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Si nanorod-based thin-film solar cells on glass: A potentially low-cost and high-efficiency all-inorganic approach

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ABSTRACT

Advances in nanofabrication for enhancing the efficiency of optical devices, such as solar cells and photo-detectors, via nanostructuring have attracted a great deal of interest. A photoconversion strategy employing nanorods (NRs) has emerged as a powerful way of overcoming the limitations of planar wafer-based or thin-film solar cells. But there is also a broad spectrum of challenges to be tackled when it comes to putting into practice cost-effective NR solar cell concepts. ROD-SOL is a 10-partner, 'nanotechnology for energy' project with end-users, equipment manufacturers and institutes from six countries forming the consortium. The aim of the project is to provide the photovoltaic market with a highly efficient (> 10%), potentially low-cost, thin-film solar cell concept on glass, based on silicon nanorods. This paper presents the project's achievements and discusses what the future might hold for nanotech-based solar energy production.

Introduction

The ROD-SOL project [1] was created to realize thin-film NR-based solar cell concepts utilizing different bottom-up and top-down NR fabrication techniques that are scalable and cost-effective. This collaborative project was comprehensive in that every aspect of the development chain – such as device simulation and realization, material characterization, and testing and benchmarking – was covered by one of the scientific or industrial partners. The benchmark included the estimation and comparison of potential manufacturing costs of the ROD-SOL cells, which in any case fall well within the range of known production costs associated with thin-film PV turnkey production lines.

Probably the most significant result of ROD-SOL is the realization of a semiconductor-insulator-semiconductor (SIS) solar cell concept based on Si NRs, no more than 2μm in length, currently exhibiting a non-optimized efficiency of ~10%. To achieve this, an Al_2O_3 insulating layer acts as a tunnelling barrier for minority charge carriers. A top-down approach via metal-assisted wet-chemical etching (WCE) is utilized to realize NRs in an n-doped Si(100) wafer and in multicrystalline Si thin films on glass. The ordered NRs are realized through patterning using nanosphere lithography (NSL). The resulting NR arrays exhibit an absorbance greater than 90%. Atomic layer deposition (ALD) then allows for a suitable application of the tunnelling barrier and a transparent conducting oxide (TCO) layer, which is then contacted with a screen-printed gold contact grid.

Lowering the cost of solar energy

The sun is our only universal source of energy, and photovoltaics (PV) allows for a broad range of applications on all scales to exploit solar energy. However, more than 90% of today's solar cells are made from bulk silicon wafers, which are expensive because of production costs, even though silicon itself is an abundant resource. In recent years increased demand has further inflated the price of solar-grade silicon. With the price of silicon accounting for at least one-third of the total price of the cell, this still makes solar energy roughly four times as expensive as energy derived from fossil fuels.

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An obvious way to lower the cost of solar energy is therefore to reduce the amount of silicon used, and thus thin-film solar cells are expected to dominate future markets. By using thin-film technology, the thickness of the silicon can be reduced from 200–300μm to 0.2–5μm – but at a price. First, the absorption length of visible light in silicon is about 200μm. Consequently, effective light trapping needs to be in place when silicon layers of only a few micrometres in thickness are used. Second, the quality of thin-film silicon on alternative substrates, for example glass, is usually limited by a large density of extended lattice defects, such as grain boundaries and dislocations, which means that high efficiencies can no longer be achieved. The efficiency of this thin-film material is poor (usually less than 10%), largely due to carrier recombination at grain boundaries that follow from the material's inherently small grains.

The most likely candidates for solving the problem of poor efficiency are nanomaterial-based approaches, often termed 'third-generation PV'. The nanocomponents under consideration are not limited to a silicon base: they can be organic or inorganic in nature, or a hybrid of the two. However, silicon is still favoured for solar cell production, despite the free path length of visible light in silicon of ~200μm, since it is non-toxic and abundant on earth. Furthermore, the properties of silicon are well understood and its processing is highly controlled as a result of decades of microelectronics research.

