



REVIEW

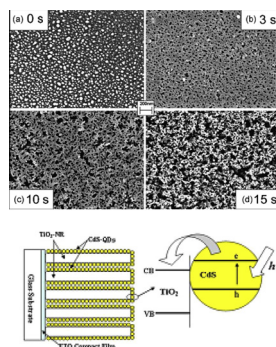
A review on solar cells from Si-single crystals to porous materials and quantum dots



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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 11 September 2013
Received in revised form 21 October 2013
Accepted 22 October 2013
Available online 6 November 2013

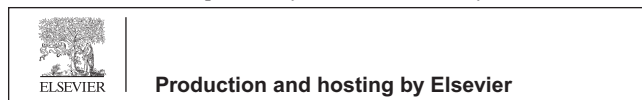
ABSTRACT

Solar energy conversion to electricity through photovoltaics or to useful fuel through photoelectrochemical cells was still a main task for research groups and developments sectors. In this article we are reviewing the development of the different generations of solar cells. The fabrication of solar cells has passed through a large number of improvement steps considering the technological and economic aspects. The first generation solar cells were based on Si wafers, mainly single crystals. Permanent researches on cost reduction and improved solar cell efficiency have led to the marketing of solar modules having 12–16% solar conversion efficiency. Application of polycrystalline Si and other forms of Si have reduced the cost but on the expense of the solar

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Peer review under responsibility of Cairo University.



Keywords:

Nanotechnology
 Porous Si
 Quantum dots
 Solar cells
 Solar energy conversion

conversion efficiency. The second generation solar cells were based on thin film technology. Thin films of amorphous Si, CIS (copper–indium–selenide) and t-Si were employed. Solar conversion efficiencies of about 12% have been achieved with a remarkable cost reduction. The third generation solar cells are based on nano-crystals and nano-porous materials. An advanced photovoltaic cell, originally developed for satellites with solar conversion efficiency of 37.3%, based on concentration of the solar spectrum up to 400 suns was developed. It is based on extremely thin concentration cells. New sensitizer or semiconductor systems are necessary to broaden the photo-response in solar spectrum. Hybrids of solar and conventional devices may provide an interim benefit in seeking economically valuable devices. New quantum dot solar cells based on CdSe–TiO₂ architecture have been developed.

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Introduction

It is now a half century of research where solar energy conversion was taking a major interest of many researchers worldwide. Photovoltaic cells, where the solar spectrum can be converted directly to electricity or photoelectrochemical cells in which the solar energy can be converted to chemical energy have attracted many research groups [1–6]. In the under terrestrial applications, solar cells based on Si have been used and still heavily in use for solar energy conversion. The technology was based on p–n junction or a Schottky barrier that enables the use of the photovoltaic characteristics of the suitable semiconductor i.e. Si [7–18].

The first generation solar cells are based on Si wafers, beginning with Si-single crystals and the use of bulk polycrystalline Si wafers. These cells are now marketed and produce solar conversion efficiencies between 12% and 16% according to the manufacturing procedures and wafer quality [19]. In Fig. 1, one of the collections of solar modules that were used for the production of electricity in separate areas is presented. The energy storage was based on lead–acid batteries.

High cost and the sophisticated technological steps have led to use polycrystalline Si instead of the single crystal wafers, of course, on the expense of the solar conversion efficiency. Continuous research has led to the development of the second generation solar cells.

The second generation solar cells are based on thin film technology in which different materials like amorphous silicon, a-Si, cadmium indium selenide, CIS, or thin silicon films on indium tin oxide, t-Si were produced. In contrast to the



Fig. 1 Solar system based on Si-single crystals.

