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REVIEW

Aligned Si nanowire-based solar cells

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Si nanowires (Si NWs), as one of the fundamental building blocks for nano sciences and technologies, have attracted significant attention recently for solar cell applications, owing to the following: (1) Si NWs can significantly reduce materials consumption, and thus the solar cells fabrication cost; (2) NWs' capability to decouple light trapping and carrier collection, which is critical to achieve high power conversion efficiency. In this paper, recent progress on aligned-Si-NW-based solar cells are reviewed from optical and electrical characteristics to experimental demonstrations. Based on the understanding of each preparation process, the issues regarding the realization of highly efficient Si NW based solar cells are discussed.

1. Introduction

Solar electricity, as a source of clean and renewable energy free from contaminations and carbon emissions, is regarded as one of the best solutions to replace fossil-based electricity for future electricity supply.¹ The direct conversion from solar energy to electricity can be realized by solar cells based on the photovoltaic

^aSchool of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore, 639798, Singapore ^bInstitute of Microelectronics, Peking University, Beijing, 100871, China. E-mail: hyyu@ntu.edu.sg (PV) effect.² Currently, Si wafer based modules dominate the PV market, with a share of >80%, largely benefiting from the mature and advanced integrated circuit industries.³ On the other hand, the cost of the Si wafer-based PV modules is still high for civil utility such that its total installation capacity is only about 0.1% of the global electricity generation (mainly distributed in the developed countries).⁴ The high costs of the PV modules partially stem from the materials consumption, *e.g.*, Si wafers alone account for about 50% of the module costs.⁵

To reduce the cost of the PV modules, several approaches have been actively pursued, including using thin and/or low quality Si wafers,⁶ and developing (advanced) thin film based



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president graduate fellowship, IEEE EDS PhD fellowship, Nanyang Assistant Professorship, Tan Chin Tuan Academic Exchange Fellowship, one highlight paper in Tech. Sym. VLSI (2007), and more recently the "Young 1000 Talent Plan" award from China. technologies.^{7,8} In particular, Si nanowires (NWs), especially the aligned ones, attract much attention for achieving high performance with lower quality and less materials.^{9,10} It is well documented that besides excellent light antireflection properties,¹¹⁻¹³ aligned Si NWs provide opportunities to design light trapping and carrier collection processes independently,^{14–18} similar to the multijunction solar cell configuration proposed by Green,¹⁹ but with much lower materials consumption.

In this paper, the progresses related to aligned Si NW based solar cells are reviewed. Firstly we discuss the optical and electrical properties of aligned Si NWs. Then we will focus on preparation and research status of the related solar cells. Following that, the issues concerning the realization of high efficient Si NW based solar cells will be pointed out.

2. Optical and electrical properties of aligned Si NW arrays

For solar cell applications, optical and electrical characteristics are the two major concerns. A solar cell firstly should have an excellent light trapping capability for generating free carriers; then effective carrier separation and collection are necessary to achieve high efficiency. The decoupling between light absorption and carrier collection in Si NWs provides opportunities to independently optimize the optical and electrical properties *via* adjusting NWs dimensions, *i.e.*, diameter, periodicity, and length *etc.* On the other hand, manufacturability, reproducibility and stability of the related solar cells should also be considered when designing the devices. Therefore, an understanding of the relationship between optical and electrical properties and NWs' dimensions, and as set of design rules to guide manufacturing are in high demand.

Aligned Si NWs have demonstrated excellent antireflection,²⁰⁻²² as compared to Si NW mats.²³ Fig. 1(a)–(c) show the SEM images of periodically aligned Si NW arrays prepared on Si wafers *via* mask-assisted Ag catalyzed wet etching, with a fixed periodicity of 500 nm, and variable diameters of \sim 385, 280, and 190 nm.²⁴ A typical cross-sectional SEM image of the sample shown in Fig. 1(b) is depicted in Fig. 1(d). The reflection



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Fig. 1 Tilted SEM images of periodically aligned Si NW arrays on Si wafer surfaces with a fixed array periodicity of 500 nm, and various diameters of (a) \sim 385, (b) 280, and (c) 190 nm. (d) shows a typical cross-sectional SEM image of the sample shown in Fig. 1(b). Reprinted with permission from ref. 24. Copyright [2010] American Chemical Society.

measurements shown in Fig. 2 demonstrate that light reflection is significantly suppressed in a wide wavelength range after incorporating the Si NW arrays, as compared to polished wafers. However, one notes that efficient antireflection is not equivalent to effective light absorption because light transmission can be significant if the dimensions of the Si NW arrays are not optimized.²⁵ Fig. 3 shows the calculated reflection and transmission spectra for the Si NW array with a square lattice, and the Si NWs' length of 2.33 μ m, array periodicity of 100 nm and



Fig. 2 Reflection spectra of the three samples corresponding to those shown in Fig. 1(a)–(c). Reprinted with permission from ref. 24. Copyright [2010] American Chemical Society.



Fig. 3 Calculated reflection and transmission spectra of a squarely arranged Si NW array with an array periodicity of 100 nm, wire diameter of 50 nm, and wire length of 2.33 μ m. The Si thin film with the same thickness serves as the reference. Reprinted with permission from ref. 26. Copyright [2007] American Chemical Society.

diameter of 50 nm.²⁶ Compared to the Si thin film with the same thickness, although the light reflection for the Si NW array is well suppressed, its light transmission is surprisingly high in the low energy region, corresponding to the high photon density regime of Si.²⁷ Accordingly, poor performance for the solar cell based on this Si NW array can be expected compared to the Si thin film counterpart. Moreover, surface defects created during NW growth also can trap photons and thermally dissipate them without contribution to electricity output. This degrades the cell performance through the thermal effect,^{1,28} owing to the reduced thermal conductivity, especially in rough²⁹ or thin³⁰ Si NW solar cells.

Fig. 4(a) shows the cross-sectional SEM image and the corresponding optical spectra of randomly aligned Si NWs on glass prepared by wet etching of laser crystallized Si thin films without



Fig. 4 (a) Cross-sectional SEM image, and (b) the corresponding optical spectra of randomly aligned Si NWs on glass prepared by wet etching of laser crystallized Si thin films without mask confinement. Reprinted with permission from ref. 31. Copyright [2009] American Chemical Society.

mask printing.31 The length and diameter of the Si NWs varies from 2300 to 2500 nm, and 20 to 100 nm, respectively. It is seen that there is significant absorption enhancement (> 20%) for wavelengths longer than ~ 1127 nm, corresponding to photon energy lower than 1.1 eV, e.g., the bandgap of Si, which is mainly from the surface defect absorption, as shown in Fig. 4(b). The surface defect absorption becomes dominant when the diameter of Si NWs is thin, owing to the increased surface-to-volume ratio. Accordingly, it necessitates quenching surface defects to relieve the solar-thermally induced cell performance degradation, especially for the Si NW-based solar cells with large surface-tovolume ratios (from the electrical aspect, surface passivation is also important to Si NW-based solar cells). Tsakalakos et al. compared the absorption spectra of the Si NW sample before and after forming gas annealing at 400 °C for 30 min.³² It is observed that after passivation, the absorption decreases noticeably in the long wavelength regime (below the energy bandgap of Si), but varies negligibly in the visible light region, indicating that the surface defects are more sensitive to nearinfrared light.

