

Quantum effects in silicon for photovoltaic applications

P. Ingenhoven^{*,1}, A. Anopchenko¹, A. Tengattini¹, D. Gandolfi¹, F. Sgrignuoli¹, G. Pucker², Y. Jestin², L. Pavesi¹, and R. Balboni³

¹ Nanoscience Laboratory, Department of Physics, University of Trento, Via Sommarive 14, 38123 Povo, Trento, Italy

² Photonics and Photovoltaics Group, Bruno Kessler Foundation, Via Sommarive 18, 38123 Povo, Trento, Italy

³ CNR-IMM Sezione Bologna, Via Gobetti 101, 40129 Bologna, Italy

Received 12 November 2012, revised 17 January 2013, accepted 17 January 2013

Published online 13 February 2013

Keywords downshifting, photovoltaics, silicon nano-crystals, tandem cell

* Corresponding author: e-mail philip@science.unitn.it, Phone: +39 0461 283172, Fax: +39 0461 282967

Quantum confinement effects in silicon might help to overcome the theoretical efficiency limit of $\sim 33\%$ of silicon cells [Shockley and Queisser, J. Appl. Phys. **32**, 510 (1961)]. The dominant loss mechanism in solar cells is the thermalization of photo-excited carriers to the band gap. Engineering of the band gap makes it in principle possible to obtain a conversion efficiency of $\sim 44\%$ [Pavesi and Turan (eds.), Silicon Nanocrystals, Fundamentals Synthesis and Application (Wiley-VCH, Berlin, 2010)]. Band gap engineering is achieved by controlling the silicon-nanocrystal (Si-NC) dimension. We currently use Si-NCs in solar cells to modify the solar spectrum in a way that the incoming light is more efficiently converted into electricity and also, to realize multiple junction cells to

minimize thermalization losses. The Si-NC energy of the band gap and the Si-NC optical properties depend strongly on the NC size, which can be controlled by the processing parameters. Therefore, light management is possible by varying the refractive index of the Si-NCs to improve the antireflective coating (ARC) and by conversion of absorbed high energy photons re-emitted in the red spectral region of light. Thus, in this approach Si-NCs are used as spectral down-shifters and for ARC optimization. Further, NCs allow the fabrication of higher band gap solar cells, to be used on top of standard silicon cells as tandem cell elements. Due to the tunability of the band gap, it is possible to construct all silicon multilayer or tandem cells. The concepts and research results for both ideas will be presented.

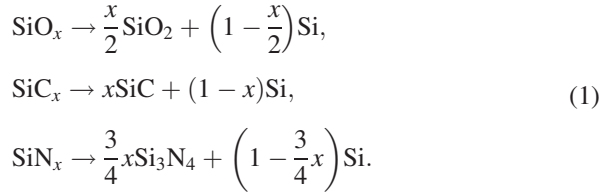
© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction: Why nanostructures? In photovoltaic solar cells, photons are converted into electron–hole pairs. These are separated by the internal field of a p–n junction. A crucial parameter is the electronic band gap. Theoretical computations show that the maximal efficiency for a single junction cell is around 30% and a band gap of 1.1 eV is needed to achieve this maximal value [1]. This value of only 30% efficiency is due to the fact that not all the photons in the solar spectrum are absorbed with the same efficiency. To overcome this limit, a large effort in the so called 3rd generation concepts is made. To use photons with energy lower than the band gap, which are not absorbed, up-conversion is exploited. In this concept, two or more low energy photons are combined into a high energy photon which has enough energy to excite an electron hole pair. On the other hand, high energy photons excite e–h pairs with a large excess energy with respect to the band-gap. The excess

energy is lost due to thermalization losses. Further, high energy photons generate e–h pairs which recombine at the surface yielding other losses. In this paper, we present two concepts to tackle these problems where nanostructures play a crucial role: namely the downshifting approach [2] and the tandem or multi-junction approach [3]. In the following, we will elaborate the concepts and present some preliminary results.