Nanomaterials-based solar power: the science of 'third-generation PV'

When Green [2] coined the term 'third-generation PV' almost 15 years ago to describe all alternative approaches to classical Si photovoltaics, it was meant as a call for new strategies to overcome the Shockley-Queisser limit and to broaden the applicability of PV as a source of renewable energy. Nanostructuring solar cells is one such strategy, as it is based on two pronounced light-trapping effects. First, resonance phenomena having geometric dimensions of the same order of magnitude as the wavelength of visible light become established, thus significantly enhancing the absorption of light within the active NR regions. Second, an array of NRs is essentially a rough surface, which again supports the enhancement

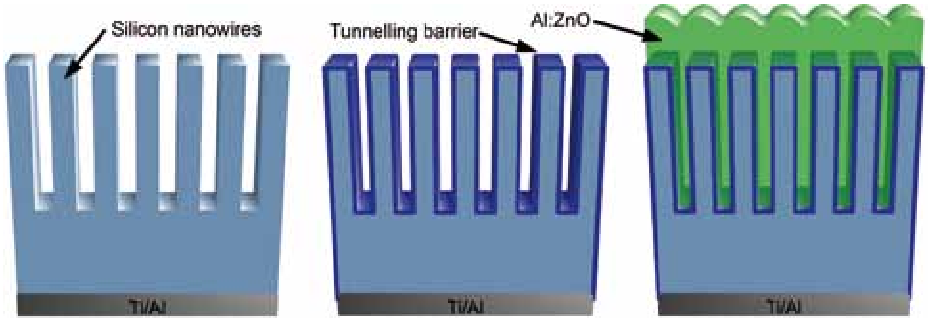

Figure 1. Schematic of a semiconductor-insulator-semiconductor (SIS) solar cell concept based on Si NRs. The Al_2O_3 insulating layer (dark blue) acts as a tunnelling barrier for minority charge carriers. A TCO layer of Al-doped ZnO (green) serves as the degenerately doped second semiconductor.

of absorption due to multiple scattering and final absorption within the NR layer. Furthermore, an NR geometry almost automatically increases the defect tolerance of the utilized semiconductor layers, eases the facile strain relaxation and allows the decoupling of the charge separation path from the photon path. Altogether this not only opens up the field for a broad range of manufacturing technologies, but also facilitates the development of new approaches regarding multijunction solar cells, which offer the potential of achieving efficiencies higher than 60%, thus overcoming the Shockley-Queisser limit.

Next generation PV and ROD-SOL

The ROD-SOL project exploits the strongly absorbing Si NRs as absorbers in a 3D solar cell architecture. The most promising cell concept is shown in Fig. 1 and is based on a semiconductor-insulator-semiconductor (SIS) cell configuration with Si NRs no longer than 10µm, with an Al_2O_3 insulating layer acting as a tunnelling barrier for minority charge carriers. A TCO layer of Al-doped ZnO serves as the degenerately doped second semiconductor. A barrier layer and TCO are deposited by ALD, a chemically self-limited and therefore suitable deposition process that permits wrapping a layer around even NRs with high aspect ratios.

A top-down approach was utilized in ROD-SOL in order to realize the NRs via metal-assisted WCE in an n-doped Si(100)-wafer (for initial trials) and ultimately in multicrystalline Si layers on glass substrates. The latter were obtained from crystallizing amorphous Si (a-Si) starting layers using furnace anneals, lasers or electron beams as sources of energy for the crystallization, either with the a-Si layer in its solid phase or liquefying it prior to re-crystallization. The NRs were initially created by a random self-aligned etching process shown in Figs. 2(a) and (c).

