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# Black silicon n-type photodiodes with high response over wide spectral range

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## ABSTRACT

Commercial photodiodes suffer from reflection losses and different recombination losses that reduce the collection efficiency of photogenerated charge carriers. Recently, we realized a near-ideal silicon photodiode, which steps closer to the physical performance limits of silicon photodiodes than any other silicon photodiode realized before. Our device exhibits an external quantum efficiency above 95% over the wavelength range of 235 – 980 nm, and provides a very high response at incident angles of up to 70 degrees. The high quantum efficiency is reached by 1) virtually eliminating front surface reflectance by forming a “black silicon” nanostructured surface having dimensions in the range of wavelength of optical light and 2) using an induced junction for signal collection, formed by negatively charged alumina, instead of a conventional doped p-n junction. Here, we describe the latest efforts in further development of the photodiode technology. In particular, we report improvements both in the short wavelength response via better control of the surface quality, and superior response to photons with energies close to the silicon bandgap.

**Keywords:** Silicon, photodiode, black silicon, induced junction, quantum efficiency, nanostructure, alumina, broadband photodiode, ideal photodiode

## 1. INTRODUCTION

Silicon photodiodes are used in wide range of applications ranging from automotive twilight detectors to medical imaging. When illuminated, they generate an output which is proportional to light level with excellent linearity over several decades of light intensity. As a first approximation within their typical range of use, when used in photovoltaic mode without bias, one electron is released per incoming photon having energy exceeding silicon bandgap. However, in practice all of these charges can't be collected as the performance of photodiodes is limited by both reflectance of incoming light and recombination of generated charges before they get collected to external circuit, resulting in typical quantum efficiencies of about 80%. The most important recombination modes are surface recombination on the (top) surface and auger recombination in doped region forming the diode pn-junction. Methods of effective passivation have been developed to reduce surface recombination and junction doping profile and anneal processes have been optimized to reduce auger recombination, but there's plenty of room for improvement. Various antireflective layers have been implemented to reduce the reflectance but they are typically optimized to some wavelength range at the cost of reduced response at other wavelengths.

Nanostructured silicon, or black silicon, with feature sizes smaller than the wavelength of visible light, can create an effective refraction index gradient and thus absorb all incident light<sup>1</sup>. These nanostructures also result in longer optical paths and wider acceptance angles for incident photons. A significant challenge included in the nanostructures is the greatly increased surface area, which makes nanostructured devices prone for surface recombination. This issue has been solved using conformal atomic layer deposited (ALD) alumina (Al<sub>2</sub>O<sub>3</sub>).<sup>2-3</sup>. Alumina passivated black silicon has been

successfully applied to silicon solar cells, resulting in excellent device characteristics<sup>4</sup>. Combining a nanostructured black silicon surface with an induced junction created via ALD deposited alumina, we recently manufactured silicon photodiodes with an external quantum efficiency above 96% over the wavelength range of 250 – 950 nm, and which exhibit a steady response at incident angles of up to 70 degrees<sup>5</sup>. Here, we describe our latest efforts in further development of our photodiode technology. In particular, we report improvements both in the short wavelength response via better control of the surface quality, and superior response to photons with energies close to the silicon bandgap.

## METHODS

### 2.1 Device fabrication

Our photodiode is illustrated in Figure 1. As substrate material, 525  $\mu\text{m}$  thick high resistivity ( $>10 \text{ k}\Omega\cdot\text{cm}$ )  $n$ -type, 100 mm diameter,  $\langle 100 \rangle$  surface oriented silicon wafers were used. Black silicon was formed on the active area ( $\text{Ø}5 \text{ mm}$ ) of the diodes by inductively coupled plasma – reactive ion etching (ICP-RIE). The process was carried out at  $-120^\circ\text{C}$  using a mixture of  $\text{SF}_6$  and  $\text{O}_2$ . To passivate the b-Si surface and to form an inversion layer near the substrate surface, a 20 nm thick  $\text{Al}_2\text{O}_3$  layer was grown on the active area via atomic layer deposition (ALD). The ALD process was carried out at  $200^\circ\text{C}$  using trimethylaluminium (TMA) and  $\text{H}_2\text{O}$  as the aluminium source and oxidant, respectively. Earlier device simulations<sup>5</sup> showed that the inversion (higher hole than electron concentration) extends down to approximately  $15 \mu\text{m}$  from the device surface. The associated depletion region edge extends down to approximately  $30 \mu\text{m}$  of depth, which corresponds to depletion depths of pn-diodes made on similar high resistivity substrates.

