Silicon doping of GaP layers grown by time-modulated PECVD

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Abstract. We study the doping in GaP layers grown on n-type silicon wafer by time-modulated plasma-enhanced chemical vapour deposition with additional flow of silane. Classical and electrochemical (ECV) capacitance-voltage methods were performed on GaP/Si heterostructures and they demonstrate high electron concentration in the GaP layer and similar profiles. In addition, glow-discharge optical emission spectroscopy revealed high silicon content in GaP, which should be responsible for the detected high n-type doping.

1. Introduction
Nowadays, many efforts are devoted to the fabrication of various optoelectronic devices based on III-V compounds on cheap silicon wafers, for example, multi-junction (MJ) solar cells (SCs). Gallium phosphide (GaP) has only 0.37% lattice mismatch with Si and exhibits good passivation properties [1] so it is one of the most perspective semiconductors for epitaxial growth on Si wafer. Also, the efficiency of single-junction SCs based on the GaP/Si heterojunction should be by 1.1% higher than in a standard silicon diffused homojunction, because the open circuit voltage, $V_{OC}$, will be higher by 49 mV and could reach up to 0.7 V according to theoretical estimations [2]. This is why a lot of work is being devoted to the development of dislocation-free growth of GaP on silicon wafers [3–7]. However, the vapor-phase and molecular beam epitaxy (VPE and MBE, respectively) methods that are currently used to produce GaP on silicon require high temperatures of 500–800°C leading to unsatisfactory quality of the heterointerface, layers deformation due to differences in thermal expansion coefficients, and deterioration of the bulk properties due to creation of a large number of threading dislocations. In addition, catastrophic drop of minority charge carriers lifetime was observed directly in the silicon wafer due to the annealing procedure of the wafer in the VPE chamber [8]. Also, high temperatures could lead to an inter-diffusion of the III, V and IV elements, during the epitaxial growth process. Note that in this case they are doping impurities for each other. Besides the above mentioned problems, there are economic ones due to strong requirements of ultra-high vacuum in the chamber, ultra-pure source of atoms, more complicated maintenance of equipment, etc. Recently, the novel method of time-modulated plasma-enhanced chemical vapour deposition (PECVD) was proposed and successfully applied to the growth of GaP layers on silicon [9]. It is based on the alternative deposition of Ga and P atoms at low temperature (<400°C). In this work, we present an initial characterization of doping in grown GaP layers by three independent measurement techniques: classical capacitance-voltage (C-V) measurements, electrochemical C-V (ECV) profiling and glow-discharge optical emission spectroscopy (GDOES).
2. Experiments and methods
Thin films of GaP with thickness of 50-75 nm were grown at 380 °C on n-type (phosphorus-doped, 2-7 Ω·cm) (100) silicon wafers by time-modulated PECVD methods using an Oxford PlasmaLab System 100 PECVD (13.56 MHz) setup. In this time-modulated method phosphine (PH3) and trimethylgallium (TMG) were alternatively changed with continuous plasma discharge due to constant hydrogen (H2) flow during the growth and purge steps. Also, additional steps of silane (SiH4) flow were introduced as a source of silicon for desirable n-type doping of GaP. The total flow and pressure were kept constant and equal to 100 sccm and 350 mTorr, respectively. Schematic views of the used characterization methods are presented in Figure 1.

Firstly, for classical capacitance measurements we fabricated a Schottky barrier on the front side of the GaP layer from vacuum evaporated gold in a BOC Edwards Auto500 equipment. Then, an ohmic contact to the bottom side of the c-Si wafer was formed by PECVD of n-type (phosphine doped) hydrogenated amorphous silicon, followed by silver deposition and further thermal annealing during 20 min at 170 °C in the air atmosphere. We measured the dependence of the device capacitance on applied reverse bias voltage using an Agilent E4980A RLC-meter [10] (Figure 1a). The obtained C-V profiling is a widely used technique to characterize semiconductor materials and structures with highly reproducible results. However, in some cases these classical C-V measurements do not allow one to obtain high resolution deep in the investigated structure [11]. For this reason, it is sometimes preferable to use a modified C-
V technique, namely the ECV profiling. Here an electrolyte is used as a rectifying contact, which could be used in a classical C-V (depletion) mode, and also for controlled dissolution of the semiconductor that helps to overcome the above mentioned limitations and obtain the full information about the concentration distribution [12]. The schematic view of the ECV technique is presented in Figure 1b. ECV measurements were performed at room temperature using an ECVPPro profiler (Nanometrics). The 0.2M NaOH solution was chosen as the electrolyte [13], and the etching current was maintained at a level of 0.5 mA/cm². During ECV profiling, the sample was etched gradually with a 1 nm step. Here, also the Agilent E4980A RLC-meter was used [14].

