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N-type Induced junction Black Silicon photodiode for UV detection

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ABSTRACT

Commercial photodiodes suffer from reflection losses and different recombination losses that reduce the collection efficiency. Recently, we realized a near-ideal silicon photodiode that exhibits an external quantum efficiency above 95% over the wavelength range of 235 – 980 nm, exceeds 100% below 300nm, 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 proportional to the wavelength of light to be detected and 2) using an induced junction for signal collection instead of a conventional doped p-n junction, virtually eliminating Auger recombination at the light entry surface. This recombination prevention is especially important in ultraviolet detection since ultraviolet photons are absorbed very close to device surface, where conventional photodiodes have high doping concentration causing loss of signal, but induced junction diode is able to collect virtually all charge carriers generated. In this paper, we analyse the performance of our photodiodes under ultraviolet radiation.

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

1. INTRODUCTION

Silicon photodiodes are used in wide range of applications ranging from automotive twilight detectors to medical imaging. When illuminated, photodiodes generate an output which is proportional to light level with linearity over several decades of light intensity. Ideally, when used in photovoltaic mode without bias, one electron-hole pair is generated and collected per incoming photon having energy exceeding silicon bandgap. However, in practice the performance of photodiodes is limited by both reflectance of incoming light and recombination of generated charges before they get collected to external circuit. The most important recombination modes are surface recombination on the (top) surface and Auger recombination in doped region forming the diode pn-junction. These phenomena are particularly harmful for ultraviolet (UV) detection since UV is absorbed and charge carriers generated at the immediate vicinity of the surface where also the dopants are usually located. Thus both surface and Auger recombination cause losses which is why many of the present day photodiodes exhibit relatively poor UV response. Methods of effective passivation have been developed to reduce surface recombination and optimization of junction doping profile and anneal processes have been performed 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.

To overcome these limitations, we recently developed n-type black silicon induced junction photodiode with atomic layer deposited (ALD) aluminium oxide (Al_2O_3) surface layer[1]. The oxide layer contains negative oxide charge that is high enough to generate an induced junction on high resistivity n-type silicon, thus removing the need of using doping for charge collecting junction formation. Simultaneously, Al_2O_3 also provides an excellent surface passivation.

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Additionally, very low reflectance and even higher effective charge was achieved by using surface nanostructuring, i.e. black silicon. Nanostructured silicon, or black silicon, with feature sizes smaller than the wavelength of visible light, creates an effective refraction index gradient and thus absorbs all incident light[2]. 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 to surface recombination. This issue was solved using conformal atomic layer deposited (ALD) alumina (Al_2O_3).[3-4] Alumina passivated black silicon has earlier been successfully applied to silicon solar cells, resulting in excellent device characteristics[5]. 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[1]. Here, we describe our latest efforts in further development of our photodiode technology specifically in ultraviolet range.

2. METHODS

2.1 Device fabrication

525 µm thick high resistivity (>10 kΩ·cm) *n*-type 100 mm diameter <100> surface oriented silicon wafers were used as starting material. Black silicon was formed on the active areas (Ø5 mm) of the diodes by inductively coupled plasma – reactive ion etching (ICP-RIE). The process was carried out at -120°C using a mixture of SF_6 and O_2. It is possible to some extent to tune the general dimensions and characteristic shape is the spikes created by selecting the process parameters. Scanning electron microscope image of a representative structure is shown in figure 1.

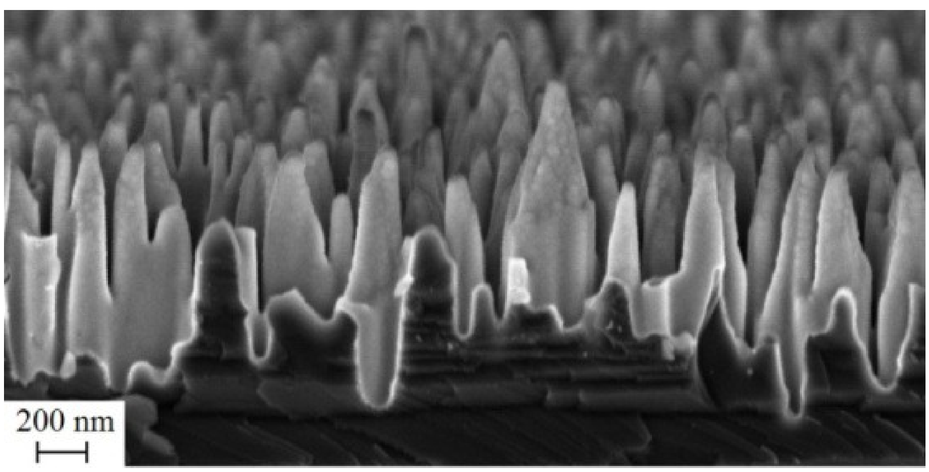

Figure 1. Scanning electron microscope image of black silicon created by inductively coupled plasma – reactive ion etching (ICP-RIE). The dimensions of the formed spikes are in the range of wavelength of optical light. As a result the effective index of refraction gradually increases from that of air to that of silicon, reducing reflectance to sub % level, thus absorbing almost all incident light.

