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# Development of Inorganic Solar Cells by Nanotechnology

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**Abstract:** Inorganic solar cells, as durable photovoltaic devices for harvesting electric energy from sun light, have received tremendous attention due to the fear of exhausting the earth's energy resources and damaging the living environment due to greenhouse gases. Some recent developments in nanotechnology have opened up new avenues for more relevant inorganic solar cells produced by new photovoltaic conversion concepts and effective solar energy harvesting nanostructures. In this review, the multiple exciton generation effect solar cells, hot carrier solar cells, one dimensional material constructed asymmetrical schottky barrier arrays, noble nanoparticle induced plasmonic enhancement, and light trapping nanostructured semiconductor solar cells are highlighted.

**Keywords:** Inorganic; Solar Cells; Photovoltaic; Nanotechnology

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## Introduction

The worldwide demand for energy is causing a dramatic environmental impact on the global climate due to the combustion of fossil fuels. In order to improve the sustainability of our society, photovoltaic solar cells, as a significant device harvesting low-carbon solar energy, have received tremendous attention recently [1,2]. The merits of photovoltaic solar cells are a lot, for example, solar cells provide clean electrical energy by directly converting solar energy into electrical energy without emitting carbon dioxide, besides, the solar energy is not limited, free of charge and distributed uniformly to all human beings. For over the past two decades, all kinds of solar cells have been extensively studied and used for practical terrestrial applications [3-5].

However, high material cost and large amount of energy needed for manufacturing solar cells have made this technology expensive with long energy payback time. This has prevented the PV power generation from rapid commercialization. One important concept to reduce the solar cell cost and to increase the conversion efficiency is to use nanotechnology, i.e., to use the nanostructured materials in solar cell [6-8]. Nanotechnology has achieved rapid development in the area of the specific optical and electrical properties of nanomaterials, assembled functional devices, and so on. Numerous nano-assembly methods can be used to impart a variety of specific optical and electrical properties of nanomaterials in photovoltaic cells [9-12]. Nano-assembly method has many advantages, such as less consumption of materials, using non-vacuum technology and a large area controlled manufacturing.

The aim of this article is to highlight the application of nanostructured materials for inorganic solar energy conversion covering a wide variety of materials. In this

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review, we briefly summarize multiple exciton generation in the semiconductor materials. We emphasize on one dimensional material constructed as asymmetrical schottky barrier arrays, which provides plasmonic light trapping in solar cells. We also highlight the light trapping structure for silicon solar cells.

## Multiple exciton generation

Multiple exciton generation (MEG) (Fig. 1), also called carrier multiplication, involves the generation of multiple electron-hole pairs from the absorption of a single photon [13,14]. As early as in 1950s, MEG has been found in the semiconductor bulk materials, known as carrier multiplication effect. However, it is considered less than reasonably useful because of very low efficiency (less than 1%). In 2004, Schaller and Klimov demonstrated for the first time that multiple exciton generation occurred with very high efficiency in semiconductor nanocrystals [15]. Thereby MEG in semiconductor nanostructures has been investigated deeply and extensively. Up to now, MEG has been demonstrated in semiconductor nanostructures (quantum dots) including PbSe, PbS [16], PbTe [17], CdS, CdSe [18], Si [19], InAs [20], and so on. Recently, MEG has also been demonstrated in InP colloidal quantum dots [21]. Beard etc. [19] have confirmed that silicon nanocrystals can exhibit strong MEG in the 0.5-3.5 eV of solar spectral region.

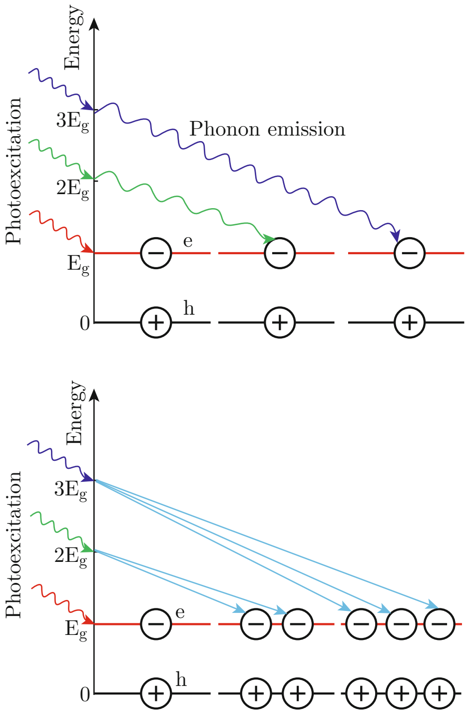

Fig. 1 The schematic drawing of a photon producing a single and multiple electronic-hole pairs.