Besides experimental demonstration, theoretical studies have also been actively pursued.25,26,33-35 Hu and Chen studied the optical characteristics of Si NW arrays with a fixed array periodicity of 100 nm, but different wire diameters and lengths.²⁶ They found that using Si NW arrays can boost light absorption mainly in the high energy regime of the solar spectrum (> \sim 2.8 eV). Light transmission for these Si NW arrays at low energy is very high (close to 100%), resulting in the total poor light trapping when compared to the flat Si thin films. Our group found that light transmission is very sensitive to the array periodicity, and it can be effectively suppressed when the array periodicity is around 600 nm, as shown in Fig. 5(c)).²⁵ In the meanwhile, effective antireflection can be well maintained (see Fig. 5(b)). From Fig. 5(a), the enhanced light absorption can be realized in the full energy range from 1 to 4 eV, covering the major energy region of the solar spectrum.²⁷ Fig. 5(d) summarizes the calculated ultimate efficiency³³ with various array periodicities, for the sake of quantitative comparison of the light trapping capability. One notes that when the array periodicity is >300 nm, the total light trapping capability of Si NW arrays becomes superior to the Si thin film with the same thickness. There is a wide "window" of periodicity variation till 1200 nm for light trapping enhancement, which offers flexibility to manufacture the related high efficient solar cells. In the meanwhile, the optimized ratio of wire diameter to array periodicity is found to be around 0.8. Following the calculations of the optical characteristics, a self-consistent explanation based on wave optics is provided below to guide the related designs for high efficient Si NW based solar cells, nanostructure surface textures-incorporated thin film based solar cells,36-39 and even for related photodetectors.⁴⁰ Here we briefly introduce the mechanism governing the interaction between nanostructures incorporated system and incident light. From the point of view of wave optics, if the feature size of the object is much smaller than the light wavelength, light could directly bypass the object. If the wavelength of the incident light is comparable with the interacted object, the light will be strongly scattered, resulting in the elongated optical path length and thus the enhanced light trapping. However, when the light wavelength is much shorter than the



Fig. 5 Calculated (a) absorption, (b) reflection, and (c) transmission spectra of Si NW arrays as a function of the array periodicity (P). The Si NWs are squarely arranged with a length of 5 μ m. The ratio of the wire diameter to P is 0.5. (d) summarizes the ultimate efficiency of Si NW arrays for different P. Reprinted with permission from ref. 25. Copyright [2009], American Institute of Physics.

object feature size, the interaction between the incident light and the objects would be dominated by the reflection process.³³

As for the Si NW arrays studied in Fig. 5, when the array periodicity (P) is much shorter than the incident light wavelength (λ) , e.g., for the case with P of 100 nm in the low energy regime (< 2 eV, corresponding to the long wavelength region, *i.e.*, λ > \sim 620 nm), the incident light easily penetrates through the Si NW array, leading to strong transmission (almost 100%, see Fig. 5 (c)), and thus very poor light trapping (Fig. 5(a)) in the corresponding energy region, although the antireflection is excellent, as indicated in Fig. 5(b). However, for this Si NW array in high energy, the scattering to the incident light is significantly enhanced due to the comparable P and λ , and the optical path length is significantly elongated, resulting in an enhanced light absorption of almost 100%. Accordingly, when P further increases, the energy region where the boosted light absorption can be observed should shift toward low energy, *i.e.*, long wavelengths. In the meanwhile, the absorption edge should also shift to low energy with increased P. Both can be observed from the absorption spectra shown in Fig.5 (a), as P increases. With the further increase in P, both light reflection and transmission, especially in the high energy regime, becomes strong due to the increased reflection area on the top and the enlarged spacing of neighboring wires at the bottom of the Si NW arrays, which leads to energy loss. If this energy loss cannot be compensated by the absorption edge shift, the total light trapping capability would be degraded, as shown by the calculated ultimate efficiency change with P in Fig. 5(d).

When fixing *P* and varying Si NWs' diameter, the optical characteristics demonstrate the similar change trend to the case of varying *P* and fixing the ratio of the Si NWs' diameter (*D*) to *P*, as summarized in Fig. 6. It can be found that D/P is optimized to be ~0.8 to achieve efficient light trapping, which is applicable in a wide *P* range from 300 to 900 nm. Our recent experimental

studies indicate that when the length of the Si NWs with the optimized *P* and *D* is > 200 nm, the enhanced light absorption can already be observed. For the Si NWs, the length of $\sim 2 \mu m$ is deemed enough for efficient light absorption. When the length exceeds 3 μm , light absorption becomes almost saturated, which indicates that highly efficient Si NW solar cells do not need very long wires, and thus materials consumption can be saved.

Recently, Bao and Ruan studied the effects of randomization in aligned amorphous Si NWs' position/diameter/length on the optical characteristics.⁴¹ They observed that the optical characteristics of the Si NW arrays are not sensitive to the position if the diameter and average spacing are fixed. However, optical absorption varies significantly for the random diameter distribution, which can be attributed to the broadened range for enhancing light scattering, and thus elongating the optical path length after incorporating the Si NWs with random diameters. In the case of random wire lengths, light absorption is enhanced for Si NW arrays with both small and large Si NW volume fractions. More significant absorption enhancement in a wider energy region is found for conditions with the larger Si NW volume fraction. In principle, the random length in Si NW arrays can create an intermediate layer with an effective refractive index lager than the air, but smaller than the underlying Si NW layer, which thus serves as an antireflection layer to suppress light reflection accordingly.^{42,43} For the higher Si NW volume fraction, the refractive index difference between air and the Si NW array becomes larger, and thus the light reflection suppression from the intermediate layer can be more significant.

Si NWs also demonstrate excellent electrical properties. The most significant electrical property potentially beneficial to the solar cell applications is the capability of forming radial (or core-shell) pn junction to facilitate carrier collection along a short collection path, *i.e.*, the radial direction.¹⁴ Based on this cell configuration, Kayes *et al.* calculated the electrical output



Fig. 6 Calculated (a) absorption, (b) reflection, and (c) transmission spectra of Si NW arrays as a function of the Si NWs' diameter (D). The Si NWs are squarely arranged with a length of 5 µm. The array periodicity is fixed at 300 nm. (d) summarizes the ultimate efficiency of Si NW arrays for different D. Reprinted with permission from ref. 25. Copyright [2009], American Institute of Physics.

