# Silicon quantum dot superstructures for all-silicon tandem solar cells: Electrical and optical characterization

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Silicon quantum dots are one possible material to realize a top cell for an all-Silicon tandem solar cell. Silicon quantum dot (Si-QD) structures for solar cells have been reported by several authors [1, 2] in recent years. Most investigations focus on sub stoichiometric Si-based dielectrics, e.g. $SiO_x$, in which Si nanocrystals form during a high temperature annealing step. The choice of the surrounding dielectric matrix plays a crucial role because it determines the crystallization process, the interface to the Si-QD and the charge carrier transport. The formation of Si-QD in $SiO_2$ has been investigated in detail [3] and their luminescence and interface defects are already well understood [4]. Nevertheless, charge carrier transport through the Si-QD network is difficult due to the large energy barrier of the surrounding $SiO_2$ matrix. Charge carrier transport through other dielectrics such as $Si_3N_4$ or SiC seems to be more feasible, but the formation of Si-QD in these materials is much more complex due to the lower enthalpy of Si-N or Si-C bonds compared to the Si-O bond.

In this paper, the effect of dopants on the structural transformations is investigated. The addition of dopants to the deposition process has a strong influence on the crystallization properties. Therefore, advanced annealing procedures have to be adapted to the desired doping level. The structural transformations are being analysed and correlated to the electrical and optical properties.

## Experimental

Non-stoichiometric Si rich films of hydrogenated amorphous $Si_xC_{1-x}$ were produced by Plasma Enhanced Chemical Vapour Deposition (PECVD) with $SiH_4$, $CH_4$, $H_2$ and in parts $B_2H_6$ (0.25% diluted in H2) as precursor gases. Si NCs form during thermal annealing from the excess Si in the deposited layer. We use annealing temperatures between 800 °C and 1000°C and different heating rates and stoichiometries in order to control size and density of the Si NCs. SiC as a dielectric matrix is doped with different fluxes of $B_2H_6$, $PH_3$. We doped in situ using 0.25% dopant gas diluted in $H_2$. The structural transformations of Si rich SiC layers due to different annealing steps were monitored by Raman spectroscopy. Raman spectra show a transition from amorphous to crystalline Si in the temperature range between 900 °C and 1000 °C. Also, we observe a strong dependence of the crystallization properties due to the addition of dopants. Dark dc conductivity reveals that both the degree of crystallization and the doping level enhance conductivity. Boron-doped samples reach $\sim 10^{-4}$ $(\Omega cm)^{-1}$ after annealing at 900 °C and $\sim 0.1$ $(\Omega cm)^{-1}$ with a 1000 °C anneal. The activation energy $E_A = E_C - E_F$ was measured with temperature activated conductivity and amounts $\sim 0.88$ eV for a phosphorous-doped sample. Furthermore, the absorption coefficient of multilayer systems of 4 nm Si quantum dots in $SiO_2$ was measured. Below the optical bandgap of 2.04 eV, no optically active defects could be detected. The shape of the absorption coefficient is in agreement with the assumption of a square-root like density of states at the band edges. The specific resistivity of the Si-QD in a $SiO_2$ multilayer system was measured to be $3.7 \cdot 10^{10}$ $\Omega cm$ and a photoresponse of the Si-QD could be shown. As a preliminary result, illumination (~0.1 suns) enhances the conductivity by one order of magnitude.

## Conclusion

The influence of dopants on the structural transformation was investigated. As a general trend, the undoped samples show a decreasing resistivity with higher degree of crystallization. Also, based on the measurements of not annealed samples we conclude an increase of conductivity solely from doping, i. e. independent on the degree of crystallization. The resistivity could be reduced from $4.4 \cdot 10^{10}$ $\Omega cm$ to $3.5 \cdot 10^6$ $\Omega cm$ by annealing at 1000 °C and further to $5.1 \cdot 10^1$ $\Omega cm$ by additional doping with boron.
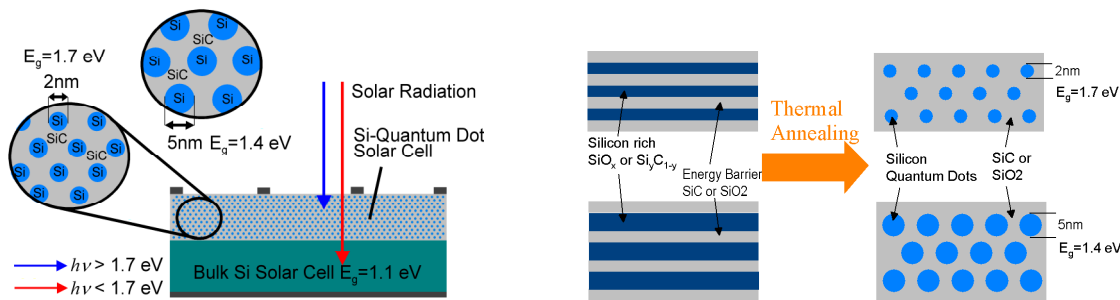
**Figure 1:** Schematical concept (left) of an all-Si tandem solar cell. The bottom cell is made of bulk crystalline Si while the top cell is realized with Si quantum dots in a dielectric matrix. The energy band gap of the top cell can be controlled by the size of the Si quantum dots (right). We choose the dielectrics $SiO_2$ and SiC as embedding matrices. $SiO_2$ is well controllable but has a high energy barrier, while SiC is more difficult to control but can be doped and shows higher carrier mobilities. Both material systems are deposited as multilayers of alternating stoichiometric and Si rich layers. Si crystallites are formed in the Si rich layers by thermal annealing between 900 °C and 1100 °C. The stoichiometric layers act as diffusion barriers in the thermal annealing step and limit the size of the Si nanocrystals.
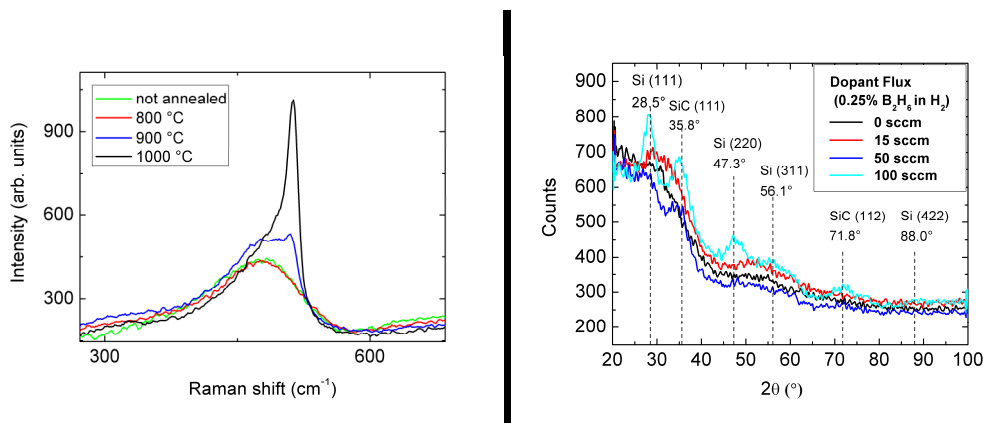


