Influence of plasma on electrophysical properties of the GaP/$n$-Si isotype heterojunction grown by PE-ALD

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Abstract. The work is devoted to studying the influence of an additional step of argon plasma treatment on the quality of the GaP/$n$-Si isotype heterojunction grown by plasma-enhanced atomic-layer deposition (PE-ALD). Deep-level transient spectroscopy measurements demonstrated that argon plasma leads to the formation of defects with a high concentration in silicon wafers, unlike the PE-ALD mode without a step of hydrogen or argon plasma treatment. In addition, GaP layers obtained by PE-ALD have defects with an activation energy of 0.40 eV and 0.62 eV for processes with and without argon plasma treatment, respectively.

1. Introduction

Nowadays, growth of III-V compounds on silicon wafers is a big challenge for science in the world. The successful development of this technology is highly important for different optoelectronic applications, for example, silicon-based multi-junction solar cells. GaP is one of the most promising semiconductors for this purpose, since GaP has only a 0.4% lattice-mismatch with silicon [1]. Furthermore, GaP-based dilute nitrides, such as InGaPN or GaPAsN, can be grown on a silicon wafer with a bandgap energy in a wide range of 1.5–2.1 eV for the fabrication of double- and triple-junction solar cells [2–4]. However, modern epitaxial methods lead to degradation of the silicon wafer quality during the growth of GaP due to the high temperature (800–900 °C) [5,6]. In this case, the time-modulated plasma-enhanced chemical vapor deposition (or plasma-enhanced atomic-layer deposition, PE-ALD) was successfully applied to the growth of thin layers of GaP on silicon wafers [7]. This method is based on alternation of P and Ga sources at low temperature (below 400 °C) in the PECVD chamber. Also, additional silane step allows one to obtain donor-doped GaP to form a $n$-GaP/$p$-Si anisotype heterojunction for the bottom subcell in prospective multi-junction solar cells. However, it was shown that an increase in the RF hydrogen plasma power during the phosphorus and gallium step leads to degradation of photoelectrical properties due to the formation of defects near the interface in the $n$-GaP/$p$-Si heterojunction [8]. A similar situation was observed for the $n$-GaP/$n$-Si isotype heterojunction fabricated with a high hydrogen plasma power, where deep defects were detected in a thin layer of the silicon wafer near the interface, but the bulk properties of silicon wafers far from the interface are not deteriorated [9]. Therefore, further optimization of PE-ALD technology is required for the growth of GaP layers on silicon wafers.
Here, the PE-ALD process is modified by excluding, as much as possible, hydrogen plasma treatment, so it was used only during the short (2 s) step of phosphine decomposition. However, according to [10], the smoothness of the AlN layer grown by ALD increased due to an additional step of argon plasma treatment. Therefore, the step of argon plasma was also added to the PE-ALD process to enhance the structural properties of GaP. In this paper, the electrophysical properties of GaP/n-Si isotype heterojunctions grown by these methods are presented.

2. Experimental details
Two different samples were grown on n-Si (100) \((n = 1 \times 10^{15} \text{ cm}^{-3})\) wafers using an Oxford Instruments PlasmaLab System 100 PECVD \((13.56 \text{ MHz})\) setup. Phosphine \((\text{PH}_3)\) and trimethylgallium \((\text{TMG})\) were used as sources of phosphorus and gallium, respectively. The first sample is a 40 nm thick GaP layer grown by the PE-ALD mode with an additional step of argon plasma treatment with a power of 200 W during 15 seconds (figure 1), and the second sample is grown without this step. Hydrogen plasma is used only during the \text{PH}_3 step in both processes. Further, 2 µm were dry etched from the bottom side of the n-Si wafer by reactive ion etching (RIE) using an Oxford Instruments Plasmalab System 100 ICP 380 to exclude possible contamination during the deposition of GaP. An ohmic contact was formed on the bottom side of the n-Si wafer using PE-ALD of 20-nm-thick highly n-doped GaP with an additional flow of silane and further indium evaporation. Then, gold contact dots with a diameter of 0.5 mm were evaporated on top of the GaP/n-Si structures to form Schottky barrier diodes to GaP layers using a BOC Edwards Auto500 setup. Capacitance-voltage measurements were performed using a precision E4980A Keysight (former Agilent) LCR-meter. Measurements of capacitance deep-level transient spectroscopy (DLTS) [11] were done using an automated installation based on a Boonton-7200B capacitance bridge in the temperature range 80–360 K.