2 Physical properties of Si nanocrystals Si-NCs can be produced in different ways. With techniques like plasma enhanced chemical vapor deposition (PECVD), low pressure chemical vapor deposition (LPCVD), co-sputtering, chemical synthesis, and ion-implantation silicon rich oxides, carbides, or nitrides are deposited. To achieve nanostructures, a phase separation is induced via a high temperature annealing treatment of at least 1000 °C, see

e.g. [3]. The material now contains nanosized particles of crystalline silicon, see Eq. (1):



The physical properties of these particles are fundamentally different from the physical properties of bulk silicon. Due to quantum confinement of the charge carriers, the band gap broadens. For un-polar bonds on the Si-NC surface, the band gap is very well described by the effective mass approximation [3]. It is important to note that the interface between the Si-NC and the surrounding matrix plays a crucial role not only for the band gap but also for the quantum efficiency of the photoluminescence. The polarity of the bond that terminates surface strongly influences the HOMO-LUMO gap [4]. Further, the height of the barrier will influence the lifetime of the excited carriers. The energy gap for a spherical crystal is given by [5]

$$E_1 \approx E_G + \left(\frac{\sqrt{3}}{2}\right)^2 \frac{\pi^2 \hbar^2}{m^* a^2}, \quad (2)$$

where a is the crystal diameter and m^* the averaged and weighted isotropic effective mass. The crystal size can be controlled by using multi-layers of alternating matrix and silicon rich oxide materials. The thickness of the silicon rich material will then define the maximal Si-NC diameter.

Another important difference to bulk silicon is that the spatial symmetry in Si-NC is broken due to the finite size of the crystals. Hence, the momentum conservation is not strict anymore. The indirect band gap of bulk silicon turns into a so called pseudo direct band gap, i.e. there are no phonons needed for the optical transition between HOMO-LUMO levels. Therefore, the optical transitions are more likely and Si-NCs can have very efficient photoluminescence, see e.g. [5–7].

This photoluminescence has a strong broad peak in the near infrared around 700–800 nm (Fig. 1). The absorption band is located in the UV and blue visible range (Fig. 1). For efficient photoluminescence, good surface passivation of the Si-NC–matrix interface is crucial. In a badly passivated surface, defect states will give rise to mid-gap states that open up more channels for non-optical relaxation of the excited stated, and hence a less efficient photoluminescence [8, 9].

For tandem or multi-junction cell concepts, it is of crucial importance to influence not only the band gap but also the conductivity. To control the conductivity, we need to know the tunnelling properties between the Si-NCs. The tunnelling coefficient is given by the approximate

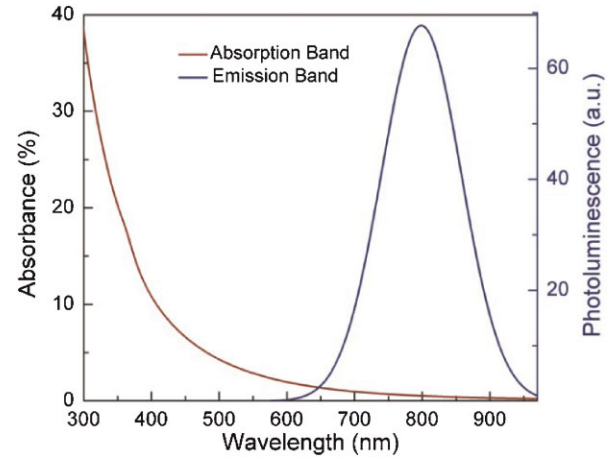


Figure 1 (online color at: www.pss-a.com) Typical absorption and emission band of SiNCs in a SiO₂ matrix [14].

relation [10]

$$T \approx 16 \exp\left(-d \sqrt{\frac{8m^*}{\hbar} \Delta E}\right), \quad (3)$$

where d is the inter Si-NC distance, m^* the carrier effective mass and ΔE the barrier height. Thus, the tunnelling probability (that is the conductivity) can be controlled by the inter Si-NC distance and the barrier height. The inter Si-NC distance can be set by the thickness of the spacer layers in a multilayer structure, as described above. Smaller distances will lead to a larger overlap of the wave functions and, hence, to a larger conductivity.

The barrier height can be influenced in two ways: by changing the band gap of the Si-NC or changing the dielectric surrounding of the dots.

For different dielectrics different barrier heights can be found (Fig. 2). Lower barrier heights will cause a larger conductivity.