The WCE approach is based on a self-organized two-step process: step one is creating Ag-nanoparticles on the Si layer or wafer surface; step two is performing metal-enhanced oxidation of the Si, combined with removal of the resulting Si oxide using hydrofluoric acid (HF) [3]. In the first step, the samples are immersed in an aqueous solution of 0.02M silver nitrate ($AgNO_3$) and 5M HF in a volume ratio of 1:1. In the second step, an etchant of 5M HF and 30% H_2O_2 in a 10:1 volume ratio is applied. Due to the nature of the etching process, the Si NRs are aligned in the <100> crystal orientation and therefore reside perpendicular or oblique to the substrate surface for Si grains of different orientation. Finally, the samples are washed in concentrated (65%) nitric acid (HNO_3) for several minutes to remove residual Ag nanoparticles from the Si NR surfaces.

With this self-aligned process, the control over NR dimensions is very limited. Even so, it was possible to realize a large area cell with ~10% efficiency as shown in Fig. 3. So far, this has been achieved with a cell size between 1.2cm × 1.2cm and 6cm × 6cm (Fig. 3a). The layer sequence of the SIS cell from Fig. 1 is obtained by ALD and the Al-doped ZnO (AZO) TCO layer is shown in the scanning electron micrograph in Fig. 2.

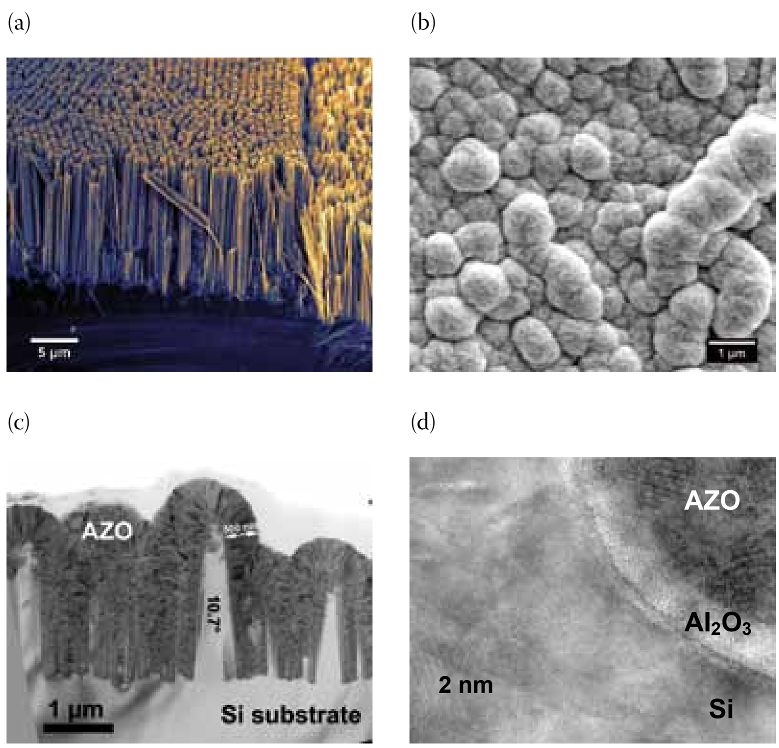

Figure 2. Scanning electron micrographs: (a) WCE Si NRs in a Si(100) wafer; (b) WCE NRs with Al_2O_3 barrier layer and degenerately doped AZO layer viewed from the top at an angle (both layers deposited by ALD). Transmission electron micrographs: (c) an SIS cell based on the concept of WCE Si NRs in Fig. 1; (d) high-resolution image of the interfacial region between the Si NRs, Al_2O_3 barrier layer (amorphous) and degenerately doped AZO layer (nanocrystalline).