Si-wafer technology, thin layer solar cells provide potentials for cost reduction in the manufacturing process due to materials savings, low temperature processes integrated cell insulation and high automation level in series production. Further advantage is the use of flexible substrates, a property that gives a good chance for these cells as second generation solar cells to take more part in the energy conversion sector, and opens new application fields such as the integration into textiles. Material combinations of Cu/In/Ga/Se what is called (CIGS-cells) as well as III/V semiconductors like GaAs are applied and solar conversion efficiencies up to 20% were reported [16,20–25]. Unfortunately, thin film solar cells represent difficult module technology, limited stability and have a small market share ($\cong 12\%$ of the total photovoltaic market). In Fig. 2 the different types of materials marketed for thin film solar cells are presented.

It is clear that thin crystalline Si films of about 2.5 μm thickness represent the most used material [26]. Cadmium telluride and amorphous Si and other thin film materials are also good candidates [27–30]. Modules of the second generation solar cells have been also marketed but they did not gain the success of the first generation solar cells, due to technological problems and module stability [31]. Losses due to polycrystallinity of thin films were investigated. It was reported that there were no clear dominant losses for Cu(In, Ga)Se₂ or CdTe solar cells and it was suggested to incorporate impurities into the absorber like Na in both Cu(In, Ga)Se₂ and CdTe and to use anti-reflection coatings. Significant problems must be solved prior to large scale development of polycrystalline thin

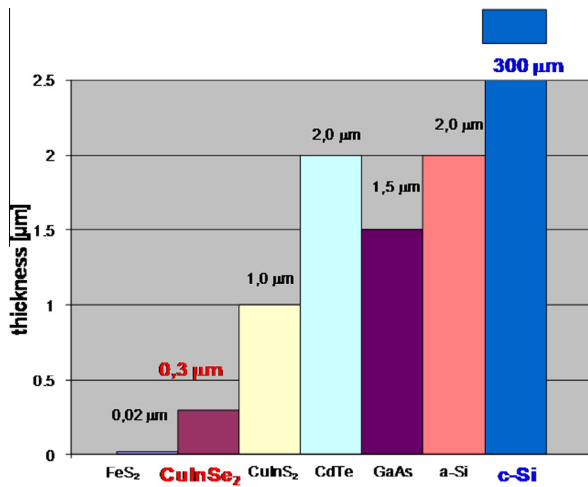


Fig. 2 Second generation solar cells, based on thin film.

film devices [31,32]. Photovoltaic structures based on polymer/semiconductor junctions have been also investigated. Schottky barrier junctions using heavily doped poly-3-methyl thiophene and CdTe or CIS were produced but the low conversion efficiency of 1% has limited their application [33].

Nanoscience and nanotechnology in conjunction with surface science, have the potential to contribute to sustainable energy systems, through more efficient use of current energy sources and enabling breakthrough solutions toward novel energy sources and systems. It is generating a great attention and building great expectations not only in the academic community but also among investors, governments, and industry. A motivation for using nano-structured materials for solar cells is growing and a specific contribution of nanotechnology to various sustainable energy sources is developed. There is

focus on light harvesting, catalysis and materials. Quantum dots, nano-porous materials like Si and TiO₂ and nano-composites play an important role in solar energy conversion [34–41]. Etching of semiconductors plays the main role in the production of micro- and nano-porous clusters [42–44].

Many researchers have demonstrated that solar cells can be made more efficient through the application of nano-technology. Quantum dots are nano-scale clusters of semiconductors that have extraordinary optoelectronic properties, which are modifiable due to quantum physical effects in dependence of the cluster size. They can be applied in solar cells, where several electron-hole pair photons can be produced. Also, the absorption bands can be optimally adjusted to the wavelengths of the irradiating light. Three dimensional grids of quantum dots are technologically possible. Such solar cell structures can lead to solar conversion efficiencies of more than 65% theoretically, which could double practically existing solar cell efficiency [25]. They can produce more electricity than conventional solar cells, which can convert one photon of the solar spectrum into only one electron-hole pair with the rest being lost as thermal by-product [25,37]. They can reduce heat waste and convert up to three electrons per photon. Therefore, they can make solar energy conversion more efficient and cost effective to compete with coal or gas as power sources. However, the current state research is still away from this value, and up to now it has not been possible to show an applied model of quantum dot module. The nano-crystal technology can be applied in near future to photo-electrochemical cells, creating a renewable source for hydrogen production. Nano-scale materials and structures exhibit many novel properties such as electric conductivity, magnetism, fluorescence, hardness and strength change which are significantly different from their macro-scale counterparts. Examples of nanotechnology applications in energy include zero loss transmission lines, super-capacitors that could replace or enhance batteries (advanced