characteristics of the concerned solar cells under different cell thicknesses, carrier diffusion lengths and trap densities, with the assumption of no light reflection and scattering effects between the incident light and Si NWs. In other words, the light absorption in the Si NWs here (100% packaging density) follows a similar behavior to the bulk material. Fig. 7 shows the calculated short circuit current density, J_{sc} , as a function of cell thickness, L, and minority carrier diffusion length, L_n , (here the shell is n doped, and the core is p doped.). Compared to planar pn junction solar cells, Si NW based ones with a radial pn junction configuration are superior in carrier collection due to the short collection length along the radial direction. Fig. 8 shows the calculated open circuit voltage, V_{oc} , as a function of L and $L_{\rm n}$. As can be seen, $V_{\rm oc}$ of Si NW based cells is more sensitive to the trap density in both the depletion and quasineutral regions due to the increased effective area of the radial pn junction, as compared to the planer ones. Especially for long and thin Si NWs (>100 μ m in length), V_{oc} approaches 0 when the trap densities in both the depletion and quasineutral regions vary from 7×10^{12} to 7×10^{18} cm⁻³. Fortunately, long Si NWs are not needed in device applications, as the efficient light absorption can already be achieved for 2-3 µm long Si NWs with optimized array periodicities and diameters, i.e., ~600 and 500 nm, respectively, as aforementioned. Moreover, the radial pn junction configuration can alleviate the negative impact of Si NWs' surface defects.44 Eventually, combined with the efficient carrier collection, the merit of radial pn junction Si NW solar cells becomes more evident compared to the planer pn junction wafer or thin film based ones.

Our recent study indicates that for Si NW incorporated solar cells, even with the planar pn junction configuration, can also facilitate carrier collection due to the improved light trapping in the Si NWs.⁴⁵ Fig. 9 schematizes the planar pn junction Si NW incorporated solar cells. The squarely arranged Si NWs are





Fig. 7 Short circuit current density, J_{sc} vs. cell thickness, L and minority carrier diffusion length, L_n for (a) a planar pn junction cell, and (b) a core-shell pn junction Si NW solar cell. Reprinted with permission from ref. 14. Copyright [2005], American Institute of Physics.



Fig. 8 Open circuit voltage, $V_{oc} vs$. cell thickness, *L* and minority carrier diffusion length, L_n for (a) a planar pn junction cell, and (b) a core–shell pn junction Si NW solar cell. In both Figures, the top plotted surface has a depletion-region trap density of 10^{14} cm⁻³, so that the carrier life times for electron and hole are 1 μ s. The trap densities in the depletion and quasineutral regions are the same for the bottom surface. Reprinted with permission from ref. 14. Copyright [2005], American Institute of Physics.

standing on a 0.8-µm-thick Si thin film substrate. The array periodicity of 500 nm and Si NW diameter of 250 nm are adopted here.³³ The doping concentrations in n⁺ emitter, p-type base, and p⁺ layer are 10²⁰, 10¹⁶, and 10²⁰ cm⁻³, respectively. A 50-nm thickness for the n^+ emitter and p^+ layer is used, which is similar to conventional thin film-based solar cells. Fig. 10(a) shows the predicted power conversion efficiency (PCE) as a function of the minority carrier (here, an electron) diffusion length, L_n . The PCE curve of the flat thin film solar cells with the same thickness, *i.e.*, 1.8 µm, serves as a reference. It is observed that cell performance is significantly boosted after incorporating the Si NW absorber, as compared to the flat ones. In the meantime, PCE for the Si NW incorporated cells is saturated when L_n is > 0.5 μ m. As a comparison, the saturation is only seen for the flat reference solar cells when L_n is ~1.2 µm, indicating the superior carrier collection efficiency and/or the high tolerance in low material qualities for the Si NW incorporated solar cells. Profiling the photogenerated carrier density distribution explains why the improved carrier collection is observed in SiNWs incorporated solar cells: it is due to the concentrated photogenerated carriers in the Si NW region (see Fig. 10(b)), originating from the excellent light confinement of NWs.



Fig. 9 Schematic of the planar pn junction SiNWs-incorporated solar cell. It consists of a 1 μ m long squarely arranged Si NW array and a 0.8 μ m thick Si supporting film. The array periodicity and Si NWs'

diameter are 500 and 250 nm, respectively.

It is worth noting that the impact of Si NWs' surface defects on characteristics should be considered electrical when manufacturing related solar cells.⁴⁶ Fig. 11 depicts the relationship between the calculated PCE and the surface recombination velocity (SRV).47 With increasing SRV from 0 to 103 cm s⁻¹, the predicted PCE has a relatively gradual decrease from 17.3% to 15.2%. However further increase of the surface recombination velocity to 10⁵ cm s⁻¹ would significantly reduce PCE to only 6.1%. Recently, several groups have started to tackle the issues on Si NWs' surface passivation. Gunawan and Guha studied the effects of Al₂O₃ passivation on the performance of Si NW based solar cells. It demonstrates that after incorporating a 10-nmthick Al₂O₃ conformal passivation layer onto the Si NWs' surfaces, PCE is improved from 1% to 1.8%, with an increment of 47 mV and \sim 5 mA cm⁻² in V_{oc} and J_{sc}, respectively.⁴⁸ Demichel et al. achieved a surface recombination velocity as low as 20 cm s⁻¹ on Si NWs using thermal oxidation and subsequent forming gas annealing, indicating an excellent passivation function of SiO₂ to Si NWs.⁴⁹ Using a thin a-Si layer, Dan et al. passiviated Si NWs, and reduced SRV by nearly 2 orders of magnitude, *i.e.*, from $\sim 3 \times 10^5$ for the as-prepared Si NWs to $\sim 4.5 \times 10^3$ cm s^{-1,50} As the traditional surface passivation and antireflection materials, a-SiN:H was also introduced to passivate Si microwire based solar cells by Kim et al., and the cell efficiency was enhanced from 8.9% to 10.6%.51 It is expected that a-SiN:H films



Fig. 10 (a) Predicted power conversion efficiency of the solar cells shown in Fig. 9 as a function of the minority carrier diffusion length, L_n , and (b) profile of the photogenerated carrier density.



Fig. 11 Predicted power conversion efficiency of the Si NWs incorporated solar cell depicted in Fig. 9 *vs.* surface recombination velocity.

are also applicable to Si NW based solar cells for surface defects passivation.