The surface area of silicon is multiplied by formation of three dimensional structures, resulting into significantly increased surface recombination. To passivate the b-Si surface and also to form an inversion layer near the substrate surface, 20 nm of Al_2O_3 was deposited via atomic layer deposition (ALD). Atomic layer deposition is literally applied at atomic layer precision, resulting in that the dielectric layer deposited will conformally cover and passivate the high aspect ratio shapes created by the ICP-RIE process. The ALD process was carried out at 200°C using trimethylaluminium (TMA) and H_2O as the aluminium source and oxidant, respectively. With earlier device simulations[1], we confirmed that the inversion (hole concentration exceeding electron concentration) extends to approximately 15 µm depth from the device surface while the corresponding depletion region reaches approximately 30 µm depth. This corresponds to depletion depth of pn-diode made on equivalently high resistivity substrate.

To create an ohmic diode anode contact to the inversion layer, a boron implanted p+ region was formed around the active area. Similarly, the backside of the wafer was phosphorus implanted for an ohmic cathode contact with the substrate. Both contacts were completed with sputtering aluminium, which was annealed at 450°C for 30 minutes. The resulting structure is illustrated in Figure 2. The basic structure and operation principle of our diodes closely resembles commercial photodiodes, making it possible to design a drop-in replacement.

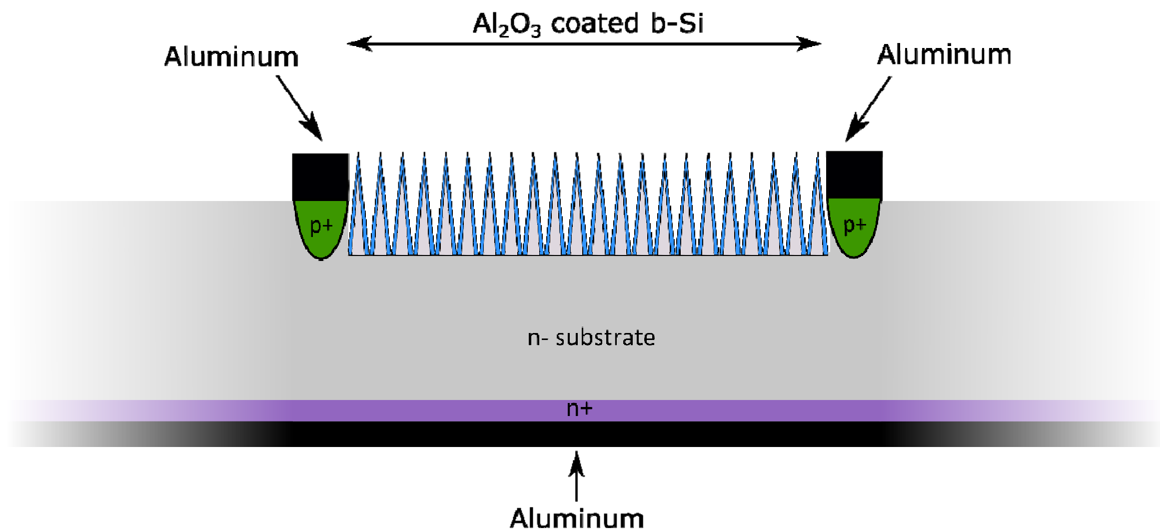

Figure 2 Schematic of the cross section of the device. Active area is formed as black silicon and then covered with alumina. Since the alumina is negatively charged, it repels electrons preventing their recombination, thus passivating the surface. It also generates an induced junction, eliminating the need for doped pn-junction. The active area is surrounded with boron implantation (green p+ regions) for ohmic anode contact. The backside is phosphorous implanted (purple n+ region) to form cathode contact. Aluminium (black regions) is sputtered on top of the doped areas to provide means for connecting the device to external circuitry.

2.2 Device characterization

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[6]. The measurements were further checked with the optical power calibration facility based on lasers[7]. The latest generation of devices 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

3. RESULTS

External quantum efficiency (EQE), i.e. the ratio of collected electrons to incident photons, is one of the most important figures of merit of photodiodes. Figure 3 shows the external quantum efficiency as a function of photon wavelength measured from our second generation of diodes further developed from the prototypes introduced in[1]. The curve was measured at zero-bias condition under a continuous-wave light source. For comparison, EQE of two other diodes have been depicted: an ultraviolet enhanced photodiode (OSI Optoelectronics UV series) which uses silicon dioxide induced inversion layer instead of a pn junction[8] and a violet enhanced photodiode (Hamamatsu S3590)[9]. The infrared region is cut out of the figure in order to highlight the UV region. The grey dashed line indicates the EQE of an ideal unity quantum efficiency photodiode, which converts every single incident photon into exactly one electron-hole pair.