Under normal circumstances, the semiconductor materials can only produce a single exciton after absorbing a photon, and the high excitation energy photon wasted by phonon emission. If a photon can generate multiple excitons, the energy conversion efficiency of nanocrystal based solar cells may be improved significantly. MEG may considerably increase the energy conversion efficiency of nanocrystal based solar cells, though harvesting the energy may be difficult because of the short lifetimes of the multiexcitons [1]. The quantum mechanical origin of MEG is still under debate and several possibilities have been suggested [22]. Among the most credible explanations of the mechanism is considered to be impact ionization.

Currently, the research of MEG in solar cell based on silicon nanostructure has just begun. To our knowledge, in p-i-n solar cell based on QD arrays, the delocalized quantized 3-D miniband states could be expected to slow the carrier cooling and permit the transport and collection of hot carriers at the respective p and n contacts to produce a higher photopotential [1,2]. In the uniform and orderly nano silicon thin films, the electronic coupling in silicon quantum dots can occur very easily, because grain boundary of amorphous silicon is extremely thin (thickness only 2∼4 atomic layers).

Solar Energy Research Institute at Shanghai Jiaotong University not only observed two Gaussian-type photocurrent peaks attributed to transitions from a tail band in the nc-Si:H/ c-Si heterostructure, but also revealed the unique electronic states of the miniband in the nc-Si:H thin film [23]. The results of the investigations of the photocurrent properties of nc-Si:H thin film may help to realize nc-Si:H/c-Si heterostructure-based optoelectronic devices.

## Nanostructure-based inorganic solar cells

### Hot carrier solar cell

A hot carrier solar cell is a device, which is to slow the rate of photoexcited carrier cooling, caused by phonon interaction in the lattice, to allow time for the carriers to be collected whilst they are still at elevated energies (“hot”), and thus allowing higher voltages to be achieved from the cell [24-27]. The schematic and band diagram of an ideal hot carrier solar cell is shown in Fig. 2.

Unlike a standard cell, which is designed to collect the carriers before the hole and the electron recombined, a hot carrier cell has to catch them before the carrier cooling stage. Therefore, carriers either have to traverse the cell very quickly or cooling rates have to be slowed in some way. For the hot carrier cell to be effective, “hot” carriers must be collected from the absorber over a very small energy range. Hence, it is also required that special contacts are used to prevent the

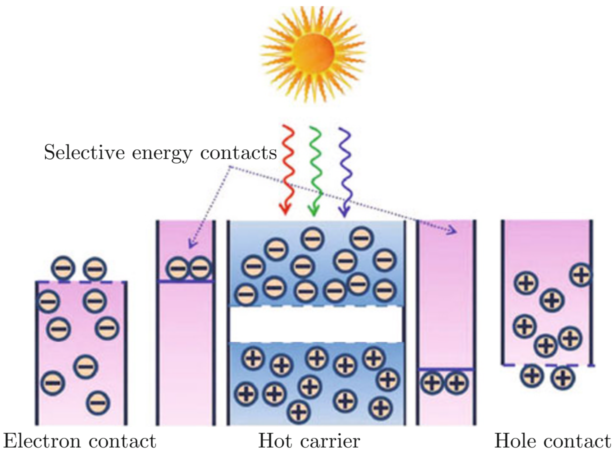

Fig. 2 Schematic and band diagram of an ideal hot carrier solar cell.

the contacts from cooling the carriers [28]. The limiting efficiency of this approach can reach 86.8% as the same as an infinite tandem cell stack. However, in order to achieve this limiting efficiency, carrier cooling rates should be reduced sufficiently or radiative recombination rates should be sufficiently accelerated, the latter being faster than the former [24].

Despite clear efficiency benefits, no real world device has ever been developed, partly because of the difficulty of a suitable absorber material [29]. Developing a hot carrier absorber material, which exhibits sufficiently slow carrier cooling to maintain a hot carrier population under realistic levels of solar concentration, is a key challenge. A candidate for the absorber material is a Quantum Dot superlattice [30]. InGaAs/GaAsP is proposed as a suitable absorber material and the GaAs surface buffer layer was reduced in thickness to maximize photon absorption in the well region. An enhanced hot carrier effect was observed in the optimized structures[31]. Besides, the hot carrier solar cell with indium nitride (InN) absorber layer, gives a highest efficiency of 37.1%, taking into account the realistic transport properties of energy selective contacts [32]. The efficiency of the hot carrier solar cell, with GaSb-based heterostructures as absorber candidates, is improved significantly compared to a fully thermalized single p-n junction of similar bandgap [33].

