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Study of photoconvertion heterojunction *n*-GaP/*p*-Si obtained by PE-ALD

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Abstract. Plasma-enhanced atomic layer deposition is an attractive method for producing *n*-GaP layers at low temperatures on *p*-Si wafers for further photovoltaic application of *n*-GaP/*p*-Si heterostructures. In this study, we explore the influence of growth conditions on the electrophysical quality of thin *n*-GaP layers. It was established from admittance spectroscopy and current-voltage characteristics that the activation energy of conductivity in GaP decreases from 0.08 eV to 0.04 eV, with an increase in phosphine flow during the phosphorous step, and a subsequent drop to an extremely low value (< 0.02 eV) when additional flow of silane was added. This leads to extreme improve photovoltaic performance of the ITO/*n*-GaP/*p*-Si sample due to suppression of inflection on the *I*—*V* curve leading to an increase in the short-circuit current and the fill factor. Fruthermore, a deep level with the activation energies ranging from 0.50 to 0.55 eV and the capture cross-section $\sigma_T = (1\text{–}10)\cdot 10^{-16}$ cm^2 was detected in all layers.

Keywords: solar cell, GaP/Si heterojunction, admittance spectroscopy, atomic-layer deposition

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Исследование фотопреобразовательных гетеропереходов *n*-GaP/*p*-Si, полученных методом PE-ALD

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Аннотация. Атомно-слоевое плазменно-стимулированное осаждение является одним из перспективных методов для формирование *n*-GaP слоев при низких температурах на подложках *p*-Si для последующего использования в качестве фотопреобразовательных структур гетероперехода *n*-GaP/*p*-Si. В данной работе, было исследовано влияние остовых параметров на электрофизические свойства *n*-GaP. Согласно измерениям спектроскопии полной проводимости и вольт-амперных характеристик показано, что энергия активации проводимости в GaP слое уменьшается с 0.08 эВ до 0.04 эВ с увеличением потока фосфина и времени его взаимодействия с подложкой во время шага осаждения фосфора, а при добавлении дополнительного потока силана на шаге осаждения фосфора она значительно уменьшается и становится меньше 0.02 эВ. Это приводит к значительному улучшению производительности солнечного элемента ITO/*n*-GaP/*p*-Si вследствие уменьшения перегиба на ВАХ, что приводит к увеличению тока короткого замыкания и фактора заполнения. Кроме того, во всех образцах был обнаружен глубокий дефектный уровень с энергией активации E_a = 0.50–0.55 eV и сечением захвата $\sigma_T = (1–10)\cdot 10^{-16}$ cm^2.

Ключевые слова: солнечный элемент, GaP/Si гетеропереход, спектроскопия полной проводимости, атомно-слоевое осаждение

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Introduction

GaP is one of the promising materials for double-junction solar cells on silicon wafers [1] since the lattice mismatch between Si and GaP is less than 0.4%, and adding nitrogen to GaP will make it possible to vary the band gap of GaP(N) in the wide range from 1.7 eV to 2.1 eV [2]. Recently, an interesting method of plasma-enhanced atomic-layer deposition (PE-ALD) at temperatures below 400 °C was demonstrated for obtaining thin layers of GaP on *p*-Si wafers [3]. This technology is based on alternative interaction of phosphorous and gallium precursors with silicon surface in PECVD chamber. The main advantage of this method is that the film growth is based on the self-limiting mechanism, i.e., it is impossible to deposit more than one monolayer in one cycle, which ensures high uniformity and conformity of the film thickness. Previously, the fundamental possibility of donor doping of a GaP film grown by the PE-ALD method with the additional silane flow was shown [4], but direct influence of silane flow on quality of doping have not been shown yet. However, this process includes argon treatment leading to the formation of defects with a high concentration in bulk silicon wafers [5]. In addition, high power of hydrogen plasma also leads to defect formation in near interface area in silicon [6]. Therefore, a more complicated growth process should be used to obtain silicon incorporation for *n*-type doping of GaP layers without deterioration of bulk properties of wafers, and direct influence of silane flow on doping will be studied here.