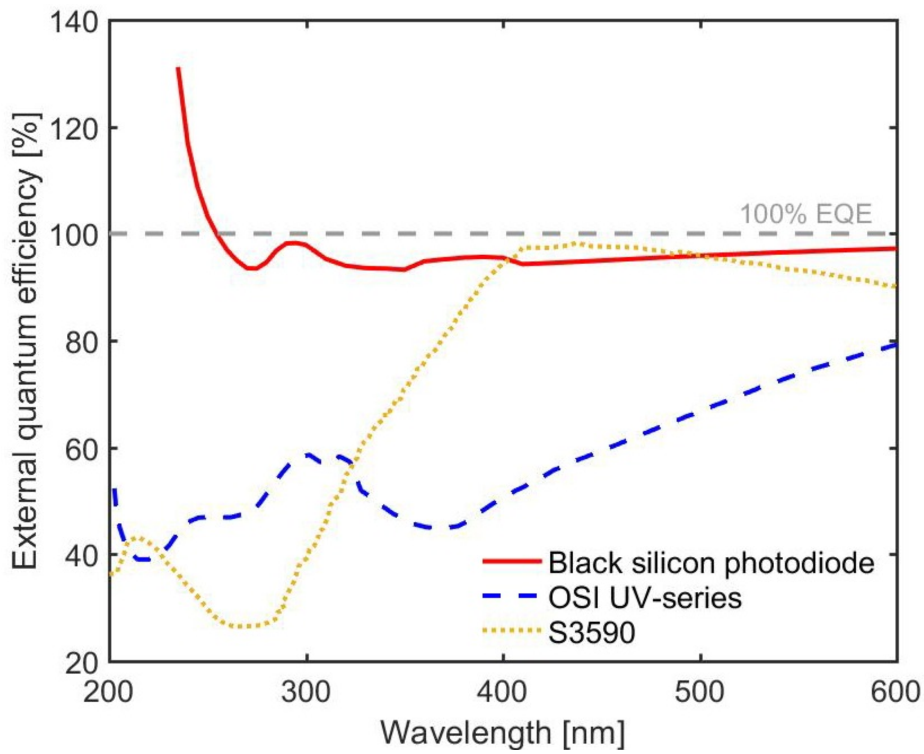

Figure 3 External quantum efficiency as a function of wavelength of the photodiode presented, as well as an ultraviolet enhanced photodiode (OSI Optoelectronics UV series) using silicon dioxide induced inversion layer instead of a pn junction[8] and a violet enhanced photodiode (Hamamatsu S3590)[9]. The EQE of an ideal photodiode (100%) is also shown.

It is evident that our device is significantly superior to the compared diodes, having close to 100% quantum efficiency over the full range of visible wavelengths. Our device also has quite exceptional performance in the ultraviolet range. The induced junction is particularly powerful there, because the UV photons are absorbed very close to the surface, and the strong electric field separates charge carriers from each other preventing immediate recombination. In conventional pn-junction photodiodes charge carriers generated close to the surface are more probably recombined due to dopant-induced Auger recombination or implantation damage. Although, the photodiode from OSI optoelectronics also utilizes induced junction, its EQE is still lower probably mostly due to optical reflections.

For short wavelengths, the energy of the incident photons is so high, that the electron released by the photoelectric effect carries enough kinetic energy to have a chance of ionizing another electron. Probability of this secondary, or impact ionization, increases with photon energy as can be seen in the response graph. With the virtually eliminated reflectance and surface recombination of our black silicon induced junction photodiode, this phenomenon results in the effective EQE increasing to over 100 % at short wavelengths.

Earlier it was thought that the excess photon energy of the ionized electron is dissipated via phonon emissions resulting in device heating. Kolodinski, et. al.[10] proved theoretically that if the photons have energy high enough, impact ionization instead of phonon emission is possible. Assuming that all the excess energy is transferred into kinetic energy of the carrier, the absolute minimum photon energy required for impact ionization is twice the bandgap. In silicon this would include photons with wavelength shorter than ≈550 nm. However, such an event would result in that the generated secondary electron would not have any kinetic energy left and would soon recombine. Thus, in practice the photon energies need to be larger. Earlier experiments and calculations, for example by Wilkinson, et. al.[11] indicated that the threshold for impact ionization is around 3.3 - 3.5 eV which translates into wavelength between 375 - 355 nm. Our results[1] indicate that the secondary ionization may start to contribute to the response already from around 400 nm downwards.

