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## Improved stability of black silicon photodiodes using aluminum oxide surface passivation

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### ABSTRACT

We have studied how high-energy electron irradiation (12 MeV, total dose 66 krad(Si)) and long term humidity exposure (75%, 75 °C, 500 hours) influence the induced junction black silicon or planar photodiode characteristics. In our case, the induced junction is formed using n-type silicon and atomic-layer deposited aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), which contains a large negative fixed charge. We compare the results with corresponding planar pn-junction detectors passivated with either with silicon dioxide (SiO<sub>2</sub>) or Al<sub>2</sub>O<sub>3</sub>. The results show that the induced junction detectors remain stable as their responsivity remains nearly unaffected during the electron beam irradiation. On the other hand, the SiO<sub>2</sub> passivated counterparts that included conventional pn-junction degrade heavily, which is seen as strongly reduced UV response. Similarly, after humidity test the response of the induced junction detector remains unaffected, while the pn-junction detectors passivated with SiO<sub>2</sub> degrade significantly, for instance, the response at 200 nm reduces to 50% from the original value. Interestingly, the pn-junction detectors passivated with Al<sub>2</sub>O<sub>3</sub> exhibit no degradation of UV response, indicating that the surface passivation properties of Al<sub>2</sub>O<sub>3</sub> are more stable than SiO<sub>2</sub> under the studied conditions. This phenomenon is further confirmed with PC1D simulations suggesting that the UV degradation results from increased surface recombination velocity. To conclude, the results presented here suggest that black silicon photodiodes containing Al<sub>2</sub>O<sub>3</sub>-based induced junction are highly promising alternatives for applications that require the best performance and long-term stability under ionizing and humid conditions.

**Keywords:** black silicon, photodiode, irradiation, humidity

### 1. INTRODUCTION

Silicon is still the dominating material for photo- and radiation detectors, as well as for indirect detection of high energy particles or X-rays. However, it is well known that the response of silicon photodetector is limited ultimately by losses due to reflection, surface recombination and bulk recombination. Recently several solutions have been proposed to overcome these losses. For instance, nanostructured silicon surface, i.e. black silicon, eliminates virtually all reflections due to gradient refractive index[1]. Secondly, Auger recombination is a major bulk loss mechanism in doped pn-junction, but it can be avoided by inducing the junction with a fixed charge incorporated in a dielectric film. Consequently, the combination of black silicon and induced junction can be used to make a photodetector with nearly ideal response [2], [3].

In many applications, the photodetector needs to operate reliably in a hostile environment that could include e.g. high relative humidity or significant doses of radiation. These issues can be averted to some degree with protective packaging but that often also dampens the signal of interest. Therefore, it would be beneficial if the detector could survive the conditions with minimal protection. The study of radiation hardness properties and environmental stability of induced junction black silicon photodiodes were targets of the project "Application of black silicon surface treatment to photodiodes

and silicon drift detectors” supported by the European Space Agency (ESA). We have recently reported radiation hardness results of conventional and induced junction black silicon PIN photodiodes in electron and proton beam irradiation[4], which indicated that induced junction photodiodes are more stable in case of electron beam irradiation. We present here further results from high-energy electron irradiation (12 MeV, total dose 67 krad(Si)) and long term humidity exposure (75%, 75 °C, 500 hours). We compare the stability of responsivity, when junction type and surface passivation layer are varied.

## 2. EXPERIMENTAL

### 2.2 2.1 Sample structures

The focus of the paper is on (surface passivation) stability of various kinds of photodiode junctions, namely silicon dioxide (SiO<sub>2</sub>) and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) passivated conventional boron implanted pn-junction, and both planar and black silicon induced junctions made by Al<sub>2</sub>O<sub>3</sub>. We present here a collection of the results from PIN and silicon drift detectors (SDD) processed during the ESA-project. The different types of PIN photodiodes were fabricated on the same n-type silicon substrate wafer (3-10 kΩcm, 500 μm-thick). They contained SiO<sub>2</sub> passivated pn-junction and both types of induced junction made by Al<sub>2</sub>O<sub>3</sub> [4] excluding aluminum oxide passivated pn-junction. The active area of PIN photodiodes was 7.9 mm<sup>2</sup>. SDDs with SiO<sub>2</sub> passivated pn-junction and active area of 29 mm<sup>2</sup> were also processed on similar substrates. During the project, SDDs were also processed on slightly different n-type wafer (>10 kΩcm, 675 μm-thick), in which the front junction was realized using Al<sub>2</sub>O<sub>3</sub> passivated pn-junction and both types of induced junctions made by Al<sub>2</sub>O<sub>3</sub>. The active area of SDDs was 19.6 mm<sup>2</sup>. SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> layer thicknesses were always 80 nm and 20 nm, respectively. These thicknesses were measured from the process control samples instead of finished detectors. Inductively coupled plasma reactive ion etching (ICP-RIE) was used to etch black silicon at cryogenic temperature and atomic layer deposition (ALD) was used to deposit Al<sub>2</sub>O<sub>3</sub>. To summarize, SDD’s entrance window and PIN photodiode junctions with different passivation layers comply the intended combinations as shown in Table I.