## SWNTs-based solar cell

The semiconducting single-walled carbon nanotubes (SWNTs) are potentially an attractive material with many unique structural and electrical properties [34-37]. Semiconducting SWNTs bear a wide range of direct bandgaps matching the solar spectrum, and show strong photoabsorption and photoresponse from ultraviolet to infrared, and exhibit high carrier mobility and reduced carrier transport scattering. In addition, like semiconductor NCs, SWNTs exhibit a strong coulomb interaction between electrons and holes, which suggests that SWNTs could also exhibit MEG [38]. They can use the incident photon that other solar cells cannot absorb to generate more electrons. Therefore, Semiconducting SWNTs are nearly ideal materials for PV applications.

In 2008, the research group of Zhang at Shanghai Jiaotong University fabricated SWNT PV solar microcells [39], shown in Fig. 3. In this cell, a directed array of monolayer SWNTs was nanowelded onto two asymmetrical metal electrodes with high and low work functions, respectively, resulting in a strong built-in electric field in SWNTs for efficient separation of photogenerated electron–hole pairs. Under solar illumination, the power conversion efficiency can reach 12.6%.

In 2010, a network of SWNTs was directly assembled onto the surface of n-p junction silicon solar cells by Zhang's group [40], shown in Fig. 4. The SWNTs network not only has high transparency, but also can significantly reduce the electrode resistance of the surface. Therefore, the collection efficiency of the hole was improved, and an enhancement of 3.92% in energy conversion efficiency was typically obtained.

In addition, in 2009 the researchers [41] at Cornell University fabricated photovoltaic cells with CNTs instead of the traditional silicon tube, shown in Fig. 5. The carbon nanotube p-n junction photodiode consist of individual SWNTs in split-gate field-effect geometry. The results clearly confirm that multiple e-h pairs can be generated and collected in a nanotube p-n junction. The e-h pair creation process observed can increase the power conversion efficiency and enhance photocurrent largely.

Cao et al. [42] reported Schottky junction solar cells by coating carbon nanotube films on individual CdSe nanobelts with open-circuit voltages of 0.5 to 0.6 V and modest power-conversion efficiencies (0.45-0.72%). In the planar device structure, the CdSe nanobelt serves as a flat substrate to sustain a network of nanotubes, while the nanotube film forms Shottky junction with the underlying nanobelt at their interface and also makes a

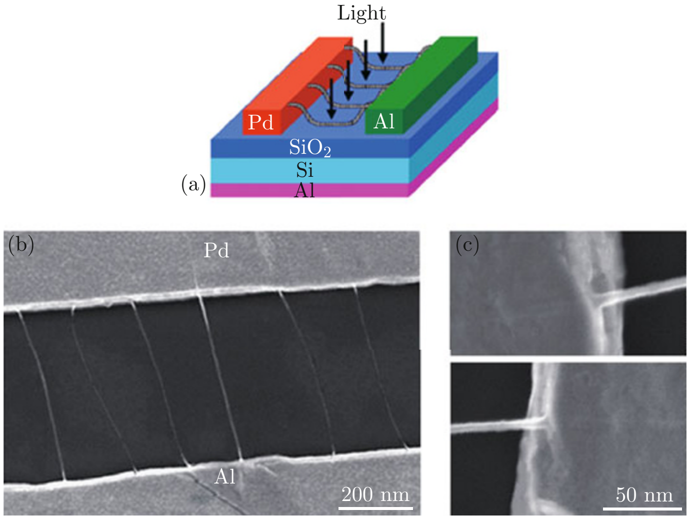

Fig. 3 Structure of the SWNT PV microcells. (a) Schematic diagram of SWNT PV cells. (b) SEM image of SWNT bundle array bridging the Pd and Al electrodes. (c) SEM images of the SWNT bundle ends nanowelded onto the metal electrodes.