Theoretically attainable responsivity has later been assessed by L. Shi, et.al.[12], including at least the impact ionization phenomenon. Figure 4 shows our measured response data in the same graph with the theoretically attainable responsivity as indicated by them. It can be seen that our response, down to wavelengths we have so far been able to measure, approaches and even surpasses the theoretical curve. The values exceeding the theoretical limit could be due to enhanced ionization within or at the tips of the black silicon spikes. According to our simulations, the induced electric field at the tips of the black silicon spikes can reach levels typically used in avalanche photodiodes. Since deeper UV photons have a reasonable chance of getting absorbed already at the spikes, limited avalanche might take place. More experiments are still needed to verify this theory.

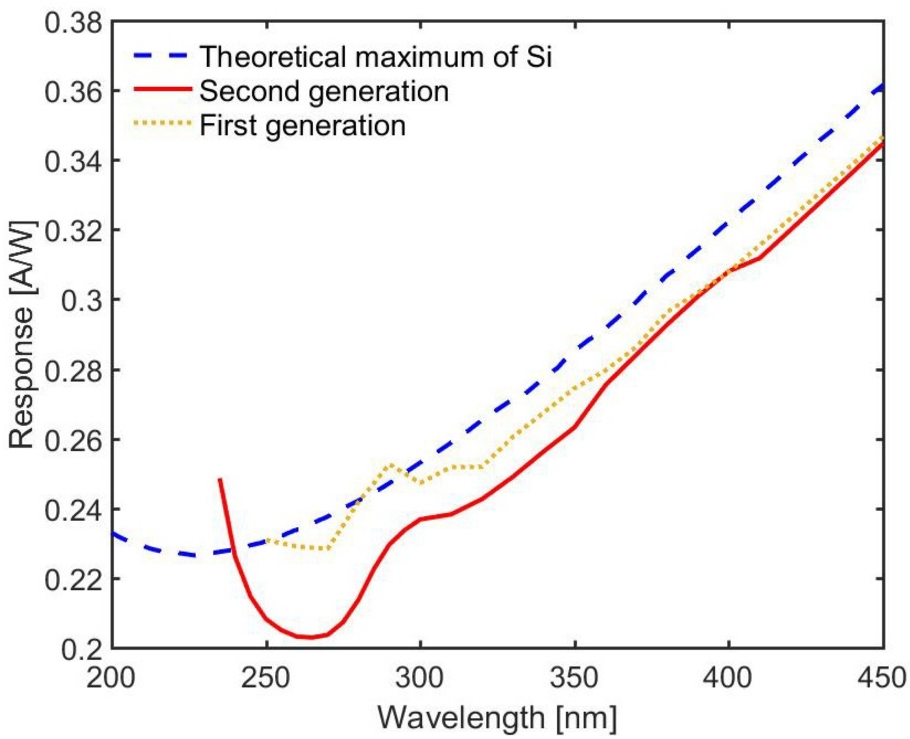

Figure 4. Spectral response measured from two first generations of our black silicon photodiodes, photodiode, plotted together with the theoretically attainable responsivity[12]. It can be seen that response of black silicon induced junction diode approaches and even exceeds the theoretical curve, potentially due to ionization at the very top of the three dimensional structures forming the black silicon.

Tolerance to UV radiation is another advantage of using alumina for inducing the junction. Previous induced junction photodiodes have usually been realized with silicon dioxide (SiO_2) on p-type silicon[13]. They utilize positive charges present in SiO_2 for inversion formation. Although, they achieve quite impressive response at UV-wavelengths, serious degradation results from exposure to UV radiation[14]. The degradation is caused by negative charges that UV light induces into SiO_2 which weakens the inversion by negating the positive charges. In Al_2O_3, the situation is the opposite. UV radiation enhances the negative charge and no degradation should be seen in the response. This is supported by our preliminary tests where we illuminated one of our photodiodes under a xenon lamp for 250 hours and did not see any change in the spectral response. Dingemans et. al.[15] have also detected a significant increase in the charge carrier lifetime of Al_2O_3 passivated samples after UV illumination. They too believe that this enhancement is due to increased negative charge in the oxide.

4. CONCLUSIONS

We have shown our recent efforts in development of n-type induced junction black silicon photodiode with near-unity spectral response in the wavelength range of 300 – 950 nm, even with high incident angles. In the wavelength range below 300 nm, the external quantum efficiency even exceeds 100% due to secondary ionization. In that region, the response of the demonstrated device is two to three times higher than that of commercially available silicon photodiodes for UV detection. As an example of the many benefits of this improvement, many fluorescence phenomena emit photons at this range, and doubling the sensitivity potentially facilitates detection of smaller concentrations of chemical compounds, or from longer distance.

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