Anomalously low ionization energy of phosphorus atoms in the electric field of silicon p-n junctions in the temperature range 10-20 K

A Shepelev, V Eremin and E Verbitskaya
Division of Solid State Electronics, Ioffe Institute, 26 Politekhnicheskaya, St.Petersburg 194021, Russian Federation

E-mail: artem.shepelev@cern.ch

Abstract. The work extends the study of the ionization properties of phosphorus atoms as trapping/emission centres in the electric field of silicon p-n junctions operating at low temperatures. The goal is describing the ionization of phosphorus atoms by a single effective parameter, the ionization energy of phosphorus energy levels $E_{\text{ion}}$. An approach to the study is based on manipulating the space charge concentration $N_{\text{eff}}$ in a nonirradiated silicon p$^+/n/n^-$ structure via filling phosphorus donors with electrons supplied by a laser pulse. Extracting the $N_{\text{eff}}$ from the experimental current pulse response shapes recorded at variable temperature and pulse repetition rate allowed building Arrhenius plot for evaluating $E_{\text{ion}}$ in the electric field. This value is shown to be 6.4±1.1 meV that is paradoxically low, being about 7 times less than the referred data.

1. Introduction
At the largest accelerator facilities such as Large Hadron Collider (LHC) in Conseil Européen pour la Recherche Nucléaire (CERN) and Facility for Antiproton and Ion Research (FAIR) in GSI Helmholtzzentrum für Schwerionenforschung (GSI), superconducting magnets are used to form particle trajectories. Due to the strict requirements for ensuring the accelerator safe operation it seems to be optimal to monitor the beam particle loss directly inside the cryogenic system in order to timely prevent local overheating of the magnet coils. For this, the use of compact silicon radiation detectors was suggested at CERN [1, 2] as a reliable way to ensure safety, which requires their operation at superfluid helium temperature and high accumulated dose of scattered particles and ambient radiation. The problem involves several aspects of the detector radiation hardness at low temperatures and is currently conducted as a novel subject of the silicon detector physics. A key condition for the proper and predictable operation of semiconductor detectors is high efficiency of charge collection in the sensitive volume [3], which is controlled by the electric field profile in the detector volume. In turn, the latter is related to the distribution of charged impurities and radiation-induced defects. Even at zero dose of radiation, dopant atoms acting as shallow energy levels in the silicon bandgap affect the profile of the electric field, which should be accounted in Si detectors development for operation at superfluid and liquid helium temperatures.

It was shown earlier [4] that the phosphorus atoms, which are shallow donors and major impurities responsible for the n-type silicon conductivity at room temperature (RT) and the effective
concentration in nonirradiated Si detectors, exhibit unusual behavior. The phosphorus donors stay positively charged in the electric field region even at $T < 15$K, despite the fact that the estimated probability of their ionization using the referred value of $0.045 \text{eV}$ is negligible. The classic Poole-Frenkel effect fails in explaining this fact, and the paradox has not yet been clarified.

This paper presents the results of the study of the ionization energy of phosphorus atoms acting as donors in the formation of the electric field in Si $p^+/n/n^+$ structures operating in the temperature range 10-20 K.

2. Experimental technique and samples

In the study, the $p^+/n/n^+$ diodes made of silicon doped with phosphorus were used. The Si resistivity was 10 k$\Omega \text{cm}$ that corresponded to the phosphorus concentration $N_D$ of $\sim 4 \times 10^{17}$ cm$^{-3}$. The thickness $d$ of the samples was 300 $\mu \text{m}$ and the $p$-$n$ junction area was $5 \times 5 \text{mm}^2$. The area was surrounded by the floating $p$ rings to prevent the low voltage breakdown. The samples allowed operation up to 300 $V$ in the temperature range 300 – 10K. The lateral dimensions of the junction were much larger than the structure thickness, which made it possible to use one-dimensional geometry for the data treatment.

