Investigation of defects in structures based on BP/Si heterojunction

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Abstract. In this work the properties of the BP/Si heterojunction interface were investigated by capacitance methods, the deep levels transient spectroscopy method and admittance spectroscopy. Admittance spectroscopy did not detect any defects, but the deep level transient spectroscopy showed response with activation energy of 0.33 eV and capture cross-section $\sigma = (1-10) \times 10^{-19}$ cm$^2$ and defect concentration ($N_T$) is in the order of $10^{13}$ cm$^{-3}$. This defect level is a trap for electron with position of 0.33 eV below the conduction band in region near the BP/Si interface.

1. Introduction

Nowadays, there is a growing interest in use of renewable energy sources, including solar energy, the main directions of development is research of new configurations of solar cells in order to increase efficiency, reduce cost and mass for delivery to near-earth orbit.

There are many types of solar cells, but silicon solar cells are the most widespread. The achieved efficiency of single-junction bifacial solar cells based on silicon heterojunction is 24.7% [1], and it has not increased since 2014. New approaches are required to further improvement the efficiency of solar cells.

For effective performance of solar cells, it is necessary to separate the photo-generated electrons and holes and collect them at opposite contacts. In most crystalline silicon solar cells, this is achieved by diffusing dopants of opposite polarity onto opposite wafer surfaces, which creates regions of very high conductivity for only one of the two carriers. Despite the proven effectiveness, this approach can limit performance due to optoelectronic losses and technological imperfections. These problems have motivated research on alternative approaches in which selective materials or structures are deposited on the surface of the c-Si wafer.

This article proposes to investigate a new approach based on the use of phosphides of group III elements, which have a high potential for use as selective contacts to silicon. For example, boron phosphide (BP) has a bandgap ($E_g > 2$ eV) significantly higher than c-Si and higher than a-Si:H which leads to parasitic absorption in short-wavelengths range of the solar spectrum in them. It will allow to contribute to an increase in short-circuit current compared to a-Si:H [2,3]. On the other hand, the negative ($-0.3 \pm 0.1$ eV) valence band offset ($\Delta E_V$) for the BP/Si heterojunction [4] provides the necessary selectivity, which makes it an excellent candidate as a selective hole contact.
Boron phosphide layers can be grown by various methods, for example, by plasma enhanced chemical vapor deposition (PECVD) [5]. This reliable industrial method allows the growth of films with high electronic quality at low temperatures over large areas. However, according to [6], for the BP layers, the synthesis is difficult due to the difference in the reactivity of B and P, which possibly explains the absence of reports on the development of a low-temperature BP formation technology. To solve this problem, it was proposed to use the plasma enhanced atomic layer deposition (PE-ALD) approach, in which the decomposition of the precursors of the B and P atoms are separated in time. This method was successfully applied to GaP layers fabrication [7].

In the near-surface region of silicon, during the deposition of the BP layer, radiation defects can form due to the treatment of the argon plasma used in the step of decomposition of trimethylboron. Thus, the purpose of this work is to investigate the properties of the BP/Si heterointerface by capacitance methods, using the deep level transient spectroscopy (DLTS) and admittance spectroscopy.

2. Experiment details
The BP films were grown in a standard Oxford PlasmaLab 100 PECVD (13.56 MHz) plasma chemical deposition setup. The gas flows of 2% trimethylboron (TMB)/H2 and 5% PH3/H2 were used as precursors for B and P respectively. The deposition was carried out on a Si substrate with a donor doping level of 10^{15} cm^{-3} at a temperature of 250 °C. Immediately before loading into the working chamber, the Si substrates were treated in a 10% HF/H2O solution to remove the natural oxide. At the first step, PH3 was decomposed at a hydrogen plasma power of 200 W for 3 s. Then, after pumping out and blowing, a TMB/H2 mixture with the addition of Ar, which is necessary to ensure the ignition of a plasma with a power of 100 W and a duration of 5 s, was poured into the chamber. After that, the chamber was pumped out again, purged, and the whole process was repeated anew. During the process, which consisted of 200 cycles, 60 nm thick layers were deposited, which corresponds to a growth rate of 0.3 nm/cycle.