3. Status on Si NW based solar cells research

Stimulated by the excellent optical and electrical properties of aligned Si NWs, fabrication of related solar cells has been active in these years. Following the paradigms of Si NWs realization, the preparation of the Si NW based solar cells can also be generally categorized into two approaches, *i.e.*, bottom-up and top-down.^{52,31}

The bottom-up method is based on the metal catalyzed vaporliquid-solid (VLS) process, firstly reported by Wagner and Ellis

in 1964.53 In 2007, Tsakalakos et al. fabricated the first Si NW based all-inorganic solar cell using this method with an Au catalyst.⁵⁴ Fig. 12 shows (a) the schematic of the solar cell configuration, and (b) SEM images of the Si NWs under various views (the cross-sectional view on the top left). Here the p-type Si NWs with an estimated doping concentration of $\sim 10^{18}$ cm⁻³, diameter of 109 \pm 30 nm and length of ~16 μ m are grown on a stainless steel foil coated by a 100-nm-thick Ta₂N film, with the precursor gases of SiH₄, H₂, HCl and B(CH₃)₃. The Ta₂N film serves as the back electrode and also prevents the interdiffusion between Si atoms and the steel substrate. As indicated by the SEM images, the synthesized Si NWs randomly distribute on the substrate owing to the non-patterned Au catalyst. The pn junction is introduced by depositing a 40-nm-thick n-type a-Si:H layer via PECVD, which also serves as a passivation layer to the Si NWs. This is followed by the ITO layer deposition with a thickness of \sim 200 nm to connect electrically the Si NWs. Then the top finger electrode consisting of 50-nm-thick Ti and 2000nm-thick Al is prepared by shadow evaporation. Fig. 13 shows (a) the measured specular reflection specular spectrum, and (b) photograph of the Si NW-based solar cell. The other one is from an a-Si thin film solar cell for comparison. It is obvious that Si NWs significantly suppress light reflection. However, the measured power conversion efficiency and external quantum efficiency of the related solar cells with the size of $1.2 \times 1.5 \text{ cm}^2$ are relatively poor, as demonstrated in Fig. 14, which can be attributed to the poor photogenerated carrier separation capability, poor pn junction, and poor electrical contact, all related to the randomly grown Si NWs.

To improve the poor electrical properties in the solar cells made of randomly aligned Si NWs, regularly aligned ones are preferred. Normally, for the regularly aligned Si NWs grown using VLS growth, pre-patterned metal catalysts are needed.^{55–58}



Fig. 12 (a) Schematic of the SiNWs based all-inorganic solar cell using a stainless steel foil as the substrate, and (b) SEM images of the SiNWs under different views. Reprinted with permission from ref. 54. Copyright [2007], American Institute of Physics.



Fig. 13 (a) Measured specular reflection spectrum (log scale) of the Si NW based solar cell (green) (the blue one is from an a-Si thin film solar cell for reference), and (b) photograph of (right) the Si NW based solar cell. The left one is from the a-Si thin film solar cell for reference. Reprinted with permission from ref. 54. Copyright [2007], American Institute of Physics.



Fig. 14 Measured (a) J-V, and (b) external quantum efficiency behaviors of the 1.2×1.5 cm² Si NW based solar cells under the AM 1.5 G illumination. Reprinted with permission from ref. 54. Copyright [2007], American Institute of Physics.

Kayes *et al.* employed photolithographically patterned oxide buffer layers to pattern and confine Au or Cu catalysts, and then prepared highly ordered vertically aligned Si NWs with area >1 cm^{2,59} They also skilfully transferred and embedded these Si NWs into polymer substrates, demonstrating the technical feasibility of flexible Si NWs based solar cells.⁶⁰ Kendrick *et al.* prepared the related radial pn junction solar cells using the similar method, and achieved a power conversion efficiency of 2.3% for a 2.5 × 2.5 mm² cell, with improved V_{oc} and J_{sc} of 500 mV and 7.6 mA cm⁻², respectively.⁶¹ More importantly, the fill factor of the illuminated *I–V* curve at AM 1.5 G is about 57%, much larger than the one from the aforementioned randomly aligned VLS grown Si NW based solar cells.⁵⁴

Here it is worth noting that the photolithography employed here would be challenging for industrial production of related solar cells with low costs. To overcome this bottleneck, several cost effective patterning techniques are explored, including a selfassembled SiO₂ or polystyrene nanosphere monolayer,^{62,57} anodic aluminum oxide (AAO)⁶³⁻⁶⁶ etc. Hsu has achieved selfassembled close-packed SiO₂ nanosphere monolayers on 4 inch Si wafers using the Langmuir-Blodgett method, paving the way for the large-area patterning required in solar cell applications.⁶² In contrast, although the well-patterned catalysts with areas larger than 1 cm² are achievable using AAO templates,⁶⁷ their applications in solar cell production would be still greatly challenging due to the high costs and low throughput associated with the redundant procedures of preparing the AAO templates etc. Recently, nano-imprint lithography, which is expected to pattern metal catalyst layers with low costs and high throughput, has also been actively studied.68 Anyway, the most important concern regarding catalyst patterning of preparing regularly aligned Si NWs for solar cell applications is that the method must be low cost, high throughput, and scalable.

Besides catalyst patterning, for VLS grown regularly aligned Si NWs, several issues need to be concerned. The first is the deep level defects introduced by Au catalyst, which can trap minority carriers and severely degrade the electrical properties and thus the cell performance.⁶⁹ The other one is the high thermal budget for cracking Si-containing radicals such as SiCl₄,⁵⁸ and for maintaining the required high substrate temperatures. To address the first issue, Cu,⁷⁰ Al,⁷¹ Sn⁷² etc. are employed to act as catalysts, which would not introduce deep level defects, and adversely act as dopants such as Al. In the meantime, they are much cheaper than Au. Putnam et al. prepared Si NWs with the minority carrier diffusion length up to 10 µm using Cu-catalyzed VLS growth.⁷³ To reduce the thermal budget, Rathi et al. employed plasma to crack Si-containing precursors, and used Sn as the catalyst, which has an eutectic temperature of 232 °C with Si, much lower than the one of 363 °C for Au with Si.⁷²

In the meanwhile, top-down processing has also been actively explored to prepare Si NWs and related solar cells. Similar to the bottom-up based approaches, the Si NWs prepared using the top-down techniques also can be grouped into two classes, *i.e.*, randomly and regularly aligned arrays. Through immersing Si wafers or thin films into the aqueous solution of AgNO3 and HF, randomly aligned Si NWs can be easily formed via an electroless etching process.74 In 2008, Garnett and Yang reported the first Si NW solar cell with a radial pn junction based on this method.75 The starting material is phosphorus doped n-type Si wafers with a resistivity of 0.6 Ω cm, corresponding to a 10¹⁶ cm⁻³ doping concentration. After obtaining the electrolessly etched Si NWs, a p-type a-Si layer was deposited using LPCVD at 450 °C with the precursor gases of disilane and boron trichloride, followed by RTP annealing at 1000 °C for 10 s in forming gas to form the ptype (estimated doing concentration: 1.7 \times $10^{19}~\text{cm}^{-3}\text{)}$ poly-Si shell. Fig. 15(a) and (b) show the schematic of the radial pn junction Si NW based cell configuration and the cross-sectional SEM image of a completed cell, respectively. The Si NWs have lengths of $\sim 18 \,\mu m$, with a packing density of $\sim 50\%$. The typical wire diameter is 350-400 nm, including the 150-nm-thick poly-Si



Fig. 15 (a) Schematic of the radial pn junction Si NWs based solar cell, (b) cross-sectional SEM image of a completed cell, (c) TEM image of the poly-Si shell and c-Si core (the inset shows the selected area electron diffraction pattern), and (d) TEM image taken from the edge of the coreshell nanowire indicating nanocrystalline domains. Reprinted with permission from ref. 75. Copyright [2008] American Chemical Society.

shell and 50–100 nm Si NWs core. TEM measurements confirm the single crystalline core and polycrystalline shell (see the inset of Fig. 15(c)), and the TEM image taken near the wire edge indicates nanocrystalline domains, as demonstrated in Fig. 15(d). I-V measurements for the solar cells with the size of 1×1 cm² confirm a $V_{\rm oc}$ of 290 mV, a $J_{\rm sc}$ of 4.28 mA cm⁻², and a power conversion efficiency of 0.46% under AM 1.5G illumination. From the I-V curves shown in Fig. 16, it is seen that the contact and junction leakage issues (as indicated by Fig. 16(b), a high diode ideality factor of 2.1 is extracted.) need to be optimized for cell performance improvement.