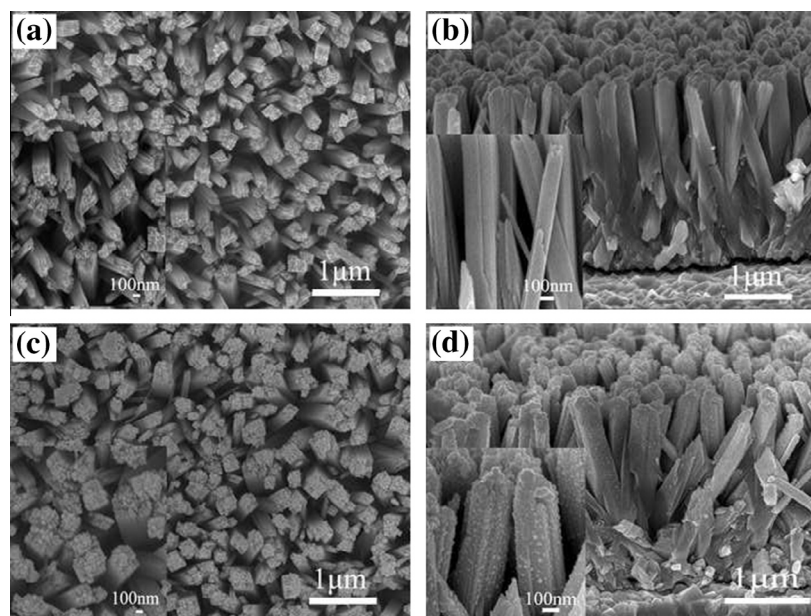


Fig. 3A Field-emission scanning electron microscopy (FESEM) images of (a) TiO₂ nanorod array (top view), (b) cross-sectional SEM image of TiO₂ nanorod array grown on FTO (fluorinated tin oxide), (c) top view and (d) cross-sectional of CdS Quantum Dot's (QDs) coated TiO₂ nanorod array.

lithium-ion batteries) and manage the energy grid more efficiently, more efficient solar cells, “green” highly efficient light bulbs, flexible electronics, cleaner coal fired power plants and more efficient fuel cells to enable the advancement of hydrogen powered cars.

Types of solar cells based on nano-technology

There are three different types of solar cells based on the advances in nanotechnology and they have emerged in the last decade:

- (i) Dye-sensitized solar cells (DSSC),
- (ii) hybrid organic solar cells, and
- (iii) quantum dot solar cells.

The capture and conversion of light energy in these solar cells is facilitated by modifying a nano-structured semiconductor interface with a dye, conjugate polymer, or semiconductor nano-crystals, respectively. Improving the efficiency of photo-induced charge separation and transport of charge carriers across these nano-assemblies remains a challenge.

The basic concepts involved in the development of nano-assemblies for light energy harvesting applications were reported elsewhere [37,39]. The thermodynamic and kinetic criteria for successful cell design were now available and understandable. Strategies for utilizing photo-induced charge separation in donor-acceptor molecules to fabricate nano-structured based solar cells were also available [45–48].