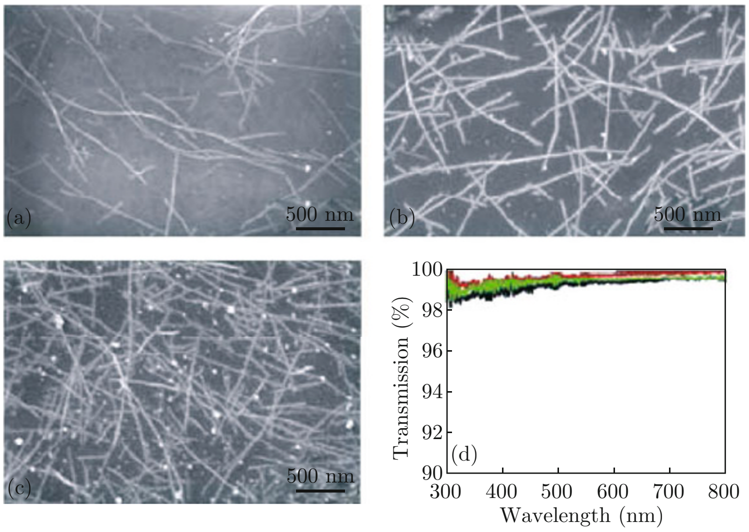

Fig. 4 SEM images of SWNT-assembled p-n junction substrate with different densities. (a) 50∼120 tubes μm$^{-2}$, (b) 150∼200 tubes μm$^{-2}$, (c) 300∼400 tubes μm$^{-2}$, (d) Optical transmission of SWNT networks with different density invisible region.

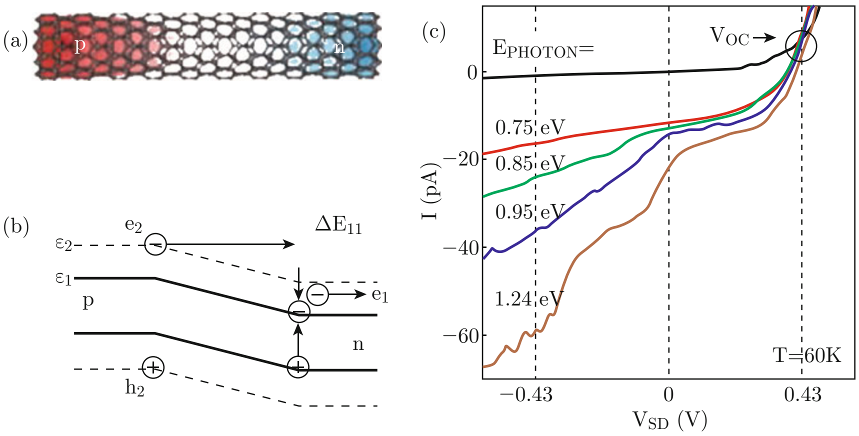

Fig. 5 SWNT p-n junction. (a) p-n junction; (b) Electronic potential energy diagram for the p-n junction with electrons and holes generated at the edges of the junction; (c) I-VSD characteristics for SWNT at various photon energies.

transparent electrode for the device. The nanotube-on-nanobelt solar cells can work either in front (nanotube side) or back (nanobelt side) illumination with stable performance in air.

## Plasmonic nanostructure-based solar cells

Inspired by optoelectronics, plasmonic nanostructures have recently attracted attention for light trapping in solar cells due to their large resonant scattering cross sections [43]. Metallic nanostructures supporting surface plasmons that excitations of the conduction electrons at the interface between a metal and a dielectric can also achieve light trapping. Metal nanoparticles deposited onto a substrate can increase the coupling of light into a substrate [44, 45]. By proper engineering of these metalloid-electric structures, light can be concentrated and 'folded' into a thin semiconductor layer, thereby increasing the absorption. Both localized surface plasmons excited in metal nanoparticles and surface plasmon polaritons (SPPs) propagating at the metal/semiconductor interface are of interest.

Plasmonic structures can offer at least three ways of reducing the physical thickness of the photovoltaic absorber layers while keeping their optical thickness constant [45], shown in Fig. 6.

Light trapping schemes are essential to capture the red and near-infrared portion of the solar spectrum. The metal island films, such as silver-, gold-, copper-island layer, can couple incident light into the waveguide modes of the detector, resulting in increased absorption [46]. Polman et al. [47] studied the light trapping geometries using plasmonic metal nanostructures integrated into coupling of light.

Yu et al. [48] discovered an engineered enhancement of optical absorption and photocurrent in a semiconductor via the excitation of surface plasmon resonances in spherical Au nanoparticles deposited on the semiconductor surface. The surface plasmon resonance wavelength depends on the nanoparticle's size, shape, and local dielectric environment. Localized surface plasmons on metallic nanoparticles can be surprisingly efficient at coupling light into or out of a silicon waveguide. Catchpole et al. [49] demonstrated a factor of 8 times enhancement in the electroluminescence from a silicon-on-insulator light-emitting diode at 900 nm using silver nanoparticles. Ferry et al. [50] demonstrated that the primary photocurrent enhancement occurs in the spectral range from 550 nm to 800 nm in the ultrathin film a-Si:H solar cell with nanostructured plasmonic back contacts. Derkacs et al. [51] investigated the surface plasmon polariton modes in Au nanoparticles deposited on the amorphous silicon film, and an 8.1% increase in short-circuit current density and an 8.3% increase in energy conversion efficiency are observed.