In 2009, Sivakov *et al.* transferred this technique to crystalline Si thin film p–i–n planar junction cells on glass substrates,³¹ which are preferred in production due to the low materials consumption and costs. Fig. 17 shows the illuminated I-V behaviors of the Si NW-based solar cell with the size of ~2.5 × 2.5 cm² at four different measurement points. Although the cell performance is improved to a certain extent (an efficiency of 4.4% with a J_{sc} of ~ 40 mA cm⁻² is achieved), it is still necessary to further improve the poor contact and junction, as indicated by the I-V curve slopes around 0.6 V and 0 V, respectively. In



Fig. 16 (a) I-V curves of the radial pn junction Si NWs based cells in the dark and under AM 1.5 G illumination, and (b) semilog plot of the same data, indicating a diode ideality factor of 2.1. Reprinted with permission from ref. 75. Copyright [2008] American Chemical Society.



Fig. 17 Illuminated I-V behaviors of the Si NW based solar cell prepared through electrolessly etching the planar p–i–n junction crystalline Si thin film cell on glass. Reprinted with permission from ref. 31. Copyright [2009] American Chemical Society.

addition, measurements at different points (see Fig. 17) show strong variation in I-V outputs, indicating the poor uniformity of the solar cell.

Here one notes that electroless wet etching for forming Si NWs in the aqueous solution of AgNO₃ and HF can be much easily scaled up because it is only limited by the solution container. During the etching process, Ag elements do not incorporate into the resulting Si NWs to form deep level defects like Au in the VLS grown ones, and the Ag particles formed in the redox reaction can be easily removed using concentrated nitric acid⁷⁵ or boiling aqua regia.⁷⁶ However, the controllability over the achieved Si NWs' diameter, spacing *etc.* is poor, leading to the resulting poor cell performance as aforementioned.^{75,31} Moreover, the electroless wet etching in the aqueous solution of AgNO₃ and HF is not applicable for etching a-Si films and heavily doped Si wafers to form Si NWs due to the peeling off of a-Si and porous Si formation in Si wafers.^{77,78}

Besides randomly aligned Si NW-based solar cells, the topdown techniques are also employed to prepare periodically aligned Si NWs for solar cell applications. In 2010, Garnett and Yang conducted a proof of concept study of the periodically aligned Si NW-based solar cells, which are prepared using deep reactive ion etching (RIE) combined with the self-assembled SiO₂ nanosphere monolayer as the mask.⁷⁹ Fig. 18 schematizes the fabrication process of the related solar cells. Firstly SiO₂ nanospheres (average diameter chosen is ~530 nm) are self assembled on n-type Si wafers via a dip-coat processing. Then RIE is done to create the Si NWs with the assistance of the self-assembled SiO₂ mask. Following that, the residual SiO₂ nanspheres are removed by HF solution, and the radial pn junction with a depth of ~ 160 nm is formed *via* boron diffusion. Here it is worth noting that to mimic the PV response of the stand-alone Si NW layer, a highly doped Si wafer is used as the substrate to eliminate the PV contribution from the substrate, and an epitaxial Si thin layer on the wafer is employed to manufacture the Si NW array. Fig. 19(a) shows the tilted SEM image of the resulting Si NW array standing on a \sim 3 µm thick Si film, with the Si NWs' diameter of \sim 390 nm, length of \sim 5 µm, and array periodicity of \sim 530 nm, corresponding to the average diameter of the starting SiO₂ nanospheres. The illuminated I-V characteristics of the related solar cell with a size of $\sim 0.67 \times 0.67$ cm² is recorded



Fig. 18 Schematic of the manufacturing process of periodically aligned Si NW based solar cells using top-down-based reactive ion etch combined with the self-assembled SiO₂ nanosphere monolayer as mask. Reprinted with permission from ref. 79. Copyright [2010] American Chemical Society.



Fig. 19 (a) Tilted SEM image of a Si NW based solar cell prepared using the method depicted in Fig. 18, with the Si NW diameters of \sim 390 nm, lengths of \sim 5 μ m, and array periodicity of \sim 530 nm, and (b) illuminated *I*–*V* behaviors of the above solar cell under AM 1.5G. The flat Si filmbased solar cell with the same total thickness of 8 μ m serves as a reference. Reprinted with permission from ref. 79. Copyright [2010] American Chemical Society.

under AM 1.5G (see Fig. 19(b)), and exhibit a PCE of ~4.83% ($V_{\rm oc}$: 525 ± 2 mV; $J_{\rm sc}$: 16.45 ± 0.19 mA cm⁻²; FF: 0.559 ± 0.002), which is ~20% higher than that of the Si ribbon solar cell with the same total thickness, *i.e.*, 8 µm.⁸⁰ Moreover, compared to the randomly aligned Si NW-based solar cells aforementioned, the pn junction quality here is much improved, *i.e.*, similar to the pn junctions in flat cells, as indicated by the flattened *I*–*V* curve around 0 V in Fig. 19(b). Here it should be noted that the electrode configuration is yet to be optimized. They further declare

that the light absorption enhancement mainly occurs in the Si NW array, and an optical path length enhancement factor of \sim 73 is achieved, which is much larger than the randomized scattering limit (\sim 25 without a back reflector).

Recently, Lu and Lal developed the periodically aligned Si NWs with a nano-conical-frustum shape, as shown in Fig. 20(a) using self-powered parallel electron lithography and RIE.⁸¹ Due



Fig. 20 (a) Tilted SEM image of a nano-conical-frustum shaped Si NW array prepared using self-powered parallel electron lithography and RIE, with Si NW top and bottom diameters of 340 and 800 nm, lengths of \sim 3.5 µm, and array periodicity of 800 nm. (b) Absorption spectrum (blue curve) of the above SiNWs array standing on a 1.5 µm Si film, with a supporter of 2 µm SOI buried oxide. The absorption spectra from (pink) a 3.5 µm Si NW array standing on the same substrate, with a quasi-uniform diameter of 340 nm and an array periodicity of 800 nm, and (black) a 5 µm flat Si film on 2 µm SOI buried oxide are for comparison. Reprinted with permission from ref. 81. Copyright [2010] American Chemical Society.