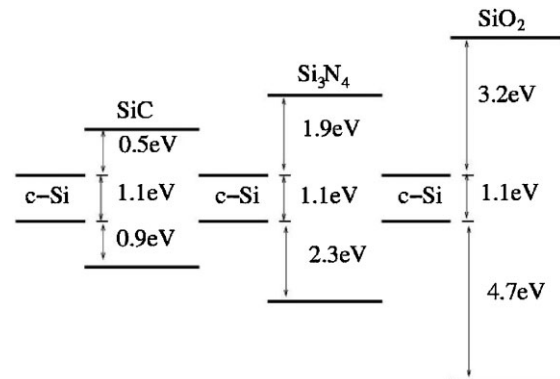


Figure 2 Band gaps of different dielectric materials and of silicon [3].

3 Photoluminescence down-shifting

3.1 Concept To utilize photoluminescence for efficiency enhancement of photovoltaic cells, two main concepts exist: down-conversion [11] and down-shifting [2].

Down-conversion and down-shifting of photons in layers located on the front side of solar cells can be used to utilize the short-wavelength part of the solar spectrum more efficiently. The down-conversion results in the generation of more than one e–h pair by high-energy photons with energy higher than $2E_g$. Although there is evidence of multiple electron generation in Si-NCs [12] it has not been used in photovoltaic applications yet.

The down-shifting process is based on absorption of blue photons and re-emission of red photons, therefore, the external efficiency of the down-shifting process is lower than unity. The downshifting process is beneficial because the lower energy photon will be converted into electrical energy more efficiently than the high energy photon, which might be lost in surface recombination processes, see Fig. 3. Shifting photons from the low efficiency band ($\lambda < 450$ nm) into the high efficiency band (around 800 nm) is theoretically beneficial for the overall cell performance.

The application of luminescent materials to overcome the poor blue response of solar cells was first described by Hovel et al. [13] in the late 1970s. Si-NCs seem ideal for this purpose as they have a wide absorption band below 450 nm, and a large Stokes shift to reduce re-absorption, see Fig. 1.

3.2 Modeling and first experimental results To model the downshifting effect, we use a transfer matrix model in combination with a phenomenological approach describing the photoluminescence re-emission of a luminescent downshifter layer, consisting of Si-NCs embedded in a silicon oxide matrix [14]. To enhance the efficiency of the silicon solar cell, we proposed using a $\text{SiO}_2/\text{Si-NCs}$ double-layer stack, as an antireflection-coating and as a

downshifter material. Optical simulations are used to calculate the optimal thickness of the SiO_2/SRO double layer stack. The photon flux is then used as a modified spectrum to evaluate the solar cell performances with an electrical simulation using Silvaco[®]. The optical characteristics of this stack were simulated and optimized as a front surface coating. The cell performances have been simulated by means of a two-dimensional device simulator and compared with the performances of a reference silicon solar cell. Modeling results show that an efficiency enhancement of about 1.5% is possible as a result of the downshifting process. In these simulations, optical conversion efficiency of only 10% of the Si-NCs photoluminescence was assumed. This means only 10% of the absorbed light is re-emitted at lower wavelength. Higher enhancements are possible for higher optical conversion efficiencies. Reports of 60% quantum efficiency in Si-NC [6] raise the hopes of achieving an enhancement of up to 8%, see Fig. 4 [14].

First experiments performed on Interdigitated-Back-Contact cells [15] lead to inconclusive results and further experiments are being performed.

4 All silicon tandem and multi-junction cells

4.1 Concept The idea is to harvest the photons according to their energy with a stack of cells with different band gaps. Theoretical calculations show that efficiencies of up to 42.5 and 47.5% can be reached for two and three cell tandem stacks [16], respectively. The band gaps for an all silicon tandem cell were calculated as 1.1 eV for silicon and 1.7–1.8 eV for the Si-NC top cell, Fig. 5.

For a three-cell tandem, the band gaps of the two top cells are optimal at 1.5 and 2.0 eV.

To realize a multi-junction cell from Si-NCs, a number of key points need to be addressed. The band gap needs to be engineered via controlled growth of the Si-NCs with specified size. This can be achieved via multilayer stacks [17], see Fig. 6.

