ECV investigation of ion-implanted photosensitive silicon structures for backside illuminated CCDs

G Yakovlev, D Frolov, A Zubkova and V Zubkov
Department of micro- and nanoelectronics, St. Petersburg State Electrotechnical University “LETI”, Prof. Popov str. 5, St. Petersburg, 197376, Russia

E-mail: gy@etu.ru

Abstract. Boron implanted Si structures used in back-side illuminated and electron bombarded charge coupled devices (CCD) were investigated by means of electrochemical capacitance-voltage (ECV) profiling. A set of test structures were specially fabricated using various energies and doses of boron implantation, as well as different materials were used as their coating layers: Al and silicon oxide. The concentration profiles of free charge carriers across the sample were experimentally obtained. Further, using Poisson equation and Fredholm equation of the first kind the distribution of free charge carrier concentration and electric field intensity in depth of the samples were calculated. By analyzing and comparison of simulated and experimentally obtained concentration profiles, the recommendations for optimization of sample parameters were proposed aiming at increase of sweeping field and decrease of surface potential impact on charge carrier transport.

1. Introduction
Fabrication of photon- and electron-sensitive devices with charge transfer implies a thinned from the back side CCD matrix with full removal of highly-doped epi-layer [1-3]. Untreated surface in such CCD does limited sensitivity to the UV radiation and low-energy electrons with short penetration depth because of the surface depletion [4, 5]. To overcome this a p⁺-area in the epi-layer is created, which provides both the bends over the surface potential caused by thinning processes, and also the sweeping field (to the front side contacts) for minority charge carriers generated by electron bombarding during device operation [6].

Ion implantation together with anneal is typically used to form highly doped area in the vicinity of the backside surface. For optimization of ion implantation it is very important to have a feedback and to investigate the obtained free charge carrier distribution profiles. One of the most useful measurement techniques for such task is the electrochemical capacitance-voltage (ECV) profiling. It shows up by wide measurement range of free charge carrier concentration (from $10^{14}$ to $10^{20}$ cm$^{-3}$) and ability to provide measurement results on depth from few nanometers up to few microns [7, 8]. The significant feature of the technique is simplified Schottky contact preparation.

The aims of this investigation are to measure the boron implanted Si samples by ECV technique, to simulate free charge carrier distribution and distribution of electric field in the samples. The results of experiments and simulation will allow making recommendations for optimization of the ion...
implantation process to increase the sweeping field and decrease the surface potential influence on charge carrier transport.

2. Samples and experimental technique

The test structures under investigation were low-doped 20 µm thick Si epi-layers with resistance of 12 Ohm·cm, grown on (100) Si substrate. Boron implantation was performed directly in the epi-layer or through coating layers. After implantation at 450°C the annealing for 60 min was used. The structure specification is shown in Table 1.

| Sample number | Implantation energy, keV | Implantation dose, ion/cm² | Coating layer material | Coating layer thickness, nm |
|---------------|--------------------------|-----------------------------|------------------------|-----------------------------|
| 1             | 13                       | 2·10¹⁴                      | -                      | -                           |
| 2             | 13                       | 5·10¹⁴                      | -                      | -                           |
| 3             | 13                       | 8·10¹⁴                      | -                      | -                           |
| 4             | 10                       | 2·10¹⁴                      | Al                     | 45                          |
| 5             | 15                       | 2·10¹⁴                      | Al                     | 45                          |
| 6             | 20                       | 2·10¹⁴                      | SiOₓ                   | 60                          |

The measurements were performed at room temperature using ECVPro profiler (Nanometrics). The aqueous solution of 0.2M NH₄HF₂ with addition of isopropyl alcohol (IPA) (up to 20% of total volume) was used to form electrolyte barrier with nominal contact area of 0.1 cm². During ECV profiling the samples were etched gradually with 5 nm step. To verify the etching depth and the surface quality the atomic force microscopy (AFM Solver NEXT) was used. The frequency of ac test signal was changed gradually from 0.1 to 5 kHz during the experiment (to eliminate the influence of series resistance on fast dropping capacitance).

In figure 1 the etching pit profile of sample #6 is shown. As it could be seen, the etching depth according to AFM measurements is 0.95 µm, which is in good agreement with ECV results (1.0 µm). The difference could be assisted, for instance, with a quite small AFM measurement area (20x20 µm) in contrast to the electrolyte contact area (0.1 cm²). The etched pit has a very sharp edge, the average surface roughness after etching is 5 nm, even better than before the etching (15 nm). It confirms the right choice of the electrolyte.