to the excellent antireflection stemming from the spatial modulation of the effective refractive index, the nano-conical-frustum shaped Si NWs show the excellent light absorption (see Fig. 20 (b)). The resulting solar cell configuration is schematically shown in Fig. 21(a). It consists of a 3.5 µm n-type (doping concentration: 2×10^{18} cm⁻³) Si NW array standing on a 1.5 µm Si film, with an array periodicity of 800 nm, and top and bottom wire diameters of 340 and 800 nm. The radial pn junction is formed via boron ion implantation, with a doping concentration of 10²⁰ cm⁻³, and an estimated junction depth of 20 nm on the side walls. Then, rapid thermal annealing at 900 °C is performed for 60 s to activate dopants and remove the implantation damage. Following that, a 20 nm SiO₂ passivation layer is coated. After the above thermal processes, the final boron doping and junction depth is 2 \times 10¹⁹ cm⁻³, and 100 nm. Fig. 21(b) shows the measured I-V characteristics of the Si NW based solar cell under the AM 1.5G illumination. In line with the excellent light absorption, the Si NW based solar cell has an enhanced performance, with a $J_{\rm sc}$ of 26.4 mA cm⁻², $V_{\rm oc}$ of 0.59 V, and power conversion efficiency of 10.8%. As a comparison, the 5 µm flat film-based control cell delivers a $J_{\rm sc}$ of 13.6 mA cm⁻², a $V_{\rm oc}$ of 0.54 V, and a PCE of 5.2%.

Besides RIE, electroless wet etching is also employed to fabricate regularly aligned Si NWs through combining selfassembled SiO₂ or polystyrene nanosphere monolayers to pattern the metal catalyst, *e.g.*, Ag.⁸² Different from VLS growth, the catalyst patterning for wet etching is performed on Si wafer or film surfaces, not on the substrate surfaces. After patterning the metal catalyst, the sample is immersed into the mixture of



Fig. 21 (a) Schematic, and (b) illuminated I-V behaviors (blue curve) of the nano-conical-frustum shaped Si NW based solar cell with the structural parameters shown in Fig. 20(a). The I-V curve (black) from the 5 µm flat Si film cell serves as reference. Reprinted with permission from ref. 81. Copyright [2010] American Chemical Society.

 $\rm HNO_3,\,H_2O_2$ and $\rm H_2O$, and the Si materials underneath Ag are etched off and then the Si NWs are formed following the below redox reaction,⁷⁷

With Ag:

$$\mathrm{H}_{2}\mathrm{O}_{2} + 2\mathrm{H}^{+} \rightarrow 2\mathrm{H}_{2}\mathrm{O} + 2h^{+},$$

$$2\mathbf{H}^+ + 2e \to \mathbf{H}_2 \uparrow,$$

With Si:

$$\text{Si} + 4h^+ + 4\text{HF} \rightarrow \text{SiF}_4 + 4\text{H}^+,$$

$$SiF_4 + 2HF \rightarrow H_2SiF_6$$

Overall reaction:

\$

$$\mathrm{Si} + \mathrm{H}_2\mathrm{O}_2 + 6\mathrm{HF} \rightarrow 2\mathrm{H}_2\mathrm{O} + \mathrm{H}_2\mathrm{SiF}_6 + \mathrm{H}_2\uparrow$$

It is obvious that the patterned catalyst-assisted electroless wet etching can prepare highly ordered Si NWs arrays with a low thermal budget and cost. Li *et al.* employed this method to fabricate Si NW incorporated solar cells on Si wafers.²¹ The solar cell with a size of $\sim 1 \times 1$ cm² exhibits a power conversion efficiency of $\sim 9.2\%$. However, compared to the Si NWs prepared by RIE, the surface for the ones prepared by electroless wet etching is much rougher,^{21,79,81,82} severely affecting the formation of high quality pn junction and electrical contact. Moreover, high defects on the rough surface would be detrimental to free carrier collection. Accordingly, post treatments are needed to smooth and passiviate the corresponding Si NWs for improving cell performance.

From the above brief review, several conclusions on aligned Si NW based solar cells can be drawn,

(i) Regularly aligned Si NWs are preferred for achieving improved cell performance due to the manipulation advantages in forming high quality pn junctions (especially for the radial ones) and electrical contacts;

(ii) Self-assembled SiO_2 or polystyrene nanosphere monolayers can be employed as a cost-effective and scalable mask for patterning metal catalysts either in VLS growth or in top-down etching;

(iii) Top-down based methods can effectively reduce the thermal budget and avoid catalyst contaminations to the resulting Si NWs, as compared to VLS (or bottom-up) based methods;

(iv) For mass production, compared to RIE, patterned catalyst-assisted electroless wet etching is preferred due to the low cost. But the rough surface of the resulting Si NWs need to be smoothed and/or passiviated for achieving a high quality pn junction and electrical contact;

(v) Dry etching using RIE can prepare Si NWs with smooth surfaces, but cost effective dry etching sources such as plasma

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 $etching^{83-85}$ should be developed for replacing RIE in solar cell applications.

Here it is worth emphasizing again that for solar cell applications, only the cost-effective, high throughput, and scalable methods are applicable.

4. Summary and prospective

In this review, the potential of aligned Si nanowires for highly efficient and cost effective solar cell applications has been discussed based on their unique optical and electrical properties. A design guideline to achieve high efficiency for Si nanowires based solar cells is introduced by optimizing the Si nanowires array dimensions (optimized array periodicities and wires' diameters are around 600 and 500 nm, respectively). At present, the most challenging tasks are believed to be related to technological developments: how to prepare cost-effectively high quality aligned Si nanowires on a large scale and high throughput manner; and how to realize the high quality pn junctions and electrical contacts on Si nanowires for effective photogenerated carrier collection. Although the best achieved power conversion efficiency for the Si nanowires based solar cells is around 11% at present, still far from the record efficiency of 25% for Si wafer based solar cells,⁸⁶ the huge potential for improving cell performance based on the unique optical and electrical properties, the much reduced materials- and energy-consumption and high tolerance of low material-quality will make aligned Si nanowires based solar cells shine in the near future.