## Nanostructure-based Thin-film Photovoltaic Cell

Compared with the traditional monocrystalline silicon solar cell, the important difference of Thin-film Photovoltaic Cell is that the electrode is transparent conductive film instead of conductive metal mesh. The p-type and n-type doping layer, called "dead zone" in Thin-film Silicon Photovoltaic Cell, make no contribution to the photocurrent. In order to increase the conversion efficiency of solar cell, the optical absorption in the doped layer should be reduced as low as possible. Therefore, in addition to reducing the doped layer as low as possible, the wide band gap material is also used as window layer to reduce the optical absorption.

Amorphous silicon solar cell has been especially popular due to its low cost, however, the low photoelectric conversion efficiency has seriously hampered their wider application. The actual conversion efficiency of amorphous silicon solar modules is only 4.8%-5.0% in industrial production. A series of methods are adopted to improve the conversion efficiency of amorphous silicon solar cell, for example, by using new wide optical band gap and low-resistivity p-type materials as window layer.

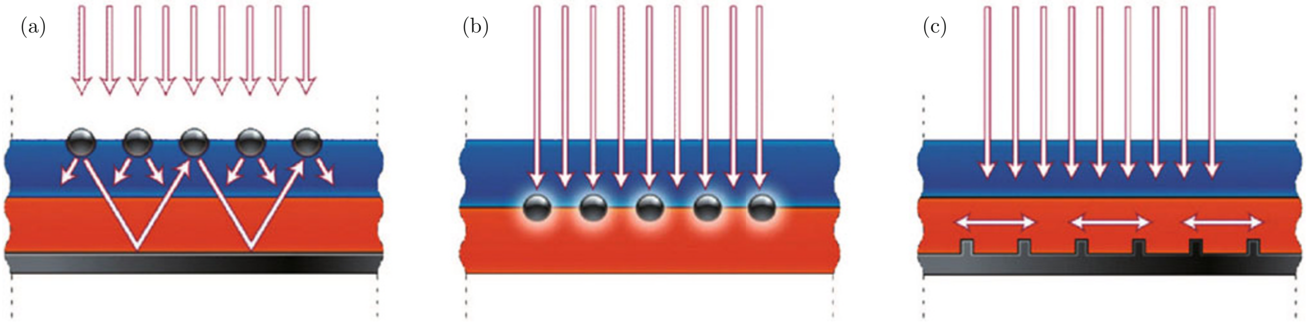

Fig. 6 Plasmonic light-trapping geometries for solar cells.

Considering the lattice matching and the impurity diffusion, the amorphous silicon thin-film solar cells use typically silicon thin film as window layer. For example, Haneman et al. [52] employed a-Si:H/SiC layer in p-i-n amorphous silicon solar cells. Kim et al. in Japan [53] adopt p-SiC/graded p-SiC compositional film. Lee and Lim in Korea [54] used a-C:H(B)/a-SiC. Khan et al. in England [55] employed polymeric amorphous carbon as p-type window within amorphous silicon solar cells. Tawada and Hamakawa et al. employed p-type a-SiC:H as window within amorphous silicon thin-film solar cells, the conversion efficiency of single-junction amorphous silicon solar cell achieved significant breakthroughs (7.14%) [56] in 1981, and reached 10.1% [57] in 1987. By 1996, Hamakawa et al. [58] utilized microcrystalline Si(C) as window layer, and the conversion efficiency of 12.5% had been achieved. The p-type μc-SiC:H was used in their work, due to its higher electrical conductivity and higher optical band gap. The role of the carbon is to change and improve the optical band gap of the thin film. The band gap of the thin film carbon can reach as high as 2.8 eV, however, if the content of carbon is too high, the photoconductance will reduce. In μc-Si thin film solar cell, the intrinsic layer is sensitive to the properties of the materials as window layer. If a-SiC: H and a-SiO: H is used directly as window layer, the thick amorphous incubation layer will appear in the intrinsic layer. Huang et al. [59] employed μc-SiC thin film as window layers in n-side illuminated μc-Si:H n-i-p solar cells. High QE current density of 26.7 mA/cm$^2$ and conversion efficiency of 9.1% was achieved. It is believed that high conductivity and transmittance of the window layer and the high hole mobility of the intrinsic layer are the key factors affecting the performance of the solar cell. It is reported that the absorption coefficient of c-SiC:H in high-energy section is much less than the absorption coefficient of n-type microcrystalline silicon and amorphous silicon.