The study was carried out using the Transient Current Technique (TCT) [5]. The method consists in recording the current responses of the detector to single-sided pulse laser injection of nonequilibrium charge carriers and their drift in the detector volume. To implement the method, a laser with a wavelength of 660 nm, the pulse duration of 48 ps and a variable pulse repetition rate was applied. The experiments were carried out in a compact helium closed cycle cryostat, which allowed cooling the samples to a temperature $T$ of 10 K. To record the current responses, LeCroy oscilloscope with analog bandwidth of 3 GHz and a sampling rate of 20 GS/s was used. The error in setting the frequency $f$ of laser pulses was $\pm 1\%$, stability of the temperature and bias voltage were $\pm 3\%$ and 0.01%, respectively.

3. Approach to estimating ionization energy of phosphorus atoms in the electric field of Si $p^+\text{-}n$ junctions

The main idea of the TCT method is that at a given time $t$ the current $i(t)$ generated in the $p^+/n/n^+$ structure and incoming to the readout circuit is proportional to the drift velocity of the weighting field $v_{dr}(E(x))$, where $E(x)$ is the electric field distribution. According to the Ramo theorem, the response is

$$i(t) = Q(t) \frac{E}{v_{dr}(E(x))},$$

where $Q(t)$ is the nonequilibrium drifting charge, $E$ the weighting field that equals $1/d$ for the planar pad detectors with a plane-parallel contacts, and $d$ the detector thickness. The drift velocity of charge carriers depends on the electric field in the sample volume and the carrier mobility $\mu$ as $v_{dr} = \mu E(x)$. The dependence is usually nonlinear since the mobility of charge carriers $\mu = \mu(E(x))$ is influenced by the electric field even in the relatively low electric field. The profile of the electric field in the detector volume is controlled by the distribution of the effective concentration of charged impurities $N_{eff}$. This dependence is described by the Poisson equation:

$$\frac{dE}{dx} = - \frac{e}{\varepsilon \varepsilon_0} N_{eff},$$

where $e$ is the elementary charge, $\varepsilon$ the silicon permittivity and $\varepsilon_0$ the vacuum permittivity.

Thus, the method makes it possible to obtain the profile of the effective concentration basing on the detector current responses.

4. Extraction of ionization energy of phosphorus atoms from the current response shapes

In a nonirradiated $p^+/n/n^+$ structure, $N_{eff}$ in the electric field at RT is uniform in the entire sample volume and equals the concentration of phosphorus atoms $N_D$. Depending on the applied bias voltage $V_{bias}$, the structure can be partially or fully depleted; the corresponding $E(x)$ profiles are shown in
The width of the space charge region $w$ is determined by the concentration of charged impurities $N_{eff}$ and the applied bias as

$$w = \frac{2\varepsilon \varepsilon_0}{e N_{eff}} V_{bias}. \quad (3)$$

The current response shape is sensitive to the electric field distribution. In a nondepleted detector ($w < d$), the current response shows an exponential decay [5] (figure 1b). At $w \geq d$, i.e., in a fully depleted sample, the current response is also exponential; however, its duration $t$ is limited by the carrier drift time $t_{dr}$ across the total sample thickness.

![Figure 1](image_url)

**Figure 1.** (a) The electric field distributions in the detector volume, and (b) current pulse responses in a partially and fully depleted detector.

The method for processing the current responses of fully depleted $p^+/n/n^+$ diodes is described in detail in [6]. The developed method gives the information on the effective space charge concentration in the detector volume, relying on the recorded detector current responses.

In the study, to quantify the value of the ionization energy of phosphorus atoms, $E_{ion}$, the influence of the laser pulse repetition rate on the shape of current response was considered. The physics of this approach is based on equation (3). It can be concluded that at a constant bias voltage, the transition from partial depletion to total depletion is possible only by reducing the concentration of charged impurities. This can be achieved by manipulating the occupancy of positively charged phosphorus atoms via increasing the concentration of electrons, which are generated by laser light and drift through the detector volume. One of the conditions for the effective filling is the comparable values of the electron emission time constant $\tau_e$ from the phosphorus atoms and the time interval between laser pulses $1/f$ (where $f$ is the repetition rate of pulses).

Thus, in the first approximation, the fraction of ionized phosphorus atoms $N_{eff} / N_D$ can be expressed as

$$N_{eff} \propto N_D \frac{\tau_e}{f-1}, \quad (4)$$

and, thus,

$$\tau_e \propto \frac{N_{eff}}{N_D f}. \quad (5)$$

The electron emission time constant is [7]:

$$\tau_e$$
\[ \tau_{e} = \frac{1}{\sigma_{e} v_{th} N_{c}} \exp \left( \frac{E_{\text{ion}}}{kT} \right), \]  

where \( \sigma_{e} \) is the electron emission cross-section, \( v_{th} \) the electron thermal velocity, \( N_{c} \) the effective density of states in the conduction band, and \( k \) the Boltzmann constant.