To facilitate an ohmic contact with the inversion layer, a region of was formed as a ring around the active area. Similarly, the backside of the wafer was phosphorus implanted to facilitate an ohmic contact with the substrate. Both contacts were completed with sputtering aluminium, which was annealed at  $450^\circ\text{C}$  for 30 minutes. From an integration perspective, our diode closely resembles commercial photodiodes, making it a possible drop-in replacement for a host of applications.

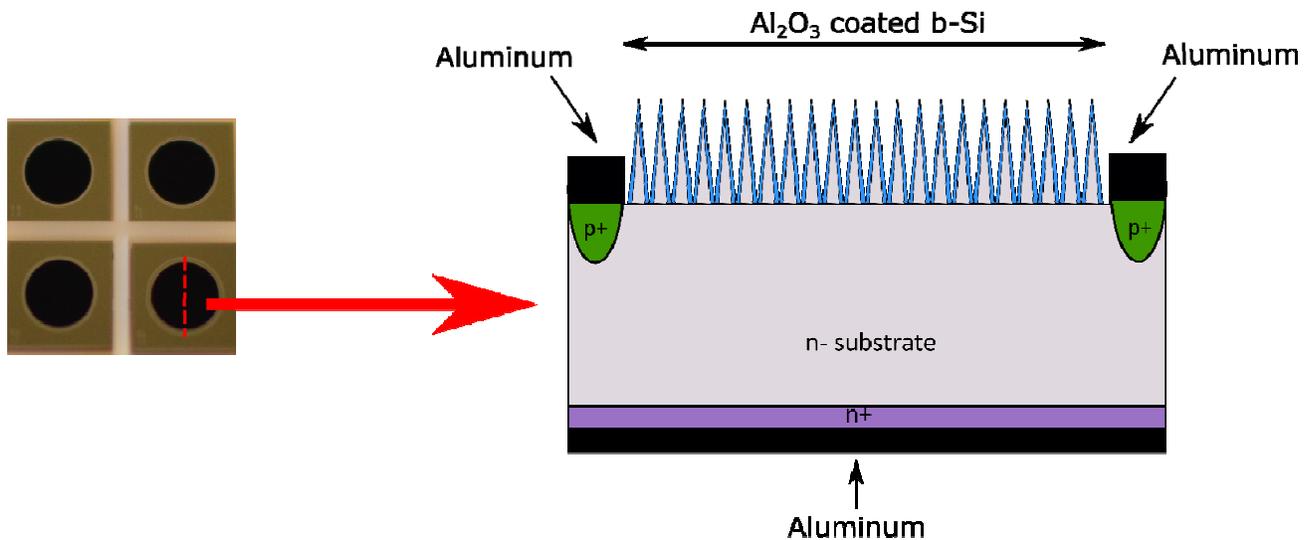


Figure 1 Left: photograph of four of our induced junction black silicon photodiodes. Right: Schematic of the cross section of the devices. Active area is formed as black silicon and then covered with alumina coated black silicon. Since the alumina is negatively charged, it generates an induced junction eliminating the need for doped pn-junction. The active area is surrounded with boron implantation (green p+ regions) which is required for ohmic anode contact. Similarly, the entire backside is phosphorous implanted (purple n+ region) to form the cathode contact. Aluminum (black regions) is sputtered on top of the doped areas to provide means for connecting the device to external circuitry.

## 2.2 Device characterization

Basic diode properties of the devices were first measured using normal current to voltage (IV) and capacitance to voltage (CV) measurements, some of which have been reported earlier<sup>5</sup>. Most of the responsivity data presented here were measured at VTT Technical Research Centre of Finland Ltd, Centre for Metrology MIKES together with National Metrology Research Institute (MRI). The responsivities were calibrated against reference trap detector, which is traceable to a cryogenic electrical substitution radiometer<sup>6</sup>. The measurements were further checked with the optical power calibration facility based on lasers<sup>7</sup>. The latest generation of devices, depicted by the purple curve in Fig. 3 was measured using a QEX7 Solar Cell Spectral Response device and calibrated against one of our own diodes, which was earlier calibrated at MRI. All measurements were performed at zero-bias conditions with a focused light beam essentially perpendicular to diode surface

## 2. RESULTS

### 3.1 Diode performance

One of the most important figures of merit of photodiodes is their external quantum efficiency, which is the ratio of the number of electrons collected to the number of photons incident on the device. Figure 2 shows the external quantum efficiency of our second generation of diodes further developed from the prototypes introduced<sup>5</sup>, measured at zero-bias condition under a continuous-wave light source. For comparison, two other diodes have been depicted: a broadband reference photodiode (Newport 818-UV) as well as the black silicon photodiode realized by SiOnyx<sup>8</sup>. The gray dashed line indicates the EQE of an ideal photodiode, which converts every single incident photon into exactly one electron-hole pair.

