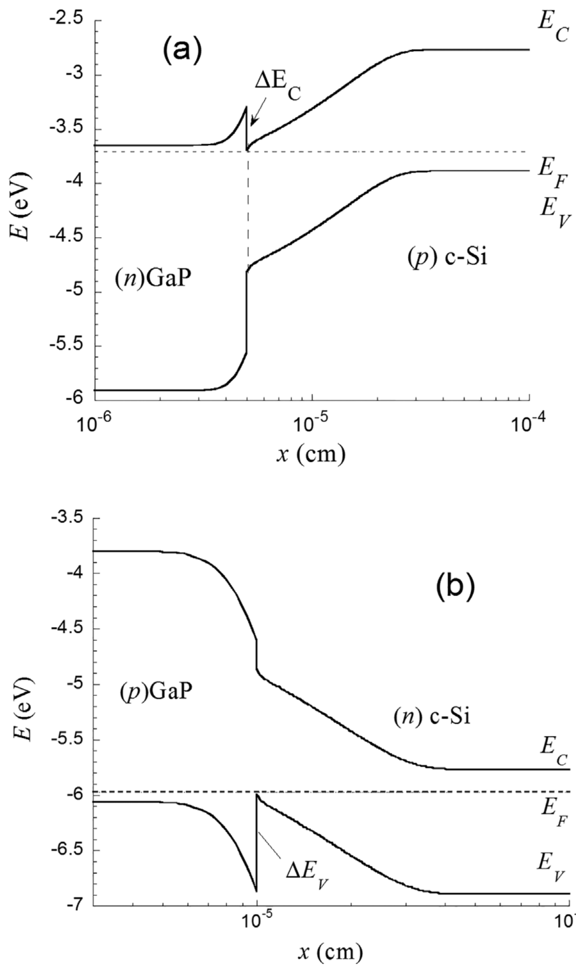

Figure 6. Calculated band diagrams of n-GaP/p-Si (a) and p-GaP/n-Si (b) heterojunctions.

formed by ΔE_C. In contrast, for the p-GaP/n-Si heterojunction the significant valence band offset forms a potential barrier which leads to total blockage of holes transport and therefore the photocurrent is limited. Thus, fabrication of n-GaP/p-Si heterojunction is of main interest.

Silicon doped n-type GaP layers of 50 nm thickness were deposited on p-type (10^{16} cm^{-3}) CZ Si (100) 4° off cut substrates using PE-ALD with constant hydrogen plasma to form n-GaP/p-Si heterojunctions. As a proof of concept the first solar cell structures based on the n-GaP/p-Si anisotype heterojunction were fabricated. The schematic view of the n-GaP/p-Si structures are presented in **Figure 7**. First type of structure was fabricated with Ti/Ag non-alloyed ohmic contacts evaporated on n-GaP to form a top electrode grid (Figure 7a). Double layer SiO_2(100 nm)/Si_3N_4(70 nm) anti-reflection coating (ARC) was deposited on the front side by PECVD. The second type of the structure was formed using ITO (100 nm) layer, which was sputtered on the top of n-GaP emitter to form contact and reduce reflection (Figure 7b). Silver past top electrode was used for electric measurements. Bottom contact was formed using indium in the both cases.

To determine the impact of GaP emitter to optical properties of solar cell a-Si:H/c-Si reference cell with the same 12 nm thick

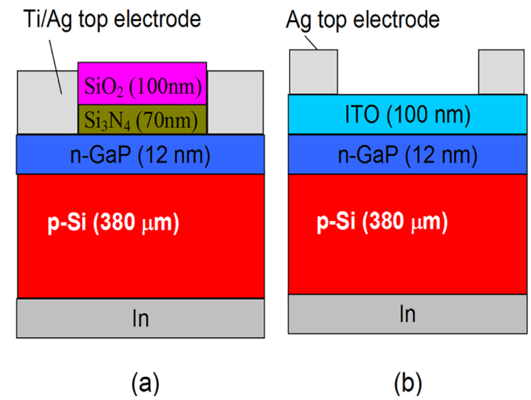

Figure 7. The schematic view of the n-GaP/p-Si solar cell fabricated by PE-ALD with SiO_2/Si_3N_4 ARC (a) and ITO layer (b).

emitter was fabricated. The deposition conditions of a-Si:H lead to 1 ms effective lifetime values on FZ Si wafers demonstrating the good passivation properties of our a-Si:H layers.

The I-V curve under one sun (AM1.5G, 100 mW cm^{-2}) illumination and external quantum efficiency (EQE) spectra of n-GaP/p-Si structures with Ti/Ag and Ag/ITO contacts are presented in Figures 8 and 9a, respectively. The metal contact geometry and thicknesses of SiO_2/Si_3N_4 ARC as well as ITO layer are far to be optimized. Thus fill factor (FF) and absolute value of EQE are relatively low. Nevertheless it is clearly seen that *I–V* curve of the structure with ITO contact exhibits a S-shape, which significantly reduce the solar cell performance compared to the structure with Ti/Ag contact. Indeed Ti/Ag contact to n-GaP has a ohmic behavior with a contact resistivity of 0.17nOhm cm^2, while ITO has non ohmic contact to n-GaP. Moreover, ITO leads to strong optical losses in the short wavelength region compared to dielectric layer ARC. Thus the design with metal ohmic contact and dielectric ARC is preferable for solar cells based on n-GaP/p-Si heterojunction.