## The light trapping nanostructured silicon solar cells

The light loss [60,61] of the solar cell comes mainly from the following three aspects: The first is surface reflection; the second is that the incident light is affected by the cover area of the electrode material; the third is that the transmission loss because the thickness of solar cell is too thin.

In order to maximize absorption of incident sunlight, many optical designs for light trapping have been proposed. For example, 1) To minimize the reflection of the incident light, the most common method is the incorporation of antireflective coatings or surface texturing. 2) To increase the path lengths of the light in the absorbing layer after the light being absorbed. For example, the light without absorption can get a second chance of incidence instead of being lost through increasing the refractive index of the absorbing layer and strengthening the back-reflection. 3) To minimize the cover area of the gate electrode, at the same time, to maximize the photocurrent output.

Most of the solar cells used in the terrestrial applications are bulk-type mono- or multi-crystalline silicon solar cells. The typical cell structure is a thin (less than 1 μm) n-type emitter layer on a thick (about 300 μm) p-type substrate. To achieve full absorption of the solar spectrum, light trapping is required over a broad spectral and angular range. To date, the light trapping method is mainly incorporating antireflective coatings or surface textures. For the antireflective effect, surface texturing is superior to the antireflective coatings, so, surface texture is one of the technologies for enhancing the conversion efficiency of the c-Si solar cells [62]. The most successful optical design for commercial monocrystalline silicon solar cell is probably the anisotropically etched pyramids on single-crystalline silicon (100) surface [63-65]. Sodium hydroxide (NaOH) or potassium hydroxide (KOH) with isopropyl alcohol (IPA) is generally used in industry for the anisotropic etching of monocrystalline silicon. For the large-scale production of polycrystalline silicon cells, antireflective coatings on siciline substrate are only used. The conversion efficiency of polycrystalline silicon cells in laboratory has reached 16.8% or above, however, the technology of surface texturing on polycrystalline silicon has not been applied to the large-scale production. The key point is how to control the interface contact, stability and uniformity of the polycrystalline silicon textured microstructure.

Thin-film structures can reduce the cost of solar cells by using inexpensive substrates and a lower quantity and quality of semiconductor material. However, the resulting short optical path length and minority carrier diffusion length necessitates either a high absorption coefficient or excellent light trapping.

Tao et al. [65] adopted a monolayer of microscale particles to achieve surface texturing. It has been experimentally found that the low reflectance from this coating becomes omnidirectional, and the coating improves the transmittance of a quartz wafer in the spectral range of 400-1100 nm. On this basis, Chen et al. [66] have recently demonstrated that incorporating the microsphere-based textures in the ITO ARC can be used as a novel approach for improving the conversion efficiency of the solar cells. The schematic of the key process steps in the fabrication of the omnidirectional ARC structure is shown in Fig. 7. The conversion efficiency of the solar cell with the ITO+MST structure changes from 7.4% to 13.5% as the incident angle increases from 0° to 60°. This results demonstrate the superior omnidirectional antireflection property of the ITO+MST structure.

Semiconducting nanowire arrays have already been shown to have low reflective losses compared to planar semiconductors. With less reflection and thermalize losses, the light trapping nanowire arrays such as ZnO nanowire arrays (Fig. 8) is an excellent surface layer as the networks. In addition, until now, various technologies for making solar cells from arrays of silicon nanowires [67,68] with radial p-n junctions are used for improving light trapping.

Yang et al. [69] demonstrated that ordered arrays of silicon nanowires (Fig. 9) increased the path length of incident solar radiation by up to a factor of 73. By changing the silicon film thickness and nanowire length, there is a competition between improved absorption and increased surface recombination.