To evaluate the electrical properties of the BP/n-Si measurements of conductivity and capacitance were carried out: spectroscopy of admittance (capacitance and conductivity depending on frequency and temperature) and DLTS to study defects in layers and at the interface. Capacitance measurements were performed on structures with a Schottky barrier Au/BP/n-Si were fabricated (Figure 1). Second, a layer of a-Si:H was deposited by PECVD and an Ag was thermally evaporated on it to form ohmic contact.

![Figure 1. Schematic representation of the structure of Au / BP / n-Si](image)

For capacitance measurements, we used an Agilent E4980A-001 precision RLC meter in frequencies range of 1 kHz to 1 MHz, and applied voltage was varied from 1.25 to -1.25 V. The admittance spectroscopy method is a measurement of the dependences of capacitance and conductivity on frequency and temperature. This method is successfully applied both to characterize defects in the bulk of semiconductor layers and to estimate the density of surface states at the interface of heterojunctions. We used a modified admittance spectroscopy method using a bias voltage, which makes it possible to separate the responses of point defects in bulk and from interface states, and to determine the spatial distribution of detected defects.
DLTS measurements were carried out using an automated setup based on a Boonton-7200B capacitance bridge and a Janis VPF 100 cryostat, which provides measurements in the temperature range of 80-360 K.

3. Result and discussion
First, I-V curve was measured at 300 K on Au/BP/n-Si structure with a Schottky barrier (Figure 2, a). Rectifying behavior is observed: exponential dependence at low forward bias voltage, and low current at reverse one, so space charge region exists and capacitance measurements can be applied.

Capacitance-frequency (C-f) dependences were measured at different temperatures at different bias voltages. C-f curves at 0 V are presented in figure 2 b. There are no any features in curves: capacitance monotonically increases with the temperature increase at all frequencies for all bias voltages. Also weak frequency dependence in the admittance spectra is observed. However, admittance spectroscopy probes the area near the border of space charge region in bulk silicon, and in explored wafer (charge carriers concentration of $10^{15}$ cm$^{-3}$) it is approximately 1 μm. The fact that no response is observed does not mean that no defects are created in Si. Admittance spectroscopy can detect the defect level, which cross the Fermi level (E$_f$). Thus, no defects located deeper E$_f$ could be detected.

![Figure 2](image-url)

**Figure 2.** a) I-V characteristic of Au/BP/n-Si structure; b) Admittance C-f characteristics bias voltage 0V.

Therefore, DLTS measurement were performed in two modes. Measurements of DLTS spectra (Figure 3, a) were performed with the bias voltage switching from -4 to +1 V and from -4 V to 0V for 50 ms to fill the defect traps for emission rates 50, 100, 200 and 500 s$^{-1}$.

After voltage returning to -4 V the capacitance transient was measured. Firstly, 0..-4V spectra does not show any defect responses as in admittance spectroscopy. On the other hand, one peak associated with some response is observed on spectra with +1 V during the filling pulse. In this case, the probed region is located at a distance not deeper than 1 μm from interface BP/Si Thus, observed response is associated with interface states in BP/Si or in near-surface region of Si.

The peak position obtained for different emission rates allows to estimate defect parameters from Arrhenius plot (Figure 3, b): activation energy $E_a=0.33$ eV, capture cross-section $\sigma_c=(1-10)\cdot10^{-19}$ cm$^2$, and the defect concentration (N$_T$) is in the order of $10^{13}$ cm$^{-3}$. Since the peak on spectra is positive the defect is a trap for electrons, and its position of energetic level is 0.33 eV below the conduction band of silicon. The observed temperature dependence has a broad feature, which can be interpreted as response from defect with some energy distribution since BP layers is amorphous, and partial amorphisation of near-surface region can be placed. Such results of capacitance measurements may indicate the negative impact of both argon plasma and the high power of TMB and PH$_3$ plasma used in the PE-ALD process.
4. Conclusion
BP layer on n-type silicon wafer was grown using plasma plasma atomic layer deposition technique. To study defect formation during the deposition admittance spectroscopy and capacitance DLTS were performed. Capacitance measurements have shown that the high-power plasma affects electrical properties of the structure since defect with \( E_a = 0.33 \) eV appeared in near-surface region on BP/Si interface Therefore, it is necessary to perform further studies of various deposition parameters influence on electrical properties of BP/n-Si heterostructures.

Thus, the possibility of the formation of thin layers the prospects of their application for hole-selective contacts to Si was demonstrated.

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