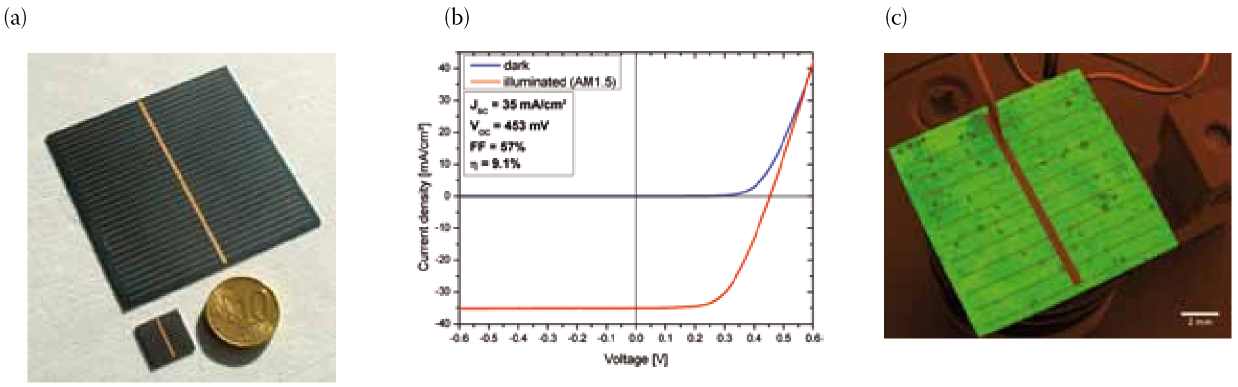

Figure 3. SIS cells based on WCE Si NRs: (a) prototypes with a screen-printed gold grid; (b) dark and illuminated (AM1.5) *I-V* curves of the same cell with an 11Å-thick Al_2O_3 tunnelling barrier layer and an AZO front-contact layer; (c) electron-beam-induced current measurements for the same SIS cell. The homogeneous green contrast indicates the generated photocurrent. The dark spots show areas that are not intact and thus only a lower effective photocurrent can be measured. These defective areas will be reduced substantially when structured etching of NRs is applied.

The same type of cell, but with better control of the optical and interfacial properties of the NRs, can be realized by structured etching of Si wafers or multicrystalline Si layers. The control over NR dimensions is accomplished by nanosphere lithography (NSL) as shown in the scanning electron micrographs in Fig. 4. Polystyrene spheres (yellow) of the desired diameters are densely packed on a Si-wafer or Si-layer surface in a Langmuir trough. Thus, a hexagonal densely packed sphere layer is realized, which then serves as a shadow mask for the deposition of a metal layer (e.g. sputtered gold shown in Fig. 4a). This lacy metal layer (blue) locally enhances the metal-assisted WCE of NRs (Fig. 4b), or the spheres themselves serve as an etching mask, such as in a dry-etching process as shown in Fig. 4(c).

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All in all, the well-separated optically and electrically controlled Si NRs that are produced from lithography-assisted etching permit a much wider range of optimization options, so that a thin-film solar cell based on Si NR with an efficiency above 15% is at hand and a 20% cell concept can also be aimed for.

Issues and problems to be solved

To achieve the highest efficiencies possible with a certain cell concept, a solar cell, being an optoelectronic device, needs optimization in terms of the most efficient optical absorption as well as of band structure engineering (given by the optimal location of the charge-separating junction within the nanocomposite material). In view of this, the proposed SIS cell concept deserves further optimization to meet its full potential. Preliminary simulations and modelling have indicated where improvements could lead.

The optimal organization of the Si NR ensembles can be derived from numerical finite-element modelling (FEM) to solve Maxwell's equations. For the purposes of optimization of solar light conversion, the scattering and absorption behaviour of the NR ensembles was studied. It was subsequently learned that a decreasing reflection occurs with increasing NR length (when the period of the NR ensemble is kept fixed). Furthermore, longer NRs act as a waveguide, leading the wave deep into the NR and permitting absorption even in the bulk Si underneath and between NRs. Comprehensive modelling shows that absorption (of green light, for example)