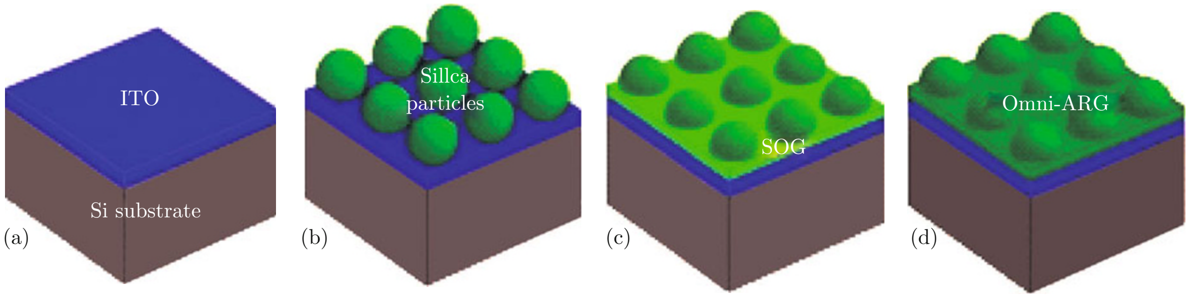

Fig. 7 Schematic of the key process steps in the omnidirectional ARC structure fabrication.

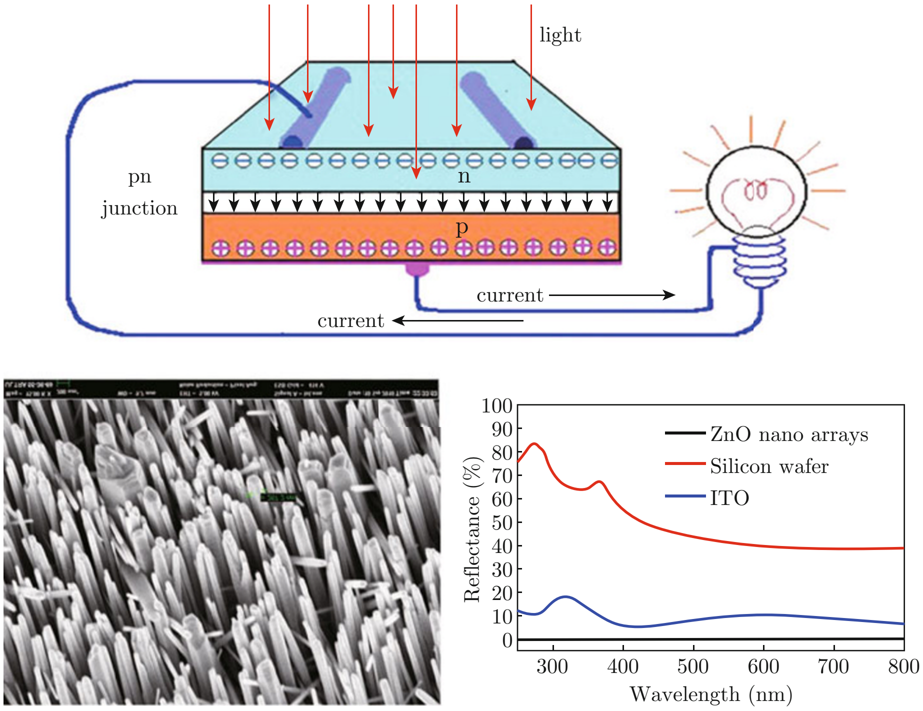

Fig. 8 Light trapping nanowire arrays as surface layer.

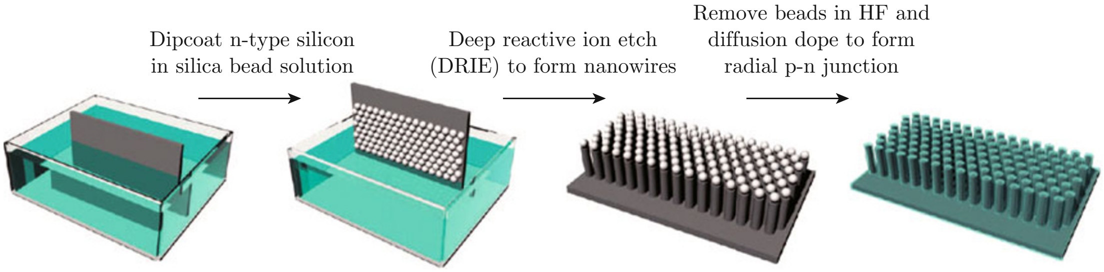

Fig. 9 Ordered silicon nanowire array fabrication scheme.

Nanophotonic structures have attracted attention for light trapping in solar cells with the potential to manage and direct light absorption on the nanoscale. While both randomly textured and nanophotonic structures have been investigated, the relationship between photocurrent and the spatial correlations of random or designed surfaces has been unclear. Light-trapping nanostructures allow for nanoscale control of the direction and absorption of light in ultrathin film solar cells.