Materials and Methods

In this study, three different GaP layers with thickness of 10–20 nm were grown using an Oxford Instruments PlasmaLab System 100 PECVD (13.56 MHz) setup on boron-doped silicon (100) wafers ($p = 1\cdot 10^{16}$ cm^{-3}) in PE-ALD mode. The main parameters were the same as in [7] except for the steps described in Table 1: lower PH_3 flux in OX856 than in OX860, and additional silane flow of 10 sccm in OX858. Indium tin oxide (ITO) layers were deposited by magnetron sputtering in first series of samples for photovoltaic measurements. Further, silver paste was applied to ITO for fabrication of metallic top contact, and bottom ohmic contact to *p*-Si was formed by indium. On the other hand, gold was evaporated in BOC Edwards Auto500 setup through a hard mask in the form of a circle with a diameter of 1 mm. Then, these samples were etched in wet solution $H_2SO_4:H_2O_2$ = 3:1 down to silicon wafer: in result, GaP/Si heterojunction remained only under gold circle. Finally, ohmic contact by indium was formed to bottom side. This series were explored by capacitance methods to probe only heterojunction *n*-GaP/*p*-Si without contribution of additional barrier ITO/*n*-GaP.

Current–voltage characteristics were measured at 25 °C using a Keithley 2400 source-meter under AM1.5G illumination provided by a SunLiteTM Solar Simulator from ABET Technologies. Admittance spectroscopy (AS) [8] measurements were performed using a precision E4980A-001 Keysight (former Agilent) LCR-meter in frequency range with test voltage amplitude of 50 mV from 20 Hz to 2 MHz in helium cryostat Janis CCS-400H/204 from 12 to 800 K.

Table 1

Different parameters of PE-ALD processes of GaP layers

Sample	Pre-PH_3 step					PH_3 step		
	t, s	PH_3, sccm	Ar, sccm	H, sccm	SiH_4, sccm	*t*, s	PH_3, sccm	H, sccm
OX856	3	30	50	200	0	3	10	200
OX860	4	40			0		20	
OX858	4	40			10		20	

Results and Discussion

Current-voltage characteristics of ITO/*n*-GaP/*p*-Si samples under AM1.5G illumination are presented in Fig. 1.

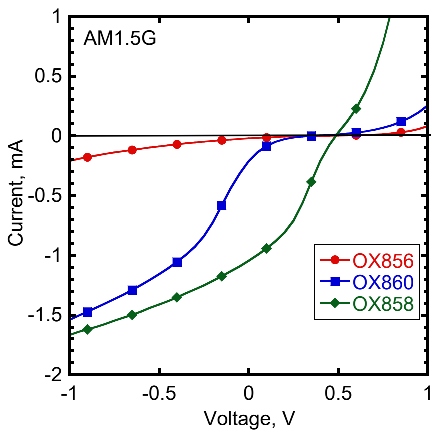

Fig. 1. Current-voltage characteristics of ITO/*n*-GaP/*p*-Si samples under AM1.5G illumination

All *I–V* curves exhibit a knee near the open circuit voltage, which leads to significant decrease of fill factor (*FF*) and even short circuit current (I_{sc}). The most pronounced drop of *FF* is observed for OX856, a medium one for OX860, and the weakest is for OX858. A possible reason explaining such behavior lies in the differences in conductivity of the GaP layer due to the growth parameters. A similar knee in the *I–V* curve could be observed for non-sufficient HIT solar cells based on a *p*-*a*-Si:H/*i*-*a*-Si:H/*n*-*c*-Si heterojunction when *p*-layer is not enough doped leading to parasitic barrier in structure and decrease of *FF*. Here, the shape of the *I–V* curve is dramatically improved when PH_3 flow increases for OX860 in both stages (Table 1), and silane flow also reduces the inflection of the *I-V* curve leading to a greatly increasing Isc. Therefore, the parameters of the PH_3 step in PE-ALD mode have a critical influence on the quality of conductivity in *n*-GaP.

Initially, gold was evaporated to these GaP layers grown on *n*-Si ($n = 1\cdot10^{16}$ cm^{-3}) wafers to form structure with Schottky diodes to explore their defect properties. However, classical rectifying behavior is not observed due to extremely high conductivity between contacts. In this case, structures Au/*n*-GaP/*p*-Si were explored by capacitance methods since gold does not form a potential barrier on Au/*n*-GaP and does not lead to contribution in total capacitance of samples. It is also confirmed by measurements of capacitance-voltage characteristics (not presented here) for all samples for 100 kHz, and estimated concentration from $1/C^2$ corresponds to the doping level in silicon wafers.