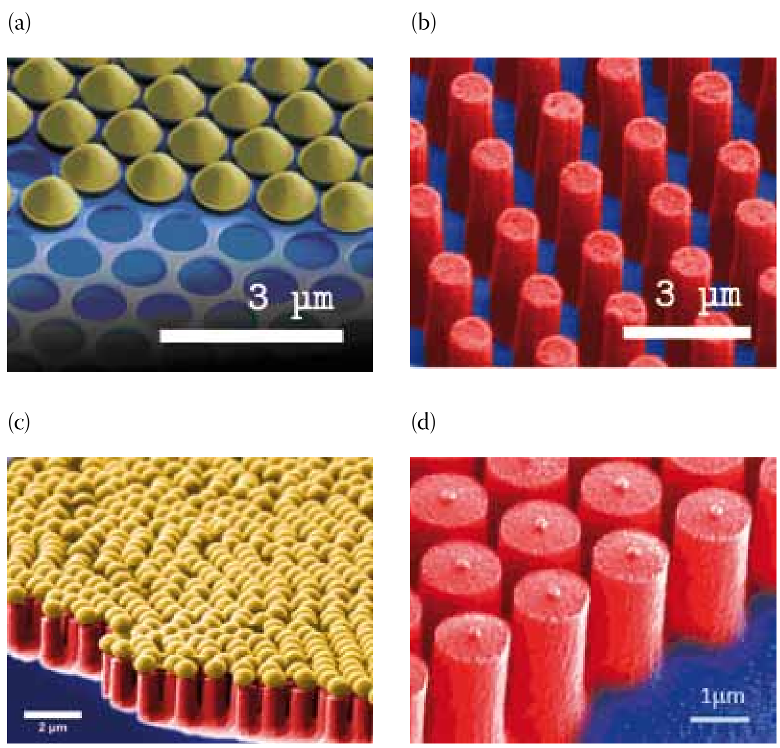

Figure 4. Scanning electron micrographs: (a) NSL assembly of polystyrene spheres (yellow), serving as a shadow mask for gold layer (light blue) deposition; (b) the lacy gold layer serves as an etching enhancer of the Si in a WCE process, thus leaving Si NRs (red) behind; (c) nanospheres (yellow) serving directly as a mask for dry etching (reactive ion etching with Bosch process) of Si wafers or layers; (d) the resulting Si NRs (red) produced by the etching process.

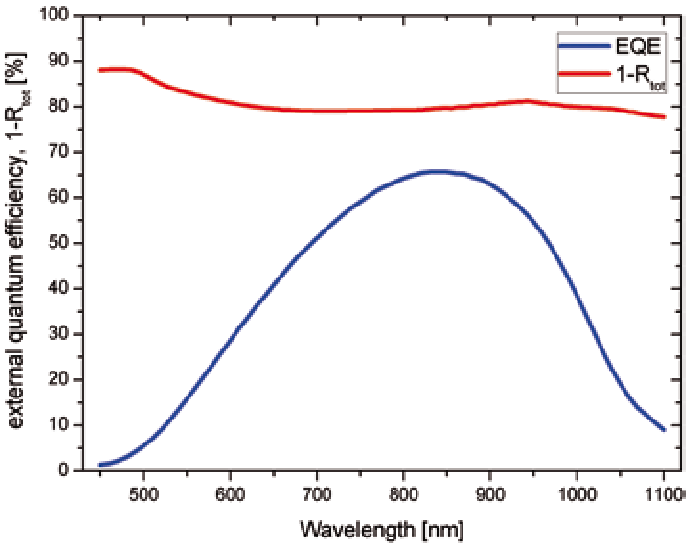

Figure 5. Comparison of the absorbed photon flux (1 – R_{tot}), where R_{tot} is a total reflection, and the external quantum efficiency EQE. The EQE describes the ratio between the extracted electron-hole pairs and the incident photons.

occurs essentially in the top 10μm of the NR ensemble. A significantly longer absorption distance is needed to gain similar absorption in flat silicon. The difference in reflection between the 2μm- and 20μm-long NR ensembles is 10%.

A comparison of the absorption profiles can be used to establish a basic rule for designing the electrical structure of the NR solar cell. In case of NRs of length 2–10μm, the SIS configuration is preferred, since significant absorption occurs in the entire NR. For longer NRs, a different cell concept using an axial p-n junction would be advantageous. A smooth effective reflection below 20% could be obtained by optimizing the diameters and lengths of the NRs.