3. The experimental results and discussion

The main feature of the investigated ion-implanted structures is high doping level in the vicinity of the surface and shallow ion distribution profile, which needs keeping in mind the surface conductivity and sharp alteration of capacitance during the experiment.

3.1. Implantation in the samples without coating layers

The obtained free charge carrier profiles for samples #1-3 (no coating layers, various implantation doses) are shown in figure 2. With the increase of implantation dose the value of concentration in peak

![Figure 1. 3D AFM plot and height histogram of the sample’s #6 etched hole.](image-url)
does increase, while the location of the peak shifts to the surface. The asymmetry of the profiles in the vicinity of the maximum and their shift could be associated with the dopant diffusion. The obtained parameters characterizing the carrier distribution in all measured samples are summarized in Table 2.

![Figure 2](image1.png)  
**Figure 2.** Apparent free charge carrier profiles of samples #1-3 (without coating layers) with various implantation doses.

![Figure 3](image2.png)  
**Figure 3.** Apparent free charge carrier profiles of samples #4-6 implanted through various coating layers.

| Sample number | Carrier concentration in peak, cm$^{-3}$ | Distance from the peak to the surface, nm | FWHM for the carrier concentration profile, nm | Distance from the electric field maximum to the surface, nm | Electric field peak value, mV/nm |
|---------------|------------------------------------------|------------------------------------------|-----------------------------------------------|------------------------------------------|-----------------------------|
| 1             | 6.5·10$^{19}$                            | 18                                       | 18                                            | 31                                       | 2.7                         |
| 2             | 6.7·10$^{19}$                            | 21                                       | 27                                            | 44                                       | 2.5                         |
| 3             | 9.5·10$^{19}$                            | 29                                       | 37                                            | 67                                       | 1.8                         |
| 4             | 2.9·10$^{19}$                            | 8                                        | -                                             | 16                                       | 5.1                         |
| 5             | 2.3·10$^{19}$                            | 14                                       | 28                                            | 38                                       | 2.7                         |
| 6             | 8.6·10$^{18}$                            | 12                                       | 32                                            | 36                                       | 2.2                         |

**Table 2.** Parameters of the measured free carrier concentration profiles and simulated electric field profiles for the investigated samples

Note that all concentration profiles in figures 2 and 3 are smeared on Debye length, which is determined by the intensity of exchange coupling between dopants and free charge carriers:

$$L_D = \sqrt{\frac{\varepsilon_0 kT}{q^2 N}},$$  
wherein the Debye length itself depends on the concentration.

### 3.2. Implantation through coating layers

The experimental free charge carrier concentration profiles of the samples implanted through Al (#4, #5) and SiO$_x$ (#6) layers are shown in figure 3. As it could be seen, the concentration profiles shift to the surface with the decrease of implantation energy (samples #4 and #5). As it was expected, these samples have smaller peak concentration than samples #1-3 because of smaller implantation dose.

### 4. Analysis

#### 4.1. The electric field simulation

The use of the coating layer allows one to shift free charge carrier concentration profile closer to the surface. Wherein, it is very important to control the maximum of the gradient of the free charge carrier
distribution, which in turn determines the position of the electric field maximum [9]. Usually, the material of the coating layer and its thickness are fixed for specific device class. For example, for visible-blind devices Al layer acts as a filter, which cut the undesirable portion of the spectra. Since the photocathode material of the electron sensitive back-side illuminated devices usually is transparent for visible range of the spectrum, the use of the Al coating layer allows one to avoid the device blooming in this spectral range. In this case only photo-generated electrons (accelerated by the bias enough to overcome the coating layer) are detected.

The main factor, which influences the sensitivity of the photodetector element, is charge collection efficiency (CCE) [10]. The necessity of the photo-generated electrons to overcome the coating layer decreases the CCE (because of the high acceleration biases). But even this condition is not enough. To obtain the highest CCE the electron should get into the sweeping electric field area. It means that it must enter the area behind the electric field intensity maximum, which is determined by the implanted concentration profile. It leads to the necessity of the acceleration bias increasing. However, if the implantation through a coating layer took place, the doping profile shifts to the surface with the consequent shift of the electric field maximum. Thus, by varying the implantation energy and dose, the electric field maximum could be shifted nearly to the interface. And now, the applied bias value is only limited by the thickness of the coating layer needed to be overcome. These conditions contribute to the sweeping field formation without “dead layer” [11, 12], which is a summarized thickness of the low CCE area. This area is limited, on one hand, by the coating layer surface, and the electric field maximum on the other hand.