**Figure 2:** Raman (left) and XRD (right) pattern and of Si nanocrystals in SiC, doped with $B_2H_6$ during deposition. The thin films were deposited on synthetic quarz substrate (Suprasil 1) by Plasma Enhanced Chemical Vapour Deposition (PECVD) with $SiH_4$, $CH_4$, $H_2$ and in parts $B_2H_6$ (0.25% diluted in H2) as precursor gases. The Raman spectra (left) show samples that were doped with 100 sccm $B_2H_6$ in $H_2$ and annealed at 800 °C, 900 °C and 1000 °C for 30 min under 1050 mbar $N_2$ atmosphere. Before annealing, a broad peak around 480 cm$^{-1}$ is observed and can be attributed to amorphous Si. The 800 °C anneal does not change the peak shape, but a 900 °C anneal results in a shoulder at 512 cm$^{-1}$ due to Si crystallites. After a 1000 °C anneal the peak is more pronounced and only a small amorphous contribution is left. The XRD pattern (right) show a series of samples with different doping level, all annealed at 900 °C for 30 min in 1050 mbar $N_2$ atmosphere. A strong influence of doping with $B_2H_6$ on crystallization can be observed.
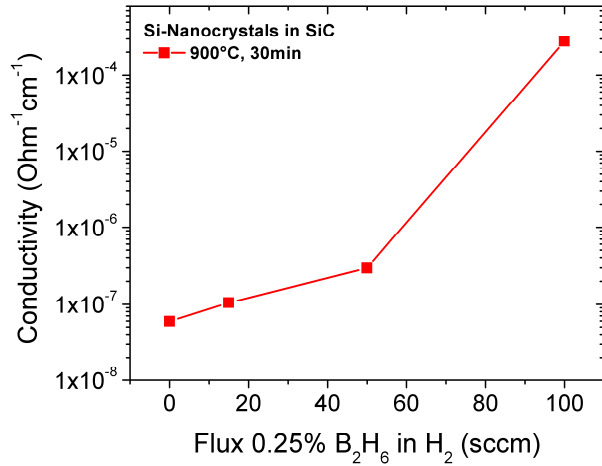
**Figure 3:** Dark dc conductivity of intrinsic and doped SiC films incorporating Si nanocrystals. Doping was realized by adding $B_2H_6$ to the precursor gases. Doping enhances the conductivity by several orders of magnitude.
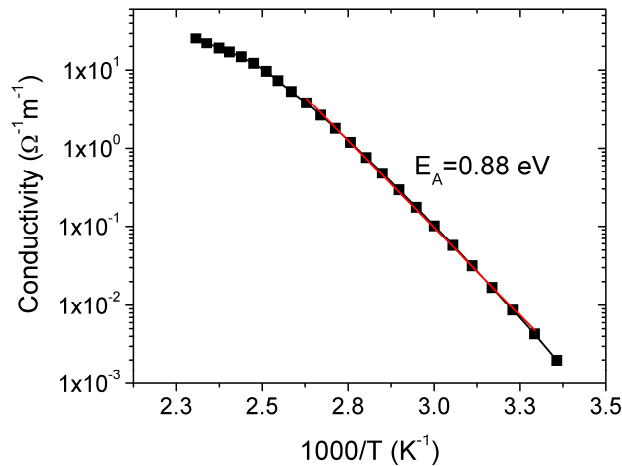


**Figure 4:** Temperature activated conductivity of phosphorous-doped SiC. Due to the mobility gap only the fraction $exp(-E_A/(k_BT))$ of charge carriers is activated above the mobility edge and contributes to conduction. $E_A$ is the activation energy, $k_B$ the Boltzmann constant and $T$ the temperature. The activation energy $E_A$ is a measure for the position of the Fermi level relative to the band edge, i.e. $E_A=E_C-E_F$ for n-type material. The temperature dependence of the conductivity was fitted over three orders of magnitude and reveals an activation energy of 0.88 eV.

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