Plasma-enhanced atomic layer deposition of Zn-doped GaP

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Abstract. The formation of p-type GaP by plasma-enhanced atomic layer deposition at a temperature of 380 °C has been studied. The incorporation of Zn impurity was detected by the method of glow discharge optical emission spectroscopy (GDOES). Strong band bending was confirmed by electrical measurements performed for the p-n homojunctions formed by deposition of p-GaP on the surface of n-type GaP substrates, which indicates the acceptor behavior of the impurity. It has been shown that p-type GaP deposited by PE-ALD can be used to form photovoltaic converters.

1. Introduction

Gallium phosphide has gained wide popularity among A\textsuperscript{III}B\textsuperscript{V} materials due to its use in devices such as LED, Hall sensors, optical filters, and solar cells. The current interest in using GaP in solar photovoltaic converters is confirmed by the results of computer simulations. It has been shown that GaP has an advantage over other semiconductor materials when used as a transparent emitter [1]. Researchers are actively working on the formation of solar cells based on GaP by epitaxial methods [2]. However, solar energy applications require scalable deposition technology such as atomic layer deposition. For the first time, the growth of GaP by the method of thermal atomic layer deposition on a GaP substrate was carried out in 1989 at Fujitsu laboratory [3]. Later in 1992, J. R Gong, S. Nakamura et al. demonstrated GaP grown by thermal ALD on a silicon substrate at temperatures of 450 – 600 °C [4]. Plasma-enhanced atomic-layer deposition allows the formation of thin layers of binary compounds at temperatures below 400 °C due to plasma activation of precursors. One of the main features of this deposition method is the possibility of obtaining uniform layers on substrates with a developed surface. This can be used to form p-i-n structures in multi-junction solar cells on structured substrates. In our previous work, we presented the possibility of obtaining n-type GaP by the PE-ALD method at a temperature of 380 °C and its use for the formation of heterostructure solar cells on p-type silicon substrates [5]. Previously doped p-type GaP layers were grown at low temperatures by reactive evaporation and sputtering [6]. The formation of a diode structure on n-type GaP substrates was shown, which clearly indicates the possibility of doping with an acceptor impurity. However, no reports were found in the literature on the production of GaP layers doped with acceptor impurities using plasma chemical deposition. This paper presents the results of deposition of p-type GaP layers by the PE-ALD method and the use of these layers for optoelectronic applications.
2. Experimental study
The GaP layers with a final thickness of 40 nm and 160 nm were grown by the PE-ALD method on GaP wafers at a temperature of 380 °C and a pressure of 350 mTorr in a PECVD Oxford Plasma Lab System 100 with capacitively coupled RF (13.56 MHz) plasma. The diameters of the top electrode and the heated sample holder were 300 and 200 mm, respectively. The evacuation was performed with a BOC Edwards iH600 dry vacuum pump. GaP substrates were treated by HCl-dip (30%) to remove native oxide immediately before loading to the PECVD chamber via a load-lock system. The process of GaP atomic layer deposition consists in the sequential deposition of monolayers of gallium and phosphorus from the precursors of trimethylgallium and phosphine, respectively. The parameters of the GaP layer growth process, including the values of flux and plasma power, were described in detail elsewhere [7]. The layers were doped with acceptor and donor impurities by adding small concentrations of diethylzinc and monosilane to the deposition process. Two types of structures were formed using p-type GaP layers: a p-n junction on an n-GaP substrate and a GaP p-i-n structure (figure 1).

After formation, an ITO layer of 100 nm was deposited onto both types of structures by reactive magnetron sputtering. The ohmic contact to the n-GaP substrates was formed by In deposition followed by annealing at 400 °C. The I-V curves were measured using an Abet Technologies AM1.5G solar simulator and a Keithley 2400 electrometer. The quantum efficiency spectra were obtained using a xenon lamp, an SLS monochromator and a reference Si solar cell.

3. Results and discussion
The elemental composition of the p-i-n structure was investigated by the method of glow discharge optical emission spectroscopy (GDOES). In this method, gradual plasma-chemical etching of the structure is performed, during which the elemental composition is determined from the intensity of atomic emission spectral lines. It was noted that a significant increase in the concentration of Zn and Si is observed at p-type and n-type GaP layers, respectively (figure 2). Thus, the incorporation of the dopants in the layers obtained by the PE-ALD method was confirmed.
Figure 2. GDOES profile of the GaP p-i-n structure deposited by PE-ALD on a GaP substrate.

The photoelectric properties of the samples were investigated by measuring the I–V characteristics. The dark I–V curves show a rectifying dependence, which indicates the presence of a space charge region for the both structures (figure 3). Moreover, the p-n junction with a p-GaP layer deposited by PE-ALD exhibits an open circuit voltage equal to 768 mV under illumination, which corresponds to the formation of strong band bending in the substrate. On the other hand, the open circuit voltage for a structure with a p-i-n junction is 127 mV. Such a small value indicates more intense nonradiative recombination in the i-GaP layer as compared to the GaP substrate.

Figure 3. I–V curves of the GaP p-n and p-i-n structures deposited by PE-ALD on n-GaP substrates.

For both structures, a smooth decrease in the external quantum efficiency (EQE) at wavelengths above 450 nm can be noted, which is a consequence of the indirect-gap absorption of gallium phosphide with a band gap of 2.26 eV (figure 4). The absolute values of the quantum efficiency of the p-i-n structure are significantly lower than those of the substrate due to the small thickness of the absorbing layer. To further increase the efficiency of such p-i-n structures, it is necessary to optimize the properties and thicknesses of the functional layers.
Figure 4. EQE of the GaP p-n junction and the GaP p-i-n structure deposited on n-GaP substrates by PE-ALD.

4. Conclusions
Investigations of the layer composition using GDOES have shown the effective incorporation of Si and Zn impurity atoms into the doped layers. As a result of the study, for the first time using the PE-ALD method, a p-type GaP layer was obtained by doping with Zn. Doping was confirmed by electrical measurements performed for p-n homojunctions formed by deposition of p-GaP on the surface of n-type GaP substrates. The resulting structures show significant photoconversion properties, which can later be used to form multi-junction solar cells by the PE-ALD method.

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