Recent trends of dye-sensitized solar cells and quantum dots

Progress in the processes that dictate the photoconversion efficiency of the dye-sensitized nano-crystalline solar cells (DSSC) and quantum dot solar cells was recently highlighted and

discussed. The photosensitization of nano-structured TiO_2 films with visible light absorbing dyes has led to the development of DSSC with efficiencies greater than 10%. Although there have been significant successes, certain challenges remain in DSSC research. The focus of recent research has been on maximizing solar conversion efficiency by molecular design, developing new nano-structure architectures and establishing the fundamental processes in light harvesting assemblies [49–62]. In this respect, porphyrin-sensitized solar cell with cobalt (II/III)-based redox system was developed and a conversion efficiency of 12.3% was reported [63]. The use of ionic liquids as a replacement for common solvents has shown promise in the development of solid state DSSC [64,65].

Continuous research in this area has led to the development of the third generation solar cells, which are based on nanotechnology [66–72]. Nano-crystals or what is more frequently called “Quantum dots” and nano-porous materials like porous Si or porous titania, TiO_2 , are the most frequently used materials. It was reported that nano-crystals can convert more than 60% of the solar spectrum that may produce more than double the electricity obtained from marketed solar cells [45,73]. The idea of the quantum dot solar cell and its theoretical approach were presented for a practical p-i-n quantum dot solar cell built on the base of the self-organized InAs/GaAs system [74]. The authors studied the advantages of the use of quantum dots in the active region for photon absorption in the long-wavelength part of the spectrum and an increase in the solar conversion efficiency was reported. Theoretical and experimental problems of quantum dot solar cells were discussed. A detailed description of the quantum dot basics and applications was reported by Nozik [75]. The author explained how the two fundamental pathways for enhancing the solar conversion efficiency i.e. an increased photo-voltage or increased photocurrent can be accessed, in three different QD solar cell configurations. However, it was emphasized that these

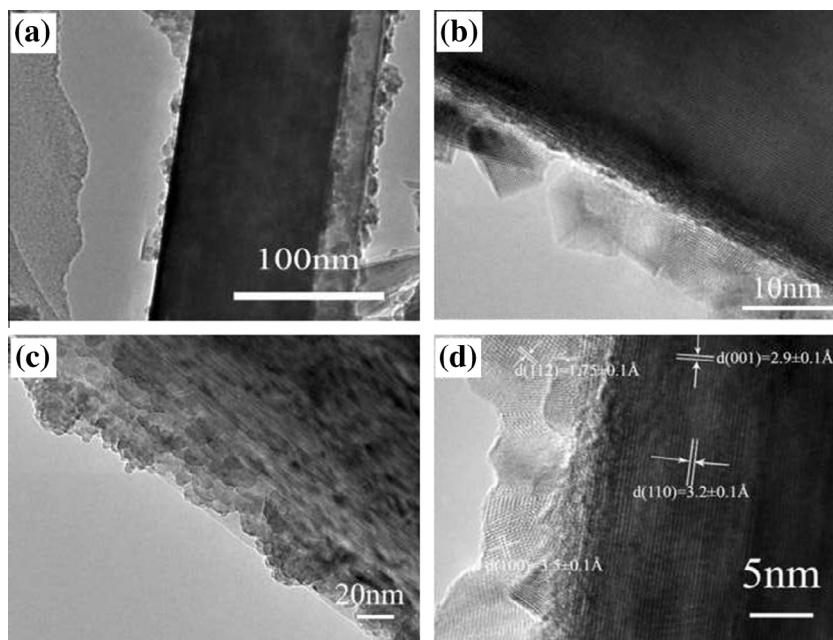


Fig. 3B CdS QDs coated TiO_2 nanorods: (a), (b) and (c) TEM (Tunneling electron microscope) image under different magnification. (d) HRTEM image.

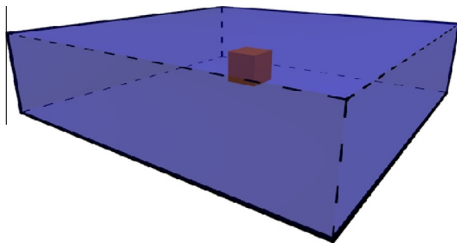


Fig. 4 Quantum dot representation.