It is evident, that our device is significantly superior to both of the compared diodes. Our device has close to 100% efficiency over the full range of visible wavelengths. Additionally, our device maintains high EQE in the near infrared with a 95% conversion up to 980 nm. The b-Si nanostructure also increases the optical path of the photons, further enhancing the efficiency close to the silicon bandgap of 1.11 eV which corresponds to approximately 1170 nm wavelength of light. For example at 1100 nm, our device still exceeds 50% EQE.

Our device also has quite exceptional performance in the UV range. Here, the the induced junction is particularly powerful, because the UV photons are absorbed very close to the surface, and the strong electric field separates charge carriers from each other preventing recombination. In conventional pn-junction photodiodes charge carriers generated close to the surface are typically recombined due to dopant-induced Auger recombination or implantation damage. Additionally, from around 300 nm downwards, the energy of the incident photons becomes so high, that the electron released by the photoelectric ionization carries high enough kinetic energy to have a chance of ionizing a secondary electron. Probability of secondary ionization increases with photon and thus also electron energy as can be seen in the response graph. This phenomenon results in an effective EQE of over 100 % at wavelengths below 300 nm. For further discussion on this phenomenon, please see<sup>9</sup>.

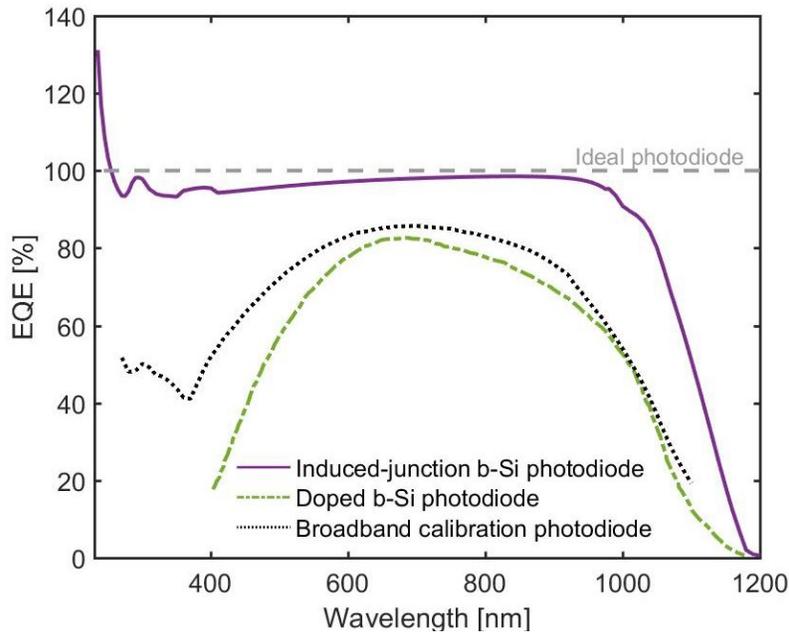


Figure 2 External quantum efficiency as a function of wavelength of the photodiode presented (purple solid line) representing our second generation of development, as well as a calibrated Newport 818-UV photodiode (black dotted line) and a doped black silicon photodiode realized by SiOnyx<sup>8</sup> (green dashed line). The EQE of an ideal photodiode (100%) is shown as a dashed grey line.

### 3.2 Process development towards 100% broadband external quantum efficiency

Here, we report on the progress to push the performance of our device even closer to 100% EQE.

Simulations performed and partially reported<sup>5</sup> indicated that an even higher EQE could be achievable with this combination of black silicon and ALD induced junction. To analyze possible causes for signal losses, more thorough simulations were performed related to for example the shape, dimensions and doping parameters of diode contacts. Additionally, devices of the first cycle were visually inspected for possible damage, which was not found. Finally, a scan across the active area of the best performing device was performed with a focused 325 nm laser beam of about 200-300  $\mu\text{m}$  in diameter. This scan revealed lower quantum efficiency regions on the active area, as can be seen in Figure 3. The shape and dimensions of these areas were characteristic to mechanical damage. The nanostructured non-reflective surface had probably been damaged during test device installation process. The second generation of our devices included improvements derived from the simulations, as well as careful handling during all process stages. This resulted in quite an impressive improvement in the long-wavelength regime, improving the EQE around 800 nm from 96% to 98.5%.

For the third round of devices, some further improvements were incorporated, still addressing some handling issues and further developing guard ring structures to improve other characteristics of the devices. This resulted in 98% or better external quantum efficiency over the entire wavelength range of 300 – 950 nm, according to preliminary measurements made by QEX7 Solar Cell Spectral Response device. Of the 2% that still remain lost, approximately 1% is lost to surface reflectance, and the other per cent due to surface and bulk recombination.