By combining (5) and (6), it can be obtained:

\[ \exp \left( \frac{E_{\text{ion}}}{kT} \right) \sim \sigma_{e} v_{th} N_{c} \times \frac{N_{\text{eff}}}{N_{D}} f^{-1}. \]

By varying the laser repetition rate and using the algorithm for extracting \( N_{\text{eff}} \) from the current response as described in [6], it is possible to build an Arrhenius plot for \( E_{\text{ion}} \) vs. \( 1/T \) taking the logarithm of equation (7). Its slope allows one to obtain the effective ionization energy of phosphorus atoms in the electric field. It should be noted here that the focus of this study is determination of \( E_{\text{ion}} \), while estimation of other parameters of the phosphorus as trapping/emission centers in silicon detectors operated at \( T = 10-20 \) K, such as the electron capture cross-section and its temperature dependence, and the influence of these on the electric field is beyond the scope of this study.

Ionization of shallow impurities in the electric field is a complex process. The potential barrier created by an impurity atom is distorted, which facilitates electron emission both above the barrier and tunneling through it. In turn, tunneling probability is significantly affected by the electron-phonon interaction via the barrier width energy dependence (so-called phonon-assisted tunneling). This process is considered in detail in [8]. However, the goal of the current study is describing the probability of ionization process by its parameterization in terms of activation energy \( E_{\text{ion}} \) (equation 6) as it is used in the Shockley-Read-Hall model [7].

5. Experimental results

Figure 2a shows the current responses of the sample at \( T \) of 11.7 K and a bias voltage of 10 V recorded at the different laser pulse repetition rates. Here and in figure 2b, the shapes of the current response are free from the influence of experimental conditions (finite penetration depth of the laser light and distortions of the signal in the readout circuit).

The change in the pulse shapes with increasing laser repetition rate (figure 2a) is clearly observed. At low frequency, \( f \leq 10 \) kHz, the current response shows gradual decay unlimited in time. Then, with increasing laser frequency to 500 kHz, the current pulse acquires a pronounced peak with a sharp drop limiting the current in time, which indicates full depletion of the structure. At \( f = 1 \) MHz, the pulse shape shows a flat top with a following sharp drop in current.

Figure 2b demonstrates evolution of the current responses at temperatures 11.3-21.7 K in the detector operating at bias voltage of 10 V and laser frequency of 500 kHz. Within this temperature range, the pulse shape corresponds to the positive \( N_{\text{eff}} \), which reduces as the temperature goes down.
Figure 2. Experimental current pulse responses obtained by TCT: (a) different laser pulse frequencies, (b) different temperatures.

The treatment of the pulse slopes gives the values of the effective concentration and thus the ratio $N_{\text{eff}}/N_D$ in equation (5), which are used for building the Arrhenius plot in accordance with equation (7). The experimental data obtained for $f = 500$ kHz and their linear approximation are shown in figure 3.

Figure 3. Arrhenius plot for estimating the phosphorous ionization energy.

Using the data in figure 3 and taking into account equation 3 in section 3, the estimated ionization energy of phosphorus atoms is $6.4 \pm 1.1$ meV.

6. Conclusion
In this work, the study of the ionization parameters of phosphorus atoms as trapping/emission centers in the electric field of silicon p-n junctions operating at $T = 11$-20 K was continued. An approach to the study based on the evolution of current pulse responses at manipulating the charged fraction of phosphorus atoms and thus, $N_{\text{eff}}$, via filling phosphorus donors with electrons, was proposed. This procedure allowed obtaining the energy of electron emission from phosphorus atoms in the electric field of p⁺-n junction. It should be noted that the estimated ionization energy is paradoxically low,
being about 7 times lower than the referred value of 45 meV, which cannot be explained even taking into account the Poole-Frenkel effect. This encourages the study to go on to get description of the observed results in terms of the electric field impact on the properties of shallow energy levels.

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