Table I Collection of structures used in this study. SiO<sub>2</sub> thickness was 80 nm and Al<sub>2</sub>O<sub>3</sub> thickness was 20 nm.

Detector structure	Junction	Passivation layer	n-type substrate
SDD	Boron implanted pn-junction	Al <sub>2</sub> O <sub>3</sub>	>10 kΩcm, 675 μm-thick
SDD	Planar or black silicon induced junction	Al <sub>2</sub> O <sub>3</sub>	>10 kΩcm, 675 μm-thick
SDD	Boron implanted pn-junction*	SiO <sub>2</sub>	3-10 kΩcm, 500 μm-thick
PIN	Boron implanted pn-junction*	SiO <sub>2</sub>	3-10 kΩcm, 500 μm-thick

\*Same boron doping profile

### 2.3 Environmental stress and electron beam irradiation

The humidity test was performed at the Helsinki Institute of Physics (HIP), in an ESPEC ENX12-7.5 environmental chamber. The detector chips were placed in the chamber without any packaging, on a 3D-printed holder designed for the tests. Both PIN and SDD devices were tested together. The holders were placed on top of a clean aluminum plate and inserted in the center of the chamber at room temperature. The test conditions in the chamber were 500 hours at 70 °C and 70% relative humidity. First, the chamber temperature was raised to 70 °C, and after that the humidity was raised to 70%, during a total ramping time of approximately 15 min.

The electron irradiation tests were performed at the Accelerator Laboratory at the University of Jyväskylä, Finland, using the RADiation Effects Facility (RADEF). The electron beam was generated using recommissioned linear electron accelerator (LINAC) Varian Clinac® medical accelerator. The dose rate was the maximum of LINAC, i.e. 0.76 krad/min (in silicon), which means that the electron beam consists of a series of 5 μs pulses with a period of 5 ms (which corresponds

to a duty cycle of 0.1%). The total dose of electron beam radiation was 66.9 krad(Si). The front junction of SDD and PIN photodiodes were under 100 V reverse bias during electron beam irradiation.

#### 2.4 2.3 External quantum efficiency measurements and simulations

External Quantum Efficiency (EQE) spectra were measured with a setup where the photodiode was illuminated with Bentham ILD-D2-QH-24 dual-lamp light source. The lamp was coupled to Bentham TMC300\_0060 monochromator where the wavelength was selected with 10 nm bandwidth and was then focused on the photodiode. The EQE values were calibrated against Newport 818-UV photodetector. In order to identify and quantify the damage mechanisms, we used the PC-1D simulator version 5.9 [5] to calculate the internal quantum efficiency (IQE) of the photodetectors as described in Refs. [4], [6]. The front surface reflection  $R_f$  was calculated using the free online calculator available by Filmtronics [7] and EQE can be obtained from the simulated IQE with:

$$EQE = (1 - R_f) IQE \quad (1)$$

The simulations used the default Auger recombination and radiative recombination parameters of the simulation tool. For the initial EQE, long (several ms) Shockley-Read-Hall bulk recombination lifetime was used. Additionally, a relatively low 100 cm/s effective back surface recombination velocity  $S_{eff}$  was used together with the mirroring effect of the back surface to get reasonable fitting of the initial EQE. Furthermore, the front surface  $S_{eff}$  was set to 10 cm/s for SiO<sub>2</sub>. The Al<sub>2</sub>O<sub>3</sub> passivation layer and induced junction was modeled with negative surface charge  $-2 \times 10^{12} \text{ cm}^{-2}$  and with surface recombination velocity of  $2.5 \times 10^5 \text{ cm/s}$  for both electrons and holes. The radiation damage and degradation due to humidity were modeled by decreasing the bulk lifetime and/or increasing the front surface recombination.

### 3 RESULTS AND DISCUSSION

#### 2.5 3.1 Electron beam irradiation

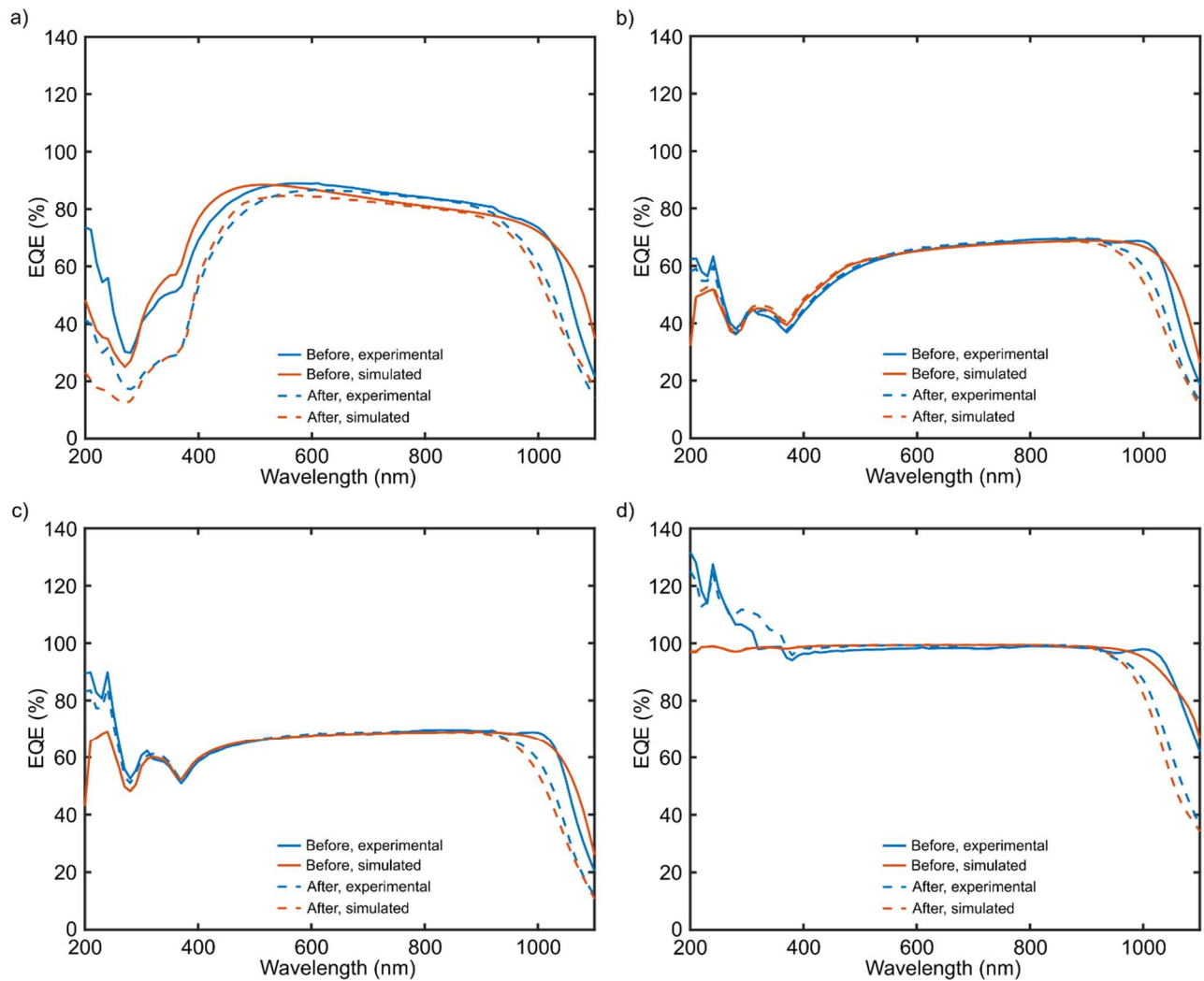


Figure 1. Measured (blue) and simulated (red) spectral response of SDDs having a) boron implanted pn-junction with SiO<sub>2</sub> passivation b) boron implanted pn-junction with Al<sub>2</sub>O<sub>3</sub> passivation c) planar Al<sub>2</sub>O<sub>3</sub> induced junction and d) Al<sub>2</sub>O<sub>3</sub> induced junction black silicon structures before (solid lines) and after (dashed lines) electron irradiation with 100 V reverse bias applied during irradiation.

Figure 1 shows the simulated and measured EQE curves of different types of SDDs before and after the 66.9 krad(Si) electron beam irradiation. For all devices, the EQE decreases at long wavelengths >900 nm. This change can be simulated by decreasing the silicon bulk lifetime to 20-40  $\mu$ s which models bulk damage generation during the irradiation. In addition, the ultraviolet response decreases in SiO<sub>2</sub> passivated boron implanted SDDs when irradiated with electron beam under 100 V reverse bias (Figure 1a). This change is similar than what has been reported earlier for SiO<sub>2</sub> passivated boron implanted PINs [4]. In case of SDDs, the impact of electron beam irradiation on EQE can be explained by using  $S_{\text{eff}}$  of  $5.5 \times 10^5$  cm/s at the Si-SiO<sub>2</sub> interface (Figure 1a), although this value is lower than  $1 \times 10^7$  cm/s which was concluded in the previous experiments [4]. This might indicate that the exact degradation rate is dependent on the processing history of the detector. However, when induced junction (Figure 1c,1d) or Al<sub>2</sub>O<sub>3</sub> passivation (Figure 1b) is used, the EQE of UV region is stable indicating that Al<sub>2</sub>O<sub>3</sub> passivation has better radiation hardness than SiO<sub>2</sub>.

### 2.6 3.2 Humidity stress

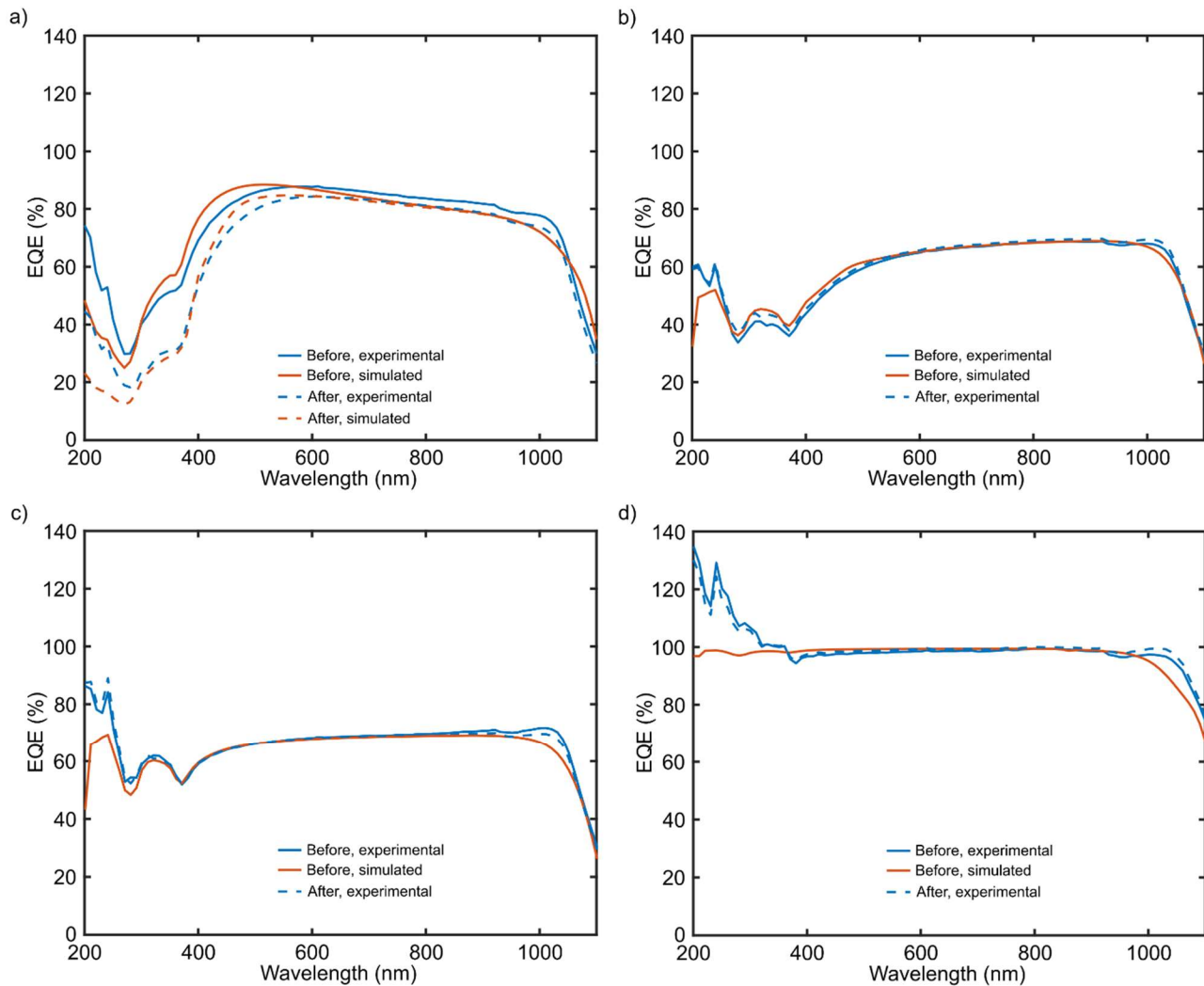


Figure 2. Measured (blue) and simulated (red) spectral response of SDD having a) boron implanted pn-junction with SiO<sub>2</sub> passivation b) boron implanted pn-junction with Al<sub>2</sub>O<sub>3</sub> passivation c) planar Al<sub>2</sub>O<sub>3</sub> induced junction and d) Al<sub>2</sub>O<sub>3</sub> induced junction black silicon structures before (solid lines) and after (dashed lines) treatment in environmental chamber.

Figure 2 shows the simulated and measured EQE curves of different types of SDDs before and after the 500 h humidity stress test. Different device types are showing clearly different EQE behavior. The EQE of boron implanted SiO<sub>2</sub>-passivated junction degraded clearly after the humidity stress as can be seen from Figure 2 a). The decrease in EQE after the test can be simulated assuming surface recombination velocity of  $5.5 \times 10^5$  cm/s at the Si-SiO<sub>2</sub> interface. Once again, when induced junction (Figure 2c,2d) or Al<sub>2</sub>O<sub>3</sub> passivation (Figure 2b) is used, the EQE of UV region is stable. The results from boron implanted SiO<sub>2</sub> passivated PIN detector before and after humidity stress are shown in Figure 3. Similar degradation is seen than in SiO<sub>2</sub> passivated SDD. With long wavelengths, no degradation is seen with any detector type.

The Al<sub>2</sub>O<sub>3</sub> film has been used as a moisture diffusion barrier [8]. It has also been reported that humidity treatment at the doped surfaces in case of SiO<sub>2</sub> passivation leads to reduction of chemical surface passivation [9] while the Al<sub>2</sub>O<sub>3</sub> surface passivation seems to be more stable [9]–[11] at least as long as no water condensates on the surface. Our results are in line with these reports suggesting that water vapor diffusion through the thicker SiO<sub>2</sub> (assuming that the oxidation reaction at the interface is not limiting) is faster than through the 20 nm thick Al<sub>2</sub>O<sub>3</sub> layer.



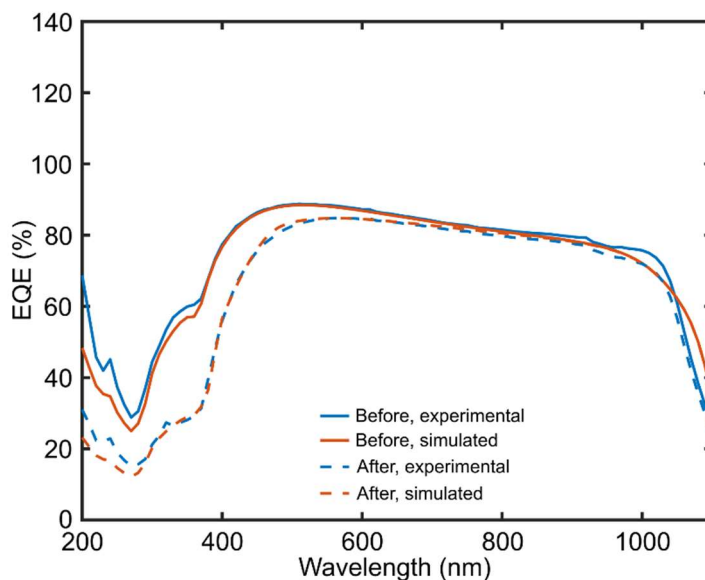


Figure 3. Measured (blue) and simulated (red) spectral response of boron implanted SiO<sub>2</sub> passivated PIN before (solid lines) and after (dashed lines) the treatment in environmental chamber.

#### 4. CONCLUSIONS

The EQE measurements before and after humidity stress showed that induced junction or pn-junction passivated with Al<sub>2</sub>O<sub>3</sub> remains unaffected whereas the response of pn-junction passivated with SiO<sub>2</sub> was severely degraded at ultraviolet wavelengths. We can conclude that Al<sub>2</sub>O<sub>3</sub> (induced junction or surface passivation) is more stable in environment containing water vapour. Similar observation was made during electron beam irradiation, in which the response of SiO<sub>2</sub> passivated pn-junction devices was almost completely lost at ultraviolet wavelengths while the response of Al<sub>2</sub>O<sub>3</sub> (induced junction or surface passivation) devices was not affected. These results suggest that black silicon detectors containing Al<sub>2</sub>O<sub>3</sub>-based induced junction are highly promising alternatives for applications that require high sensitivity together with long-term stability under ionizing and/or humid conditions.

#### ACKNOWLEDGEMENTS

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