Numerous methods have been developed to fabricate Si NW arrays, among which metal assisted wet chemical etching of Si substrates is a promising method in combination with nanosphere lithography to synthesize large areas of ordered Si NWs. Fabrication of porous Si by metal assisted chemical etching was first proposed by Li and Bohn [70] in 2000. Mikhael et al. [71] produced Silicon nanowires (SiNWs) by nanosphere lithography and metal assisted chemical etching (Fig. 10). Chim et al. [72] have developed a simple and low-cost method to fabricate high-density and well-aligned Si NWs through metal-assisted chemical etching using metal nanodots as a hard mask (Fig. 11).

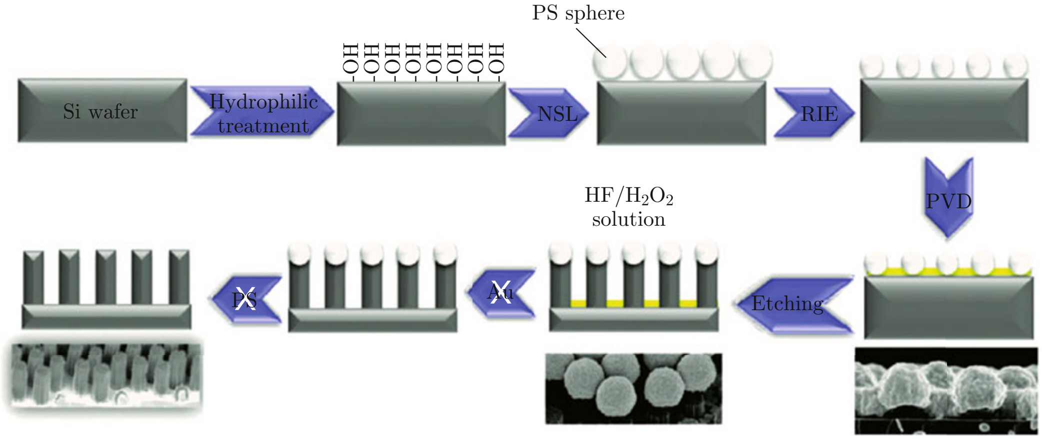

Fig. 10 Schematic diagram showing the overall process to produce Si NW arrays by Au chemical etching combined with nanosphere lithography.

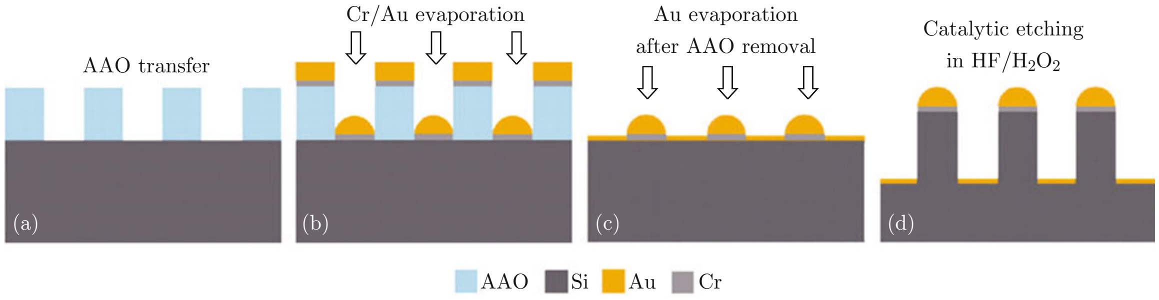

Fig. 11 Schematic of the SiNW fabrication process.

The theory predicts that periodic photonic nanostructures should outperform their random counterparts in trapping light in solar cells. A direct comparison with a cell deposited on the random pyramidal morphology of state-of the-art zinc oxide electrodes, replicated onto glass using nanoimprint lithography, demonstrates unambiguously that periodic structures rival random textures [73].

## Conclusion

In this review, we made a brief introduction of multiple exciton generation, and discussed the recent advances on inorganic solar cells by nanotechnology. The inorganic solar cells have achieved exciting development due to the fact that nanomaterials have unique optical and electrical properties. However, the most important challenge regarding nanostructure-based inorganic solar cells is how to enhance the conversion efficiency to achieving the goal of scalable applications and promising market foreground, and there are still difficulties in the development of nanostructure-based inorganic solar cells, particularly on how to take the full advantage of the unique electrical and optical properties of the nanomaterials. Nevertheless, various problems that commonly occur in solar cells might be partially solved in the near future with advances in nanotechnology.

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