Admittance spectroscopy were performed in the temperature range from 60 to 400 K for different applied voltage bias. The *C–f* curves for different temperatures for V_{DC} = 0 V and +0.8 V are presented in Fig. 2. The admittance spectroscopy is based on the measurement of the capacitance and conductance of *p–n* junctions using a small signal alternating voltage at different frequencies and at various temperatures. If the Fermi level (or quasi Fermi level) crosses the defect level in the space charge region, we may detect an additional contribution to the capacitance. This leads to a step-like behavior in the capacitance versus frequency as in *C*–*f* in Fig. 2.

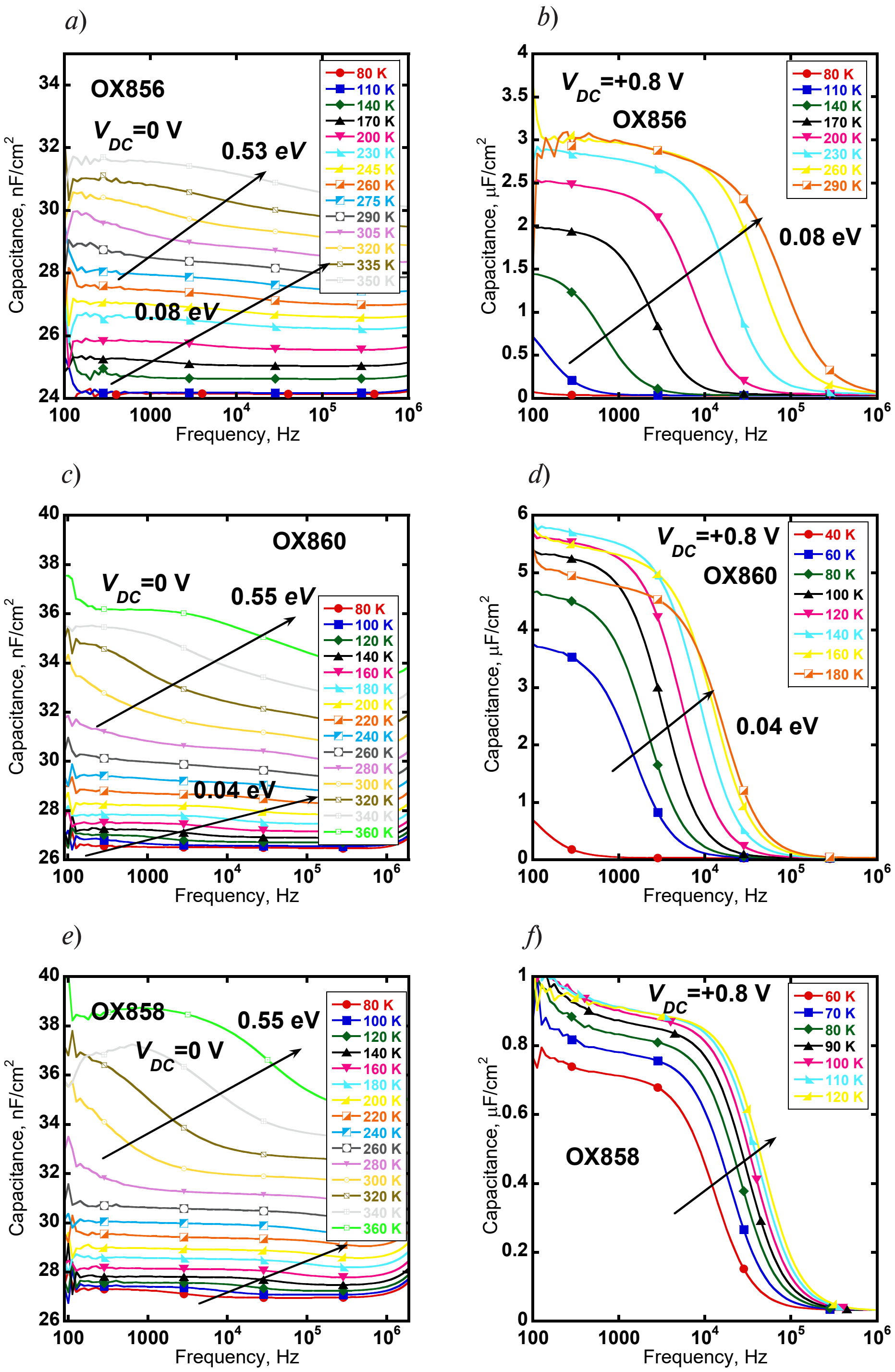

Fig. 2. *C*–*f* curves for different temperatures for V_{DC} = 0 V (*a*, *c*, e) and V_{DC} = +0.8 V (*b*, *d*, *f*)