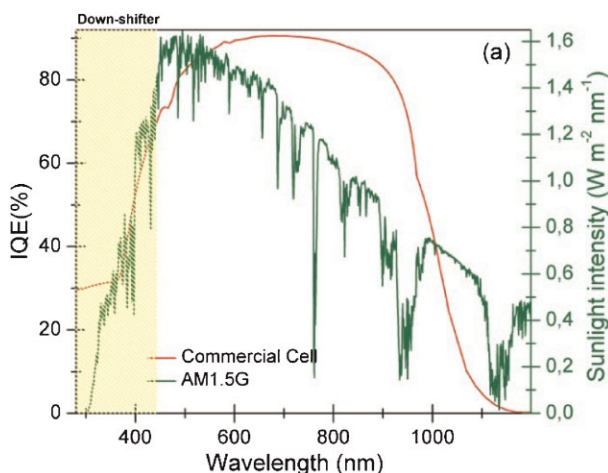


Figure 3 (online color at: www.pss-a.com) Internal quantum efficiency of a typical commercial solar cell (red) and the solar spectrum (green) [14]. Note the low response in region below 450 nm.

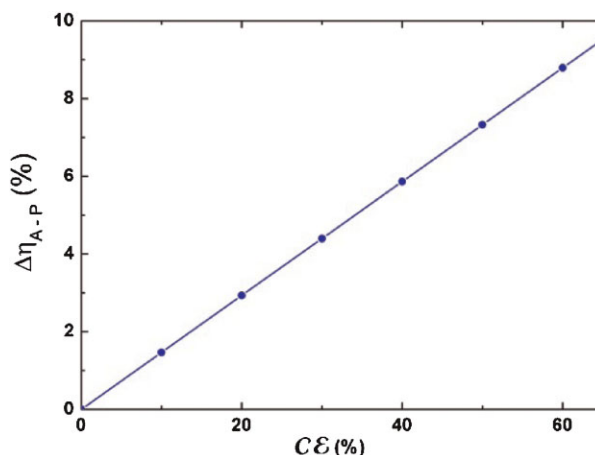


Figure 4 Our model predicts that efficiency enhancements of the solar cell are linear with respect to the optical quantum efficiency of the photoluminescence [14].

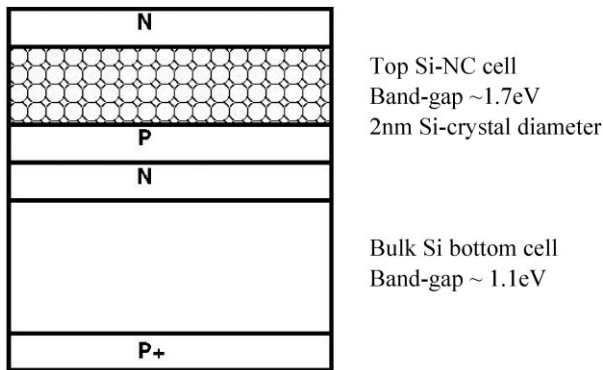


Figure 5 Schematic view of an all silicon tandem cell with a nanocrystalline top cell and a bulk silicon bottom cell [3].

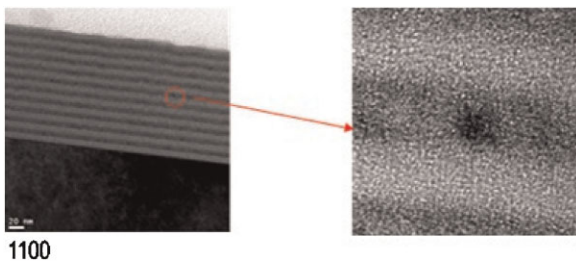


Figure 6 (online color at: www.pss-a.com) TEM pictures of Si-NC multilayers with SiO₂ spacer layers.