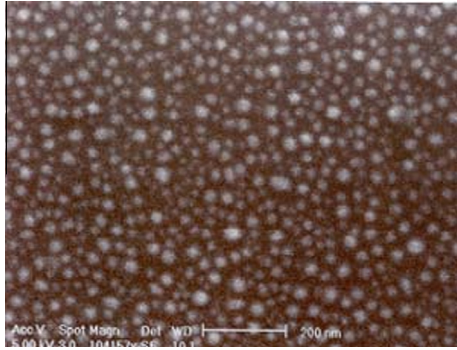


Fig. 5 Quantum dot layer (SEM).

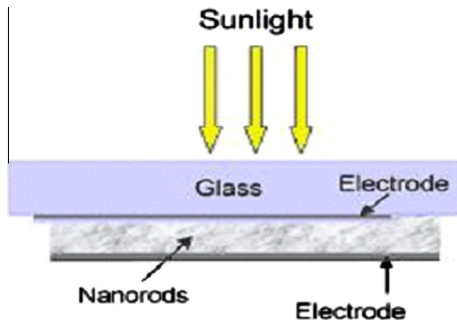


Fig. 6 Diagram of a nano-solar cell.

potential high-efficiency configurations are speculative and there was no experimental evidence that demonstrates actual enhanced conversion efficiencies in any of these systems. Many

trials have been made to produce efficient and stable quantum dot solar cells [37,39,73,76,77].

In Figs. 3A and 3B some pictures and scanning electron micrographs, showing the nano-crystals and nano-rods, and their cross sections that are used to fix the nano-crystals and produce the well-functioning solar cells, are presented. Fig. 4 shows a representative quantum dot and Fig. 5 presents the SEM of a quantum dot layer. Some simple low-cost wet-chemical route for synthesis of ZnO nanowire/nanoparticle composite electrodes integrated in dye-sensitized solar cells was recently presented. The composite photo-anodes have led to much better photovoltaic properties than for bare nanowire or nanoparticle ensembles and an efficiency of 4.7% was obtained [78]. Recent research on ZnO quantum dots and nano-rods and also TiO₂-coated ZnO nanowire arrays leads to promising applications. The dye-sensitized cells of this type gave solar conversion efficiency of 6–9% [61,62,79,80]. Investigations on modified and hybrid solar cells are recently presented [81–83].

In Fig. 6, a diagram of solar cell based on quantum dots and nanowires under sunlight illumination is presented. Efficiencies of about 10% have been obtained without optimization of the preparation conditions. It could be doubled by optimizing the charge collection.

In Fig. 7 the charge transfer process occurring in a nano-structured QDs modified TiO₂ nano-rod array electrode is presented. In the simple cell the electron-hole pairs are created in the CdS quantum dots after absorption of sun light. The electrons are injected in the conduction band of TiO₂ and the holes are collected at the dot surface. In this way, the charges can be separated producing electric current through the two electrodes, i.e. the front and back contacts.

Porous silicon

Porous silicon (PSi) is a form of the chemical element Si which contains nano-porous holes in its microstructure, rendering a large surface to volume ratio in an order of 500 m²/cm³. It was discovered in 1990 that porous silicon formed on crystalline silicon wafers using electrochemical etching exhibits photoluminescence and electroluminescence. Since then, the research in this area was increased intensively and extensively. Fig. 8 presents the progress in the field of research in this area in the last decades.