A similar behavior of the curves is observed for all samples at V_{DC} = 0 V (left panels in Fig. 2). A first step on the *C–f* curve can be seen at low temperatures of 80–240 K and a second one at higher temperatures, 300–360 K (the sequence of steps is indicated by arrows). As shown, the position of the turn-on frequency (*f* where $-f \cdot dC/df$ has maxima) shifts toward higher frequencies with a temperature increase, allowing to obtain the Arrhenius plot and estimate the parameters of the defect, activation energy E_a and the capture cross section σ_T.

Parameters of high-temperature responses (300–360 K) are almost the same for all samples since the position of the turn-on frequency is similar for the same temperature, amounting to E_a = 0.50–0.55 eV and σ_T = (1–10)·10^{-16} cm^2. The parameters do not depend on the process conditions so the differences in the *I–V* curves can hardly be explained by its influence. Furthermore, a similar defect was detected by DLTS in our previous work where it was associated with a deep defect level in GaP layer, but its nature is still unclear.

In contrary, the parameters of low temperature response depend on the deposition conditions. Low temperature feature is characterized by low values of σ_T (1·10^{-20} cm^2) and E_a being equal to 0.08 eV and 0.04 eV for OX856 and OX860, respectively. For OX858 E_a is too low to be estimated (E_a < 0.02 eV). Thus, the highest value of E_a is observed in OX856, then increasing of phosphine flow leading to decreasing of Ea in OX860, and the lowest one is in OX858 with additional flow of silane. The *C–f* curves were also measured at V_{DC} = +0.8 V (Fig. 2, *b*, *d*, *f*) to prove the difference in E_a for the samples. In this case, in addition to the capacitance of space charge (which is closer to the GaP layers) a diffusion capacitance should dominate in the total capacitance. The absolute value of the capacitance at low frequency is much higher compared to that at 0 V being typical for diffusion capacitance. However, high amplitude steps are detected for all samples, and their responses correspond well to the low temperature response observed at 0 V with the same values of E_a. In fact, if we consider the equivalent circuit the space charge capacitance is connect in parallel to diffusion capacitance, i.e. contribution of each should be presented in the equivalent capacitance. Only the contribution of series capacitance could provide such high amplitude steps. When series capacitance is much lower compared to diffusion capacitance the total capacitance is determined by series capacitance. If the series capacitance is shunted by conductivity, for example due to temperature activation, the total capacitance is determined by diffusion capacitance. Similar behavior has already observed for *a*-Si:H/*c*-Si heterojunctions [9]. An activation of the conductivity of doped *a*-Si:H layer leads to appearance of low temperature response in the admittance spectra. An activation of GaP conductivity could explain the observed behavior of the admittance spectra at +0.8 V as well as dependence of the E_a on deposition conditions. Also it is in good correlation with our suggestion from *I–V* curves: lower E_a leads to better conductivity in GaP with silane flow. Therefore, detected response is related to conductivity of GaP layers, and it can be controlled in future experiments.

Conclusion

Plasma-enhanced atomic layer deposition is attractive method for formation of *n*-GaP layers on *p*-Si wafer for further photovoltaic application. Here, we explore influence of growth conditions on electrophysical quality of thin *n*-GaP layers. Admittance spectroscopy and current-voltage characteristics were used to establish a decrease in the activation energy of conductivity in GaP with increasing phosphine flow during the phosphorous step from 0.08 eV to 0.04 eV, with a subsequent drop to extremely low values when additional flow of silane was added. This serves to greatly improve the photovoltaic performance of ITO/*n*-GaP/*p*-Si sample. Moreover, a deep level with E_a = 0.50–0.55 eV and σ_T = (1–10)·10^{-16} cm^2 was detected in all layers.

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