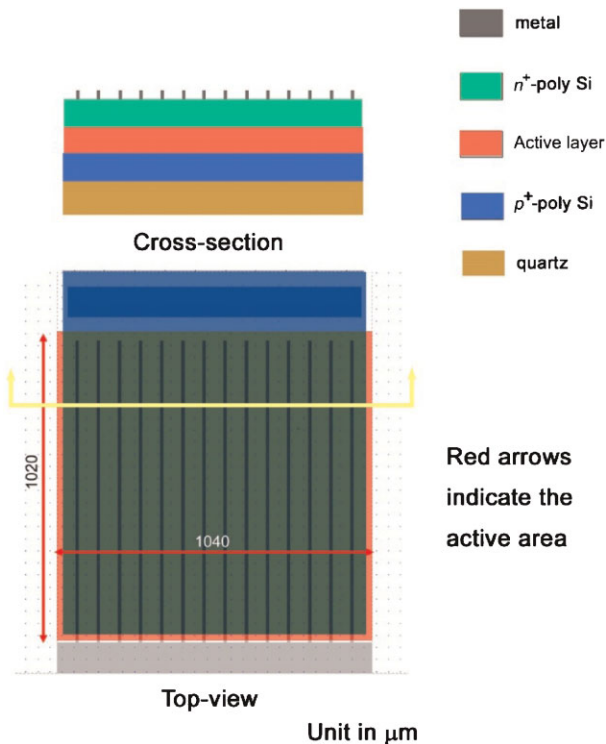


Figure 7 (online color at: www.pss-a.com) Schematic view of the Si-NC top cell devices, deposited on quartz [21].

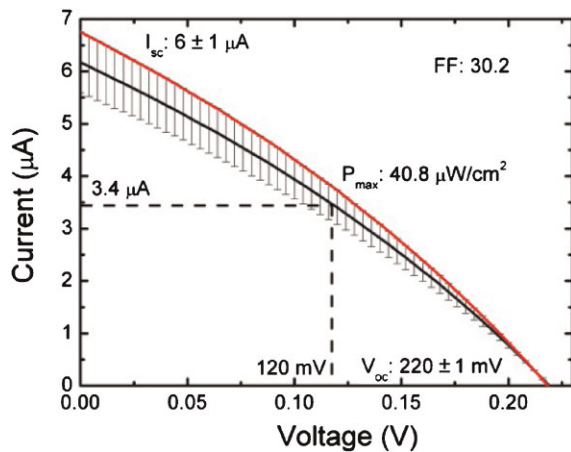


Figure 8 (online color at: www.pss-a.com) Current–voltage measurements from a multilayer nanocrystalline photocell [21]. The size of the Si-NCs was estimated to be 5 nm in a SiO₂ matrix.

An effective junction needs to be incorporated into the Si-NC layer. The doping of nanocrystals shows a fundamentally different behavior to that of bulk doping. Nevertheless, rectifying p–n junctions have been fabricated from nanocrystalline silicon materials [18–20]. The conductivity can be influenced by different barrier heights and different crystal distances, see Section 2.

4.2 Preliminary results To test the performance of the top cell structures, all Si-NC cells were deposited on quartz. Deposition on quartz instead of silicon was used to separate clearly the influence of the bulk silicon to that of the nanocrystalline layer. On silicon wafers, light will be absorbed not only in the nanocrystals but mainly in the bulk silicon. Further, it is difficult to separate the electrical properties of the nano-crystals from the bulk silicon if deposited on silicon. However, polycrystalline electrodes were used and make a complete separation of the bulk and nano properties difficult. Three different kinds of active layers were deposited via PECVD, an amorphous silicon (a-Si)/SiO₂ superlattice, a silicon-rich silicon oxide (SRO)/SiO₂ superlattice and a silicon-rich silicon nitride (SRN)/Si₃N₄ superlattice, see Fig. 7. The structures show a clear photovoltaic effect, see Fig. 8. The best photoresponse was found for amorphous silicon (a-Si)/SiO₂ superlattice, which had the highest silicon content. For this layer also, the conductivity measurements showed the highest results among the examined samples. Nevertheless, due to the high serial and shunt resistances only a very low efficiency of 0.041% was obtained [21].

5 Conclusions We have presented two approaches to overcome the fundamental thermodynamic limits of a single junction solar cell. The strong photoluminescence of the Si-NCs raises hopes for the use of this material as a luminescent downshifting layer. Nevertheless, much work and research is needed to fine tune the system. Light

management, better absorption–re-emission ratio are only two points that need to be addressed. Maybe a well balanced combination of different nanoparticles such as plasmonic layers to enhance the photoluminescence of the Si-NCs is a feasible way. For the tandem cell geometry, it is necessary to improve the electrical transport properties of the Si-NC top-cell, to ensure efficient carrier extraction. More work is also necessary in band-gap tuning and appropriate doping profiles.