![Figure 1. Schematic view of plasma-enhanced atomic layer deposition with an additional step of argon plasma treatment.](image)

3. Results and discussion
According to the capacitance-voltage characteristics measured at 80 K and 100 kHz (see figure 2), GaP layers are fully depleted even at zero applied voltage. An increase in the reverse bias voltage leads to high band bending in the thin GaP layer without a significant change in the capacitance value. Therefore, the grown GaP layers have a background donor doping concentration lower than \(5 \times 10^{17} \text{ cm}^{-3}\). However, at a bias voltage lower than -1.5 V, the space charge region penetrates into silicon, which leads to a sharp drop in capacitance, and the concentration of free charge carriers, estimated from the Mott-Schottky plot, correlates with the doping concentration in the n-Si wafer. Therefore,
DLTS measurements were performed under the following conditions: $V_{\text{init}} = -2$ V, $V_{\text{pulse}} = 2$ V, $t_{\text{pulse}} = 50$ ms to explore possible defects in silicon near the GaP/$n$-Si interface.

![Figure 2](image-url). Capacitance-voltage characteristics measured at 80 K and 100 kHz for the GaP/$n$-Si isotype heterojunctions.

The obtained DLTS spectra for different rate windows are presented in figure 3a and figure 3b for the GaP layer grown with and without a step of argon plasma treatment, respectively. As a result, series of peaks are detected in the sample grown with the argon step, which are associated with a defect with activation energy $E_a = 0.32–0.35$ eV and an extremely high capture cross-section $\sigma_T = 1\times10^{-10}$ cm$^2$. On the other hand, no responses are observed in GaP/$n$-Si grown without argon treatment. Therefore, argon plasma with a power of 200 W leads to the formation of radiation defects in a silicon wafer during the PE-ALD of GaP layers. Nevertheless, the results for both samples are significantly different from the ones for GaP/$n$-Si grown with a step of activation by hydrogen plasma with a power of 200 W, where two deep defects with $E_a = 0.30$ eV and $E_a = 0.80$ eV and a high concentration were observed in the high-temperature range [12], and the photovoltaic performance of the GaP/$p$-Si anisotype heterojunction was very poor [8]. Consequently, the PE-ALD mode without hydrogen plasma reduces the defect concentration in the silicon wafer, and the mode with argon plasma treatment requires further optimization, for example, using a lower plasma power or shorter step duration.

When a forward bias voltage is applied during the filling pulse, it allows one to fill in the possible defect levels, which are located in the GaP layers. Therefore, DLTS measurements were performed under the following conditions: $V_{\text{init}} = 0$ V, $V_{\text{pulse}} = 2$ V, $t_{\text{pulse}} = 50$ ms. The obtained DLTS spectra for different rate windows are presented in figure 3c and figure 3d for the GaP layer grown with and without a step of argon plasma treatment, respectively. As a result, both samples have similar behavior: one series of very broadened peaks, which are associated with responses from defect levels with a certain energy distribution, leading to a non-exponential capacitance transition. According to the Arrhenius plot, the medium activation energy of this defect is lower for the sample with argon plasma treatment ($E_a = 0.40$ eV) compared to that without Ar plasma ($E_a = 0.62$ eV), and, moreover, its concentration is higher in the first one due to the higher amplitude of the DLTS signal. Perhaps, these defects are responsible for the concentration of free carriers in GaP layers at room temperature, so their nature would be clarified in further experiments.
4. Conclusions
Finally, the influence of an additional step of argon plasma treatment on the quality of GaP/n-Si isotype heterojunction grown by plasma-enhanced atomic-layer deposition was explored by deep-level transient spectroscopy. It was shown that argon plasma leads to the formation of defects with a high concentration in silicon wafers unlike the PE-ALD mode without a step of hydrogen or argon plasma treatment. In addition, the GaP layers obtained by PE-ALD have defects with an activation energy of 0.40 eV and 0.62 eV for processes with and without argon plasma treatment, respectively.

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