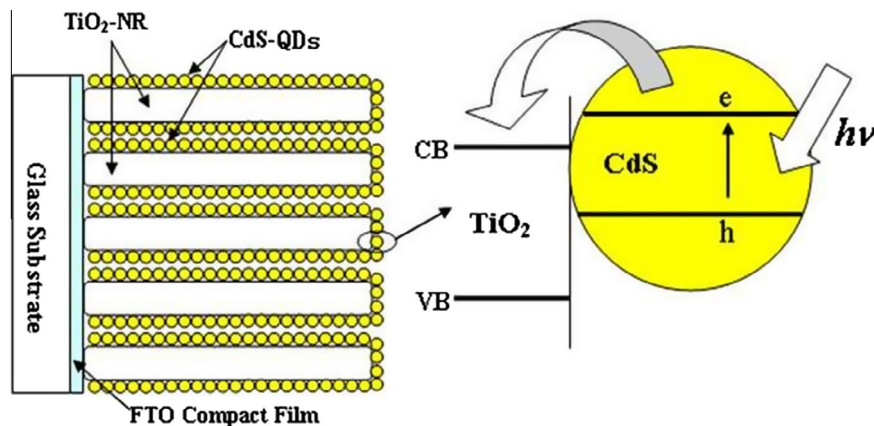


Fig. 7 Charge-transfer processes between CdS and TiO₂ in a QD/nanowire based solar cell.

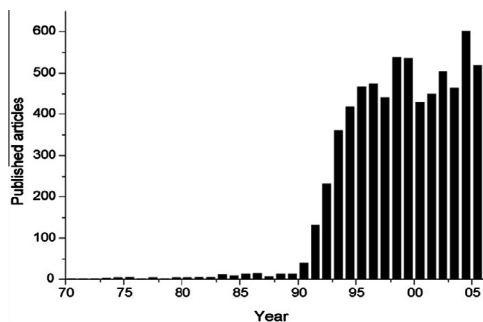


Fig. 8 The progress of research on porous Si.

Fabrication and pore morphology of porous silicon

There are numerous physical and chemical methods to produce porous semiconductors. Among these techniques, chemical and electrochemical techniques possess two main advantages:

1. Cost effectiveness, and
2. Three-dimensional processing.

Wet etching of semiconductors

Wet etching of semiconductors, e.g. Si, is basically a material dissolution that can proceed via several mechanisms: chemical, electro-less, photochemical, anodic or cathodic etching.

Chemical etching

During chemical etching, simultaneous bond exchange proceeds between undissociated molecules in the solution and surface atoms. Chemical bonds between the surface atoms and the bulk atoms are broken while new bonds are formed with the reactants; surface atoms thus move to the solution. Such phenomena are not potential dependent. Both anisotropic

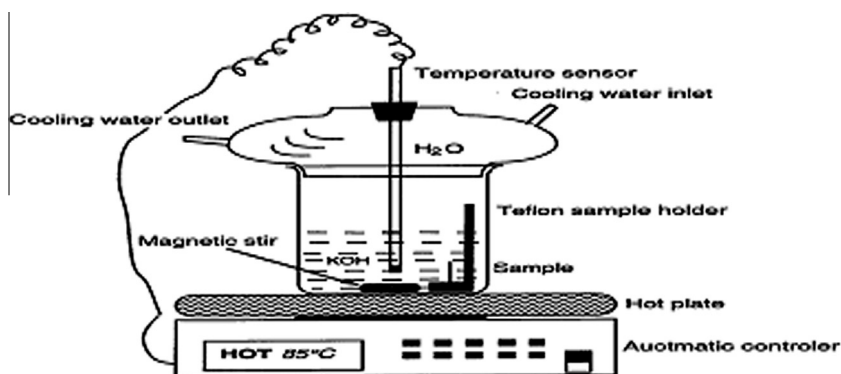


Fig. 9 The chemical etching cell.