Finally, GaP/n-Si heterojunctions were explored by GDOES [15]. The schematic view of the method is presented in Figure 1c. The sample is placed in a chamber under argon RF-plasma. Argon ions are used to progressively sputter the sample and the removed atoms enter the plasma where they are excited. Then, they relax and emit photons with characteristic wavelengths for each atom, which are registered by the spectrometer. As a result, the profile of atomic content can be obtained.

3. Results
The C-V dependence (not shown here) was measured for Schottky barriers on GaP/n-Si at 1 MHz, and the free charge carrier concentration profile (N_{CV}-W) was estimated (Figure 2a). Firstly, high electron concentration is observed near the surface, which further quickly decreases with depth. Then, it becomes almost constant with a value of 1×10^{15} cm^{-3} that exactly corresponds to the doping concentration of the silicon wafer (2-7 Ω·cm). The estimated high concentration at low depth is corresponding to the free carrier concentration in the GaP layer rather than in silicon since we showed the absence of high phosphorous diffusion into a p-Si wafer during the same growth process of GaP in our previous work [16]. However the absolute value of the depth obtained from C-V measurements is larger than the total thickness of the GaP layer. This discrepancy could be explained by an imperfect bottom contact to the wafer that leads to a shift of the capacitance and thus of the estimated probed depth. However, the GaP layer could be fully depleted and we clearly observe the part of the GaP/n-Si heterojunction profile lying in the wafer.

The results of the ECV profiling technique is shown on Figure 2b. The global shape of the N_{CV}-W curve is similar to that of the classical C-V of Figure 2a, however there are two main differences. The first one is the shift of the depth scale to lower values by 30-50 nm, which can partially confirm our suggestion of imperfection of bottom contact to n-Si for the sample with Schottky barrier explored by the classical C-V. The second one is the peak on the N_{CV}-W curve observed at a value of W=60 nm corresponding to the thickness of GaP and position of the GaP/Si interface [17]. Furthermore, we observe high electron concentration in the GaP layer (>1×10^{17} cm^{-3}) as we assumed. This demonstrates that the used growth process by the time-modulated PECVD method allows one to obtain desirable highly doped n-GaP layers. The ECV method shows a more complete quantitative picture of the concentration profiling in the GaP/n-Si heterojunction compared to the classical C-V measurements in our structures with very thin n-GaP layer.

The results of GDOES profiling for Ga, P and Si atoms are shown in Figure 2c. The GaP layer was removed very rapidly (2 seconds) due to its low thickness, and for larger etching time the silicon response has a constant value indicating that the Si wafer is probed. Despite this fact, we could definitely conclude the existence of a significant silicon concentration in GaP. It should be larger than 10^{18} cm^{-3} but the precise value will be estimated after complete calibration of the used equipment in future experiments. The GDOES spectra demonstrate the possibility of high silicon incorporation in the GaP layers during the described growth process, and it is likely to be the origin of the high electron concentration estimated above from C-V methods.
Figure 2 (a, b, c). N_{CV}-W profiling obtained by classical (a) and electrochemical (b) C-V techniques (the zoomed peak is in the inset), and GDOES spectra of (c) of GaP/Si structure.

4. Conclusion
We explored GaP layers grown on n-Si wafers with additional flow of silane by time-modulated PECVD method. The GaP/n-Si heterojunction was explored by classical and electrochemical C-V techniques that showed similar qualitative dependence of free electron concentration on thickness of the space charge region, however the ECV method showed more reliable values for the probed thickness. Both techniques demonstrate that the GaP layer has high electron concentration. In addition, the GDOES technique showed that a high silicon content was incorporated in the GaP layer which is thus likely to be the cause of the high electron concentration detected by the capacitance techniques.

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