In all cases, the NR surface should be well passivated, and strong repellent fields should be present at the glass-Si heterointerface. Further optimization of the back-contact area is required here, just as the ALD layers need optimizing to fulfil different property requirements, comprising a proper tunnelling barrier and passivation of the surface states of the NRs. The *I-V* curves of the SIS cells show a tail ranging from 0.6–0.9V, indicating a non-ideal back contact. It is in this contact area that the major source of improvement of the cells is seen. This assessment is supported by the *I-V* curves showing that our SIS cell has a poor fill factor (FF ~68%), again pointing to non-ideal collection properties and thus non-ideal contacts. However, the good news is that the SIS cell consequently has good collection properties and a good electrical structure, and both V_{oc} and I_{sc} can be enhanced by improving the FF.

From additional external quantum efficiency (EQE) measurements and optical absorption measurements (given by the measured total reflection R_{tot} according to [1 – R_{tot}]) presented in Fig. 5, it can be concluded that, for an improvement of the SIS solar cell efficiency, the following steps could be beneficial:

1. To improve the short-circuit current (I_{sc}), a thicker absorber region (taller NRs of the order of 10μm) and/or better back contact with an optical reflector should be used.

2. To improve the open circuit voltage (V_{oc}), a back-contact surface field that repels holes, and thus lowers the recombination losses, should be applied.

3. To improve both I_{sc} and V_{oc}, a thinner contact layer that absorbs less light essentially of the low-wavelength type should be created.

Fig. 5 shows an example of EQE and absorption (1 – R_{tot}) measurements. The absorption does not precisely represent the absorption in the SIS solar cell, but rather the total incident flux that is reduced by the amount of reflected light. But, because the contacts of the SIS solar cell are completely transparent, the non-reflected light is absorbed in the SIS solar cell and/or in the silver back contact.

The difference between the (1 – R_{tot}) and the EQE curves therefore comprises the generated (but not collected) carriers, i.e. the recombined carriers, and the photon flux that did not contribute to carrier generation, but on the contrary is absorbed in the back contact. Since the EQE shape from 900nm to 1200nm represents a characteristic band-gap cut-off of the absorption in Si, it is assumed that the EQE maximum at 900nm represents to a large extent the absorbed photon flux rather than recombination losses. Therefore, the difference between EQE and (1 – R_{tot}) at 900nm could be largely attributed to the photon flux that was absorbed in the back contact. Part of this loss could also be attributed to the back-contact recombination.

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A significant loss of the generated carriers may be observed in the low and middle wavelength region of the absorbed spectra. These losses can be attributed to the non-ideal position of the junction, where the n-type AZO layer might be too thick and thus absorb too large a portion of the low-wavelength photons.

Outlook

NR-based solar cell architectures have a long way to go yet in terms of research and optimization. Despite the encouraging results of the project so far in achieving ~10% efficiency with ~2μm long, still random Si NRs (without having yet implemented known ways to improve the cell), there are still tremendous challenges ahead for a successful commercialization of the ROD-SOL technologies.

That said, an exploitation strategy for ROD-SOL solar cells based on NRs has been developed by industry partners BISOL, PICOSUN and AIXTRON. Cost structure calculations show good potential for high-efficiency, low-cost ROD-SOL cell production. Another partner, IHS iSuppli, has developed cost models of three turnkey thin-film lines for manufacturing solar modules, taking into account ROD-SOL manufacturing requirements.

It should be recognized that, if a module efficiency of 15% can be achieved with Si NRs (which does not seem out of reach), the costs of ROD-SOL energy production on an industrial scale will compare well to those of current state-of the-art thin-film production lines. In order to reduce costs, monolithic integration instead of wafer-based concepts will be investigated, along with ways of avoiding vacuum and high-temperature processes, as well as the use of ordered NR ensembles to take advantage of the superior control of physical properties and device parameters. In addition, extensive electrical and optical modelling will yield deeper insight into the transport properties of NRs, and optimization of the technology, though a laborious task, seems straightforward at this stage.

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