The low values of open circuit voltage Voc (0.5 V) for both types of solar cells are related to the low bulk lifetime of the used

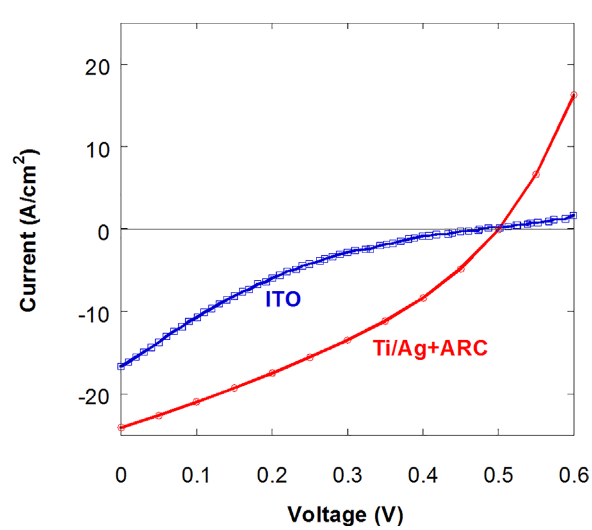

Figure 8. The I-V curve under AM1.5G illumination of n-GaP/p-Si structures with Ti/Ag and ITO contacts.

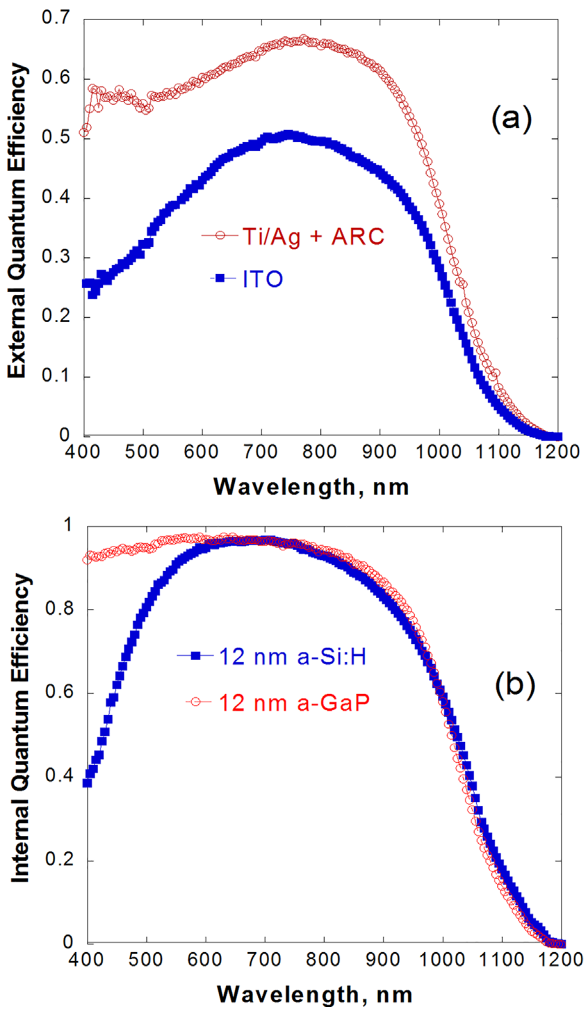

Figure 9. The external quantum efficiency (EQE) of n-GaP/p-Si structures with SiO_2/Si_3N_4 ARC and ITO (a). The internal quantum efficiency (IQE) of a-Si:H/c-Si reference cell and n-GaP/p-Si structure with the same emitter thickness of 12 nm (b).

Si substrate (about 10 µs) and by the poor back contact properties. The a-Si:H/c-Si reference cell demonstrates the same V_{oc} values of 0.5 V.

To estimate the potential of the n-GaP/p-Si heterostructures with zero reflection losses the internal quantum efficiency (IQE) spectrum was calculated as IQE=EQE/(1-R) (**Figure 9**b). A significant increase of short circuit current due to enhanced quantum efficiency in the short wavelength region could be achieved due to low absorption of GaP emitter. Indeed, comparing IQE of the structures with the same thickness (12 nm) of GaP and a-Si:H emitters a drop of quantum efficiency in the short wavelength range due to strong absorption in a-Si:H is observed for a-Si:H/c-Si. On the contrary, the IQE of n-GaP/p-Si is much higher in short wavelengths due to weak absorption in the GaP layer. Thus the obtained results demonstrate a high potential of the PE-ALD technology for new silicon based photovoltaic heterostructures.

3. Conclusions

Possibility of GaP deposition on Si wafers at temperature below 400 °C by plasma technology was shown. The advantage of the ALD mode with alternatively changing the phosphorus and gallium atom source flows, which allows one to obtain better structural and optical properties, compared to the continuous mode was demonstrated. For the first time anisotype heterojunction solar cell structures based on Si doped n-GaP deposited on p-Si substrate were fabricated by PE-ALD at a temperature less than 400° C. The demonstrated results are promising because the proposed technology is easily scalable for mass production.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

atomic layer deposition, GaP/Si heterojunction, plasma technology, solar cell

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