The analytical expression for the electric field intensity distribution could be obtained from the Poisson equation

\[
\frac{\partial^2 \varphi(x)}{\partial x^2} = -\frac{\rho(x)}{\varepsilon_0}.
\]  

(2)

Using the single donor assumption, after the math operations one could get

\[
E(x) = \frac{kT}{q} \frac{1}{n(x)} \frac{\partial n(x)}{\partial x}.
\]  

(3)

where \( n(x) \) is the free charge carrier distribution. We used this formula to obtain the electric field distribution in the investigated samples.

The electric field distribution for the sample #4, calculated from the experimental free charge carrier profile, is shown in figure 4. The peak value of the electric field intensity is 5.1 mV/nm (5.1 \( \times \) 10\(^4\) V/cm). Sample #4 has the highest (of all measured samples) the electric field peak intensity. The electric field maximum is shifted to the surface by the coating layer and is located at depth 16 nm from the surface. The peak electric field intensity values and its locations are summarized in Table 2. To our knowledge, based on the experience of numerous measurements (most are not presented in this paper), for getting high values of sweeping electric field the surface carrier concentration must be greater than 10\(^{19}\) cm\(^{-3}\).
4.2. Ion implantation simulation

It is useful to compare the results obtained in our investigation with the simulation by TRIM software, which is frequently used for estimation of implanted profiles. There are lots of works, where free charge carriers concentration profiles are obtained by CV-technique, which is widely used for semiconductor characterization. However, the concentration profiles obtained by conventional CV are limited by space charge area penetration (~100 nm for $5 \times 10^{17} \text{cm}^{-3}$ and for similar samples as in this paper it will be ~25 nm [13, 14]), while ECV (due to possibility of etching) allows one to obtain full profile information, even for the samples with very broad range of noticed concentrations.

The TRIM output is the doping profile, so to provide the comparison it is necessary to recalculate the doping profile to free charge carrier distribution. The latter is not identical to the doping profile because of the Debye tailing. When calculate, we do assume that all impurity is ionized (this is the case for room temperature).

The standard math processing for this is the convolution with known broadening function. However, in our case the broadening function isn’t constant and is dependent on concentration through the Debye length (1). The impurity ions and free charge carriers are charged oppositely, therefore the higher the dopant concentration is, the higher the attractive force between ions and free carriers and the less the Debye length become.

Our recalculation was based on the Fredholm equation of the first kind:

$$y(x) = \int K(x,x') f(x') dx'$$

where $f(x')$ is the doping distribution, $K(x,x')$ is the equation core (the broadening function), determined by the Debye length:

$$K(x,x') = e^{-|x|/\Lambda_D(x')}$$

We show in figure 5 two free charge carrier profiles for sample #3: (1) obtained from the experiment and (2) simulated by TRIM and processed by Fredholm equation. As one can see, there is a small (not more than 30 nm) mismatch between experimental and simulated position of extremum. We explain this mismatch by the extremely low annealing temperature in contrast to the standard Si implantation technology. Note that TRIM does not take into account the annealing temperature and its duration. The default TRIM settings are based on the suggestion that all impurity is built into the lattice and is electrically active, while the interaction between charged ions isn’t taking into account.
Moreover, in our case ion implantation took place with quite low energies (10–45 keV). The use of TRIM for simulation in this energy range could lead to the error around 30% [15], so generally TRIM is used for energies around 0.2-1 MeV. We conclude that these features are the main reason of the experimental and simulation mismatch.

5. Conclusion

In this work the specially prepared Si samples, implanted by boron with various energies and doses directly and through coating layers (Al and SiO\textsubscript{x}), were investigated. Free charge carrier profiles of the samples were obtained by electrochemical CV technique. From the experimental data the electrical field distributions in the surface vicinity were obtained. It was shown that for the formation of high sweeping field under the illuminated surface, the concentration profile must be sharp with the surface value not less than 10\textsuperscript{19} cm\textsuperscript{-3}. To obtain this it is necessary to provide ion implantation through the coating layer, wherein the doping distribution maximum must be located inside this layer. The optimal conditions, at which the electric field maximum is located in the vicinity of the surface, could be obtained by varying of implantation dose and energy for the given coating layer thickness. So, the experiment and simulation gave for 45 nm thick Al coating layer the following optimal implantation parameters: energy – 10 keV, dose – 2·10\textsuperscript{14} ion/cm. For the sample with these parameters the electric field maximum (5.1·10\textsuperscript{4} V/cm) is located at depth around 16 nm from the surface. The use of the ion implantation with the optimal parameters allows one to compensate decreasing of CCE after sample thinning, and also allows one to decrease accelerated bias with no drop of the device sensitivity. The comparison between experimental carrier concentration profiles and TRIM simulations was made. The mismatch between the simulation and experimental data could be attributed to neglecting of TRIM for the technology process features, particularly the annealing temperature.

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