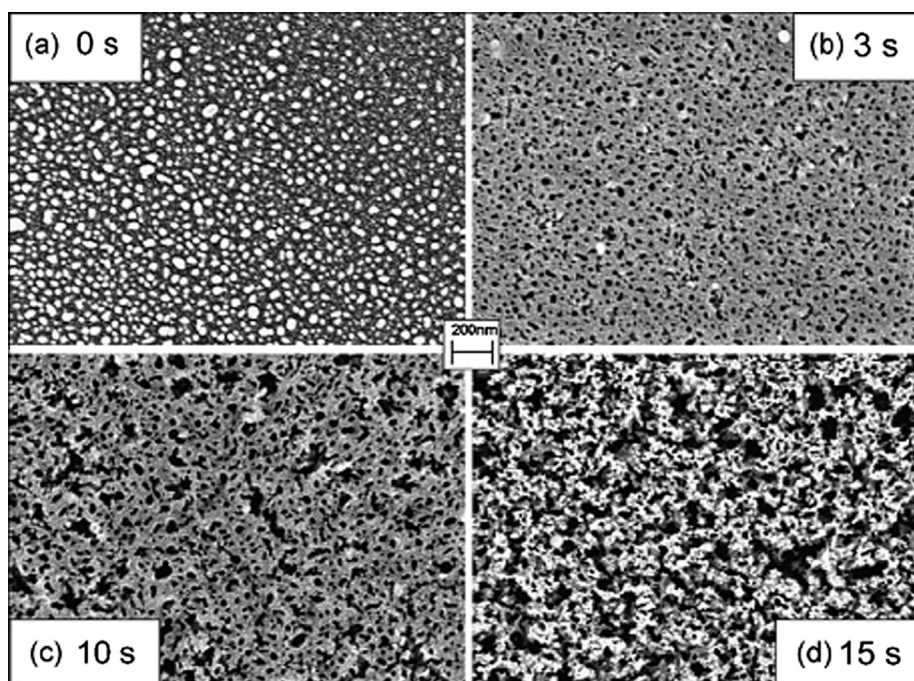


Fig. 10 SEM plane view of a Ag loaded p-type (100) Si surface (a) and the porous Si layer produced by HF (40%), H₂O₂(35%) and (H₂O) by volume (25/15/4) after 3 s (b), 10 s (c), and 15 s (d).

silicon and isotropic silicon chemical etching are widely used in micro-electronics. Etching in alkaline aqueous solutions containing inorganic (LiOH, NaOH, KOH, RbOH, CsOH, or even NH_4OH) or organic (ethylenediamine, hydrazine, tetramethyl-ammonium hydroxide, choline, and amine gallates) commands leads to anisotropic Si dissolution in which OH^- or H_2O are the active species.

Isotropic Si etching is achieved in acidic media that contain fluoride ions i.e. (HF) according to the following equation:

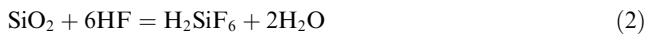
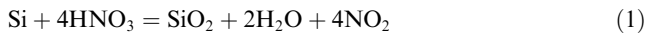


Fig. 9 represents a simple chemical etching system, where the specimens are fixed in a Teflon holder. The specimens were subjected to surface etching from one side leaving the other for electrical contacts.

Table 1 Photovoltaic parameters of n-Si/oxide and n-Si/PSL/oxide solar cells under simulated solar spectrum at 298 K.

| Photovoltaic cell | J_{ph} (mA cm^{-2}) | V_{oc} (mV) | FF | η (%) |
|-----------------------------|---|----------------------|------|------------|
| n-Si/ SnO_2 /M | 29 | 550 | 0.57 | 9.12 |
| n-Si/PSL/ SnO_2 /M | 31.5 | 580 | 0.67 | 12.10 |
| n-Si/ TiO_2 /M | 29 | 590 | 0.61 | 10.40 |
| n-Si/PSL/ TiO_2 /M | 31.5 | 670 | 0.71 | 14.84 |

Electrochemical metal deposition is utilized to fabricate micro- and nano-structures and to facilitate the etching process. In such cases, metal deposition by displacement reaction or electro-less deposition without reducing agent in electrolyte is often used. Immersion deposition is the simplest electrochemical process and a favorable process to control a very small amount of deposits; furthermore, silicon is the preferred