However, both concepts show promising first results. The theoretical study [14] on downshifting shows a possible enhancement, and some Si-NC cells show a photovoltaic effect [21].

Acknowledgements This work is supported by EC through the FP7 ICT-248909 LIMA project.

References

- [1] W. Shockley and H. J. Queisser, *J. Appl. Phys.* **32**, 510 (1961).
- [2] Y. Jestin, in: *Comprehensive Renewable Energy*, Vol. 1, edited by A. Sayigh (Elsevier, Oxford, 2012), p. 563.
- [3] L. Pavesi and R. Turan (eds.), *Silicon Nanocrystals, Fundamentals Synthesis and Application* (Wiley-VCH, Berlin, 2010).
- [4] D. König, J. Rudd, M. A. Green, and G. Conibeer, *Phys. Rev. B* **78**, 035339 (2008).
- [5] T. Fangsuwannarak, E. Pink, Y. D. Huang, Y.-H. Cho, G. Conibeer, T. Puzzer, and M. A. Green, *Proc. SPIE* **6037**, 60370T-1.F (2005).
- [6] R. J. Walters, J. Kalkman, A. Polman, H. A. Atwater, and M. J. A. de Dood, *Phys. Rev. B* **73**, 132302 (2006).
- [7] B. G. Lee, D. Hiller, J.-W. Luo, O. E. Semonin, M. C. Beard, M. Zacharias, and P. Stradins, *Adv. Funct. Mater.*; DOI: 10.1002/adfm.201200572 (2012).
- [8] C. Delerue, G. Allan, and M. Lannoo, *Phys. Rev. B* **48**, 11024 (1993).
- [9] M. Jivanescu, D. Hiller, M. Zacharias, and A. Stesmans, *EPL* **96**, 27003 (2011).
- [10] K. Boer, *Survey of Semiconductor Physics* (Van Nostrand Reinhold, New York, 1990).
- [11] W. R. Taube, A. Kumar, R. Saravanan, P. B. Agarwal, P. Kothari, B. C. Joshi, and D. Kumar, *Sol. Energy Mater. Sol. Cells* **101**, 32 (2012).
- [12] M. C. Beard, K. P. Knutsen, P. Yu, J. M. Luther, Q. Song, W. K. Metzger, R. J. Ellingson, and A. J. Nozik, *Nano Lett.* **7**(8), 2506 (2007).
- [13] H. J. Hovel, R. T. Hodgson, and J. M. Woodall, *Sol. Energy Mater.* **2**, 19 (1979).
- [14] F. Sgrignuoli, G. Paternoster, A. Marconi, P. Ingenhoven, A. Anopchenko, G. Pucker, and L. Pavesi, *J. Appl. Phys.* **111**, 034303 (2012).
- [15] G. Galbiati, V. D. Mihailetchi, A. Halm, R. Roescu, and R. Kopecek, *Energy Procedia* **8**, 421 (2011).
- [16] F. Meillaud, A. Shah, C. Droz, E. Vallat-Sauvain, and C. Miazza, *Sol. Energy Mater. Sol. Cells* **90**, 2952 (2006).
- [17] A. Anopchenko, A. Marconi, E. Moser, S. Prezioso, M. Wang, L. Pavesi, G. Pucker, and P. Bellutti, *J. Appl. Phys.* **106**, 033104 (2009).
- [18] X. J. Hao, E.-C. Cho, G. Scardera, Y. S. Shen, E. Bellet-Amalric, D. Bellet, G. Conibeer, and M. A. Green, *Sol. Energy Mater. Sol. Cells* **93**, 1524 (2009).
- [19] Xj. Hao, E.-C. Cho, C. Flynn, Y. S. Shen, S. C. Park, G. Conibeer, and M. A. Green, *Sol. Energy Mater. Sol. Cells* **93**, 273–279 (2009).
- [20] S. Park, E.-C. Cho, D. Song, G. Conibeer, and M. A. Green, *Sol. Energy Mater. Sol. Cells* **93**, 684 (2009).
- [21] Z. Yuan, C. Schuster, G. Pucker, A. Anopchenko, A. Marconi, and L. Pavesi, *Proc. 7th IEEE Int. Conf. on Group IV Photonics*, p. 90 (2010).