References

- 1 P. Würfel, *Physics of solar cells: From principles to new concepts*, Wiley-Vch, Weinheim, 2005.
- 2 The photovoltaic effect, http://photovoltaics.sandia.gov/docs/ PVFEffIntroduction.htm.
- 3 M. Pagliaro, G. Palmisano and R. Ciriminna, *Flexible solar cells*, Wiley-Vch, Weinheim, 2008.
- 4 C. A. Wolden, J. Kurtin, J. B. Baxter, I. Repins, S. E. Shaheen, J. T. Torvik, A. A. Rockett, V. M. Fthenakis and E. S. Aydil, *J. Vac. Sci. Technol.*, A, 2011, 29, 030801.
- 5 Thin Film Solar cells: Fabrication, Characterization and Application, ed. J. Poortmans and V. Arkhipov, John Wiley & Sons Ltd., Chichester, England, 2006.
- 6 A. Fujisaka, S. Kang, L. Tian, Y. L. Chow, and A. Belyaev, "Implantcleave process enables ultra-thin wafers without k_{erf} loss," Photovoltaics World, pp. 21–24, Issue: May/Jun 2011.
- 7 C. O'Brien, "Why less is more: how thin-film manufacturing is finding momentum," Photovoltaics World, pp. 22–25, Issue: Jan/Feb 2011.
- 8 J. Zhu, C. M. Hsu, Z. Yu, S. Fan and Y. Cui, *Nano Lett.*, 2010, **10**, 1979.
- 9 Nanotechnology for photovoltaics, ed. L. Tsakalakos, Taylor & Francis Group, LCC, 2010.
- 10 O. Gunawan, K. Wang, B. Fallahazad, Y. Zhang, E. Tutuc and S. Guha, Prog. Photovoltaics, 2011, 19, 307.
- 11 K. Hadobás, S. Kirsch, A. Carl, M. Acet and E. F. Wassermann, *Nanotechnology*, 2000, **11**, 161.
- 12 K. Peng, Y. Xu, Y. Wu, Y. Yan, S. T. Lee and J. Zhu, *Small*, 2005, 1, 1062.
- 13 V. V. Iyengar, B. K. Nayak and M. C. Gupta, Sol. Energy Mater. Sol. Cells, 2010, 94, 2251.
- 14 B. M. Kayes, H. A. Atwater and N. S. Lewis, J. Appl. Phys., 2005, 97, 114302.
- 15 B. Tian, X. Zheng, T. J. Kempa, Y. Fang, N. Yu, G. Yu, J. Huang and C. M. Lieber, *Nature*, 2007, **449**, 885.
- 16 V. V. Kislyuk and O. P. Dimitriev, J. Nanosci. Nanotechnol., 2008, 8, 131.

17 M. D. Kelzenberg, S. W. Boettcher, J. A. Petykiewicz, D. B. Turner-Evans, M. C. Putman, E. L. Warren, J. M. Spurgeon, R. M. Briggs, N. S. Lewis and H. A. Atwater, *Nat. Mater.*, 2010, 9, 239.

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- 18 S. W. Boettcher, J. M. Spurgeon, M. C. Putman, E. L. Warren, D. B. Turner-Evans, M. D. Kelzenberg, J. R. Maiolo, H. A. Atwater and N. S. Lewis, *Science*, 2010, **327**, 185.
- 19 M. A. Green and S. R. Wenham, Appl. Phys. Lett., 1994, 65, 2907.
- 20 J. Y. Jung, Z. Guo, S. W. Jee, H. D. Um, K. T. Park and J. H. Lee, Opt. Express, 2010, 18, A286.
- 21 X. C. Li, J. S. Li, T. Chen, B. K. Tay, J. X. Wang and H. Y. Yu, *Nanoscale Res. Lett.*, 2010, 5, 1721.
- 22 W. Q. Xie, J. I. Oh and W. Z. Shen, *Nanotechnology*, 2011, 22, 065704.
- 23 R. A. Street, P. Qi, R. Lujan and W. S. Wong, *Appl. Phys. Lett.*, 2008, 93, 163109.
- 24 H. P. Wang, K. Y. Lai, Y. R. Lin, C. A. Lin and J. H. He, *Langmuir*, 2010, 26, 12855.
- 25 J. S. Li, H. Y. Yu, S. M. Wong, X. C. Li, G. Zhang, P. G. Q. Lo and D. L. Kwong, *Appl. Phys. Lett.*, 2009, **95**, 43113.
- 26 L. Hu and G. Chen, Nano Lett., 2007, 7, 3249.
- 27 Air Mass 1.5 Spectra, American Society for Testing and Materials, http://rredc.nrel.gov/solar/spectra/am1.5/#1962.
- 28 Theory of solar cell, http://en.wikipedia.org/wiki/Theory_of_solar_cell. 29 A. I. Hochbaum, R. Chen, R. D. Delgado, W. Liang, E. C. Garnett,
- M. Najarian, A. Majumdar and P. Yang, *Nature*, 2008, **451**, 163. 30 I. Ponomareva, D. Srivastava and M. Menon, *Nano Lett.*, 2007, **7**,
- 1155.
- 31 V. Sivakov, G. Andrä, A. Gawlik, A. Berger, J. Plentz, F. Falk and S. H. Christiansen, *Nano Lett.*, 2009, 9, 1549.
- 32 L. Tsakalakos, J. Balch, J. Fronheiser, M. Y. Shih, S. F. LeBoeuf, M. Pietrzykowski, P. J. Codella, B. A. Korevaar, O. Sulima, J. Rand, A. Davuluru and U. Rapol, *J. Nanophotonics*, 2007, 1, 013552.
- 33 J. S. Li, H. Y. Yu, S. M. Wong, G. Zhang, X. W. Sun, P. G. Q. Lo and D. L. Kwong, *Appl. Phys. Lett.*, 2009, **95**, 033102.
- 34 C. Lin and M. L. Povinelli, Opt. Express, 2009, 17, 19371.
- 35 J. Zhu, Z. Yu, G. F. Burkhard, C. M. Hsu, S. T. Connor, Y. Xu, Q. Wang, M. McGehee, S. Fan and Y. Cui, *Nano Lett.*, 2009, 9, 279.
- 36 J. S. Li, H. Y. Yu, S. M. Wong, G. Zhang, G. Q. Lo and D. L. Kwong, *IEEE Electron Devices Meeting*, 2009, 511.
- 37 F. Wang, H. Y. Yu, J. S. Li, X. W. Sun, X. C. Wang and H. Y. Zheng, Opt. Lett., 2009, 35, 40.
- 38 J. S. Li, H. Y. Yu, Y. L. Li, F. Wang, M. F. Yang and S. M. Wong, *Appl. Phys. Lett.*, 2011, 98, 021905.
- 39 Y. L. Li, H. Y. Yu, J. S. Li, S. M. Wong, X. W. Sun, X. Li, C. Cheng, H. J. Fan, J. Wang, N. Singh, P. G. Q. Lo and D. L. Kwong, *Small*, 2011, DOI: 10.1002/smll.201100950 (published online).
- 40 C. A. Keasler and E. Bellotti, Appl. Phys. Lett., 2011, 99, 091109.
- 41 H. Bao and X. Ruan, Opt. Lett., 2010, 35, 3378.
- 42 H. Bao and X. Ruan, Proc. SPIE, 2010, 7772, 7772J.
- 43 Z. Fan, R. Kapadia, P. W. Leu, X. Zhang, Y.-L. Chueh, K. Takei, K. Yu, A. Jamshidi, A. Rathore, D. J. Ruebusch, M. Wu and A. Javey, *Nano Lett.*, 2010, **10**, 3823.
- 44 S. M. Wong, H. Y. Yu, J. S. Li, Y. L. Li, N. Singh, P. G. Q. Lo and D. L. Kwong, *IEEE Electron Device Lett.*, 2011, **32**, 176.
- 45 S. M. Wong, H. Y. Yu, J. S. Li, G. Zhang, P. G. Q. Lo and D. L. Kwong, *IEEE Electron Device Lett.*, 2010, 31, 335.
- 46 J. E. Allen, E. R. Hemesath, D. E. Perea, J. L. Lensch-Falk, Z. Y. Li, F. Yin, M. H. Gass, P. Wang, A. L. Bleloch, R. E. Palmer and L. J. Lauhon, *Nat. Nanotechnol.*, 2008, **3**, 168.
- 47 J. S. Li, S. M. Wong, Y. L. Li and H. Y. Yu, *IEEE Photovoltaic Spec.* Conf., 35th, 2010, 1469.
- 48 O. Gunawan and S. Guha, Sol. Energy Mater. Sol. Cells, 2009, 93, 1388.
- 49 O. Demichel, V. Calvo, A. Besson, P. Noé, B. Salem, N. Pauc, F. Oehler, P. Gentile and N. Magnea, *Nano Lett.*, 2010, 10, 2323.
- 50 Y. Dan, K. Seo, K. Takei, J. H. Meza, A. Javey and K. B. Crozier, *Nano Lett.*, 2011, **11**, 2527.
- 51 D. R. Kim, C. H. Lee, P. M. Rao, I. S. Cho and X. Zheng, *Nano Lett.*, 2011, **11**, 2704.
- 52 C. Y. Kuo, C. Gau and B. T. Bai, *Sol. Energy Mater. Sol. Cells*, 2011, 95, 154.
- 53 R. S. Wagner and W. C. Ellis, Appl. Phys. Lett., 1964, 4, 89.

- 54 L. Tsakalakos, J. Balch, J. Fronheiser, B. A. Korevaar, O. Sulima and J. Rand, *Appl. Phys. Lett.*, 2007, 91, 233117.
- 55 J. Westwater, D. P. Gosain and S. Usui, Jpn. J. Appl. Phys., 1997, 36, 6204.
- 56 J. MaioloIII, B. M. Kayes, M. A. Filler, M. C. Putnam, M. D. Kelzenberg, H. A. Atwater and N. S. Lewis, J. Am. Chem. Soc., 2007, 129, 12346.
- 57 B. Fuhrmann, H. S. Leipner, H. R. Höche, L. Schubert, P. Werner and U. Gösele, *Nano Lett.*, 2005, 5, 2524.
- 58 I. Lombardi, A. I. Hochbaum, P. Yang, C. Carraro and R. Maboudian, *Chem. Mater.*, 2006, 18, 988.
- 59 B. M. Kayes, M. A. Filler, M. C. Putnam, M. D. Kelzenberg, N. S. Lewis and H. A. Atwater, *Appl. Phys. Lett.*, 2007, **91**, 103110.
- 60 K. E. Plass, M. A. Filler, J. M. Spurgeon, B. M. Kayes, S. Maldonado, B. S. Brunschwig, H. A. Atwater and N. S. Lewis, *Adv. Mater.*, 2008, **20**, 1–4.
- 61 C. E. Kendrick, H. P. Yoon, Y. A. Yuwen, G. D. Barber, H. Shen, T. E. Mallouk, E. C. Dickey, T. S. Mayer and J. M. Redwing, *Appl. Phys. Lett.*, 2010, 97, 143108.
- 62 C. M. Hsu, S. T. Connor, M. X. Tang and Y. Cui, *Appl. Phys. Lett.*, 2008, **93**, 133109.
- 63 H. Masuda and K. Fukuda, Science, 1995, 268, 1466.
- 64 T. Gao, J. Fan, G. Meng, Z. Chu and L. Zhang, *Thin Solid Films*, 2001, **401**, 102.
- 65 C. W. Liu, C. Y. Kuo, C. P. Wang, S. H. Shiau, C. Gau and B. T. Dai, Jpn. J. Appl. Phys., 2007, 46, 6343.
- 66 Y. Lei, W. Cai and G. Wilde, Prog. Mater. Sci., 2007, 52, 465.
- 67 M. S. Sander and L. S. Tan, Adv. Funct. Mater., 2003, 13, 393.
- 68 L. J. Gao, Adv. Mater., 2007, 19, 495.
- 69 W. M. Bullis, Solid-State Electron., 1966, 9, 143.
- 70 Y. Yao and S. Fan, Mater. Lett., 2007, 61, 177.

- 71 Y. Ke, X. Weng, J. M. Redwing, C. M. Eichfeld, T. R. Swisher, S. E. Mohney and Y. M. Habib, *Nano Lett.*, 2009, 9, 4494.
- 72 S. J. Rathi, B. N. Jariwala, J. D. Beach, P. Stradins, P. C. Taylor, X. Weng, Y. Ke, J. M. Redwing, S. Agarwal and R. T. Collins, J. Phys. Chem. C, 2011, 115, 3833.
- 73 M. C. Putnam, D. B. Turner-Evans, M. D. Kelzenberg, S. W. Boettcher, N. S. Lewis and H. A. Atwater, *Appl. Phys. Lett.*, 2009, **95**, 163116.
- 74 K. Peng, A. Lu, R. Zhang and S. T. Lee, Adv. Funct. Mater., 2008, 18, 3026.
- 75 E. Garnett and P. Yang, J. Am. Chem. Soc., 2008, 130, 9224.
- 76 Z. Huang, H. Fang and J. Zhu, Adv. Mater., 2007, 19, 744.
- 77 X. Li and P. W. Bohn, Appl. Phys. Lett., 2000, 77, 2572.
- 78 F. Voigt, V. Sivakov, V. Gerliz, G. H. Bauer, B. Hoffmann, G. Z. Radnoczi, B. Pecz and S. Christiansen, *Phys. Status Solidi A*, 2011, **208**, 893.
- 79 E. Garnett and P. Yang, Nano Lett., 2010, 10, 1082.
- 80 J. Yoon, A. J. Baca, S. I. Park, P. Elvikis, J. B. Geddes III, L. Li, R. H. Kim, J. Xiao, S. Wang, T. H. Kim, M. J. Motala, B. Y. Ahn, E. B. Duoss, J. A. Lewis, R. G. Nuzzo, P. M. Ferreira, Y. Huang, A. Rockett and J. A. Rogers, *Nat. Mater.*, 2008, 7, 907.
- 81 Y. Lu and A. Lal, Nano Lett., 2010, 10, 4651.
- 82 K. Peng, M. Zhang, A. Lu, N. B. Wong, R. Zhang and S. T. Lee, *Appl. Phys. Lett.*, 2007, 90, 163123.
- 83 C. H. Hsu, H. C. Lo, C. F. Chen, C. T. Wu, J. S. Hwang, D. Das, J. Tsai, L. C. Chen and K. H. Chen, *Nano Lett.*, 2004, 4, 471.
- 84 S. Ravipati, C. J. Kuo, J. Shieh, C. T. Chou and F. H. Ko, *Microelectron. Reliab.*, 2010, **50**, 1973.
- 85 L. Sainiemi, V. Jokinen, A. Shah, M. Shpak, S. Aura, P. Suvanto and S. Franssila, *Adv. Mater.*, 2011, 23, 122.
- 86 M. A. Green, Progr. Photovolt.: Res. Appl., 2009, 17, 183.