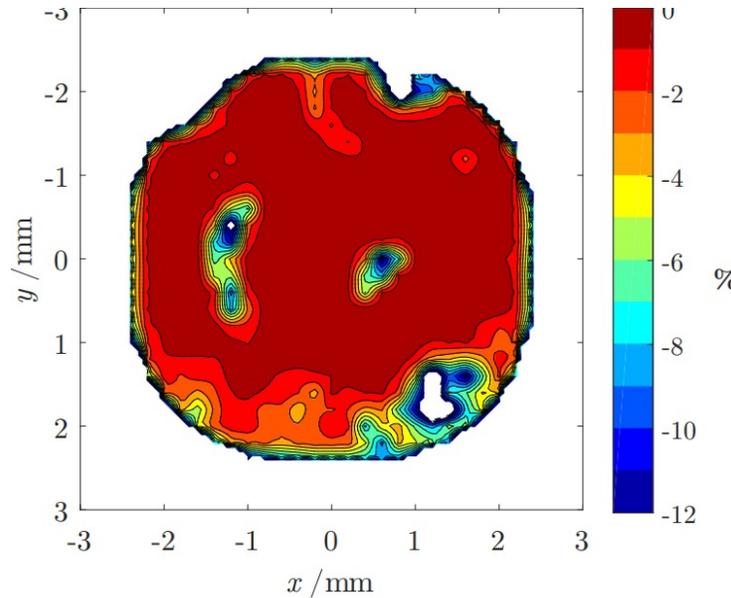


Figure 3 Relative response across a black silicon induced junction photodiode scanned with a 325 nm laser beam focuses to about 200-300  $\mu\text{m}$  in diameter. The overall response of this device was  $\sim 96\%$  including the clearly damaged areas.

Figure 4 shows results from these three generations of manufactured devices. The first one we reported earlier<sup>5</sup>, which exhibited slightly over 96% EQE for the wavelength range of 250 – 950 nm, the second one achieved higher response in IR range, and the third one achieved the  $\sim 98\%$  level across the same range.

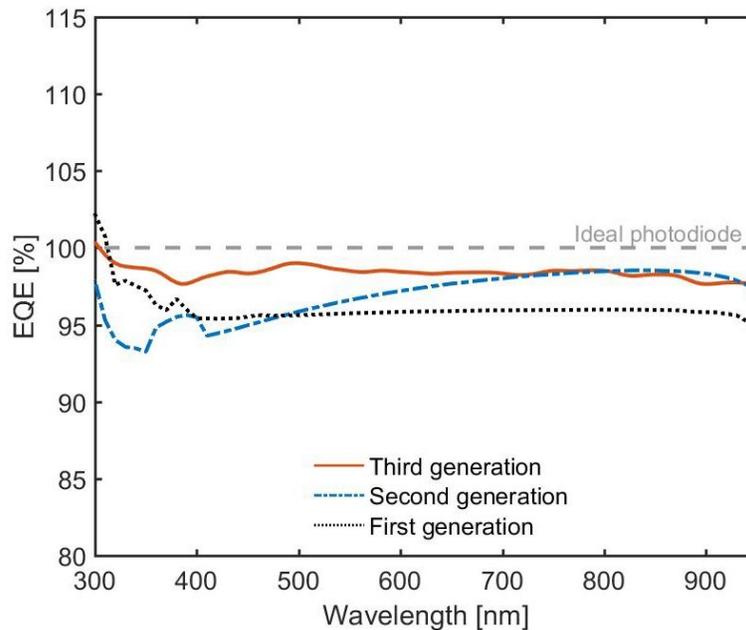


Figure 4 External quantum efficiency as a function of incident light wavelength for three generations of our devices. The first one (black dotted line) we reported earlier<sup>5</sup>, the second one (blue dashed line) achieved higher response in IR range, and the third one (red solid line) achieved the  $\sim 98\%$  level. The first and second generation were measured at VTT Technical Research Centre of Finland Ltd, Centre for Metrology MIKES together with National Metrology Research Institute (MRI) and the third generation is a preliminary result obtained with QEX7 Solar Cell Spectral Response device.

### 3. CONCLUSIONS

We have demonstrated a silicon photodiode with near-unity spectral response in the wavelength range of 250 – 950 nm, even with high incident angles. Here, we report for the first time the superior quantum efficiency of our diode in the NIR regime, close to the silicon bandgap, exceeding 50% at 1100 nm, as well as new data from deeper in the UV regime. We also showed that additional cycles of learning after our prototype device<sup>5</sup> further enhanced the performance of our diode. Preliminary results from our latest generation of devices exhibit over 98% EQE over the wavelength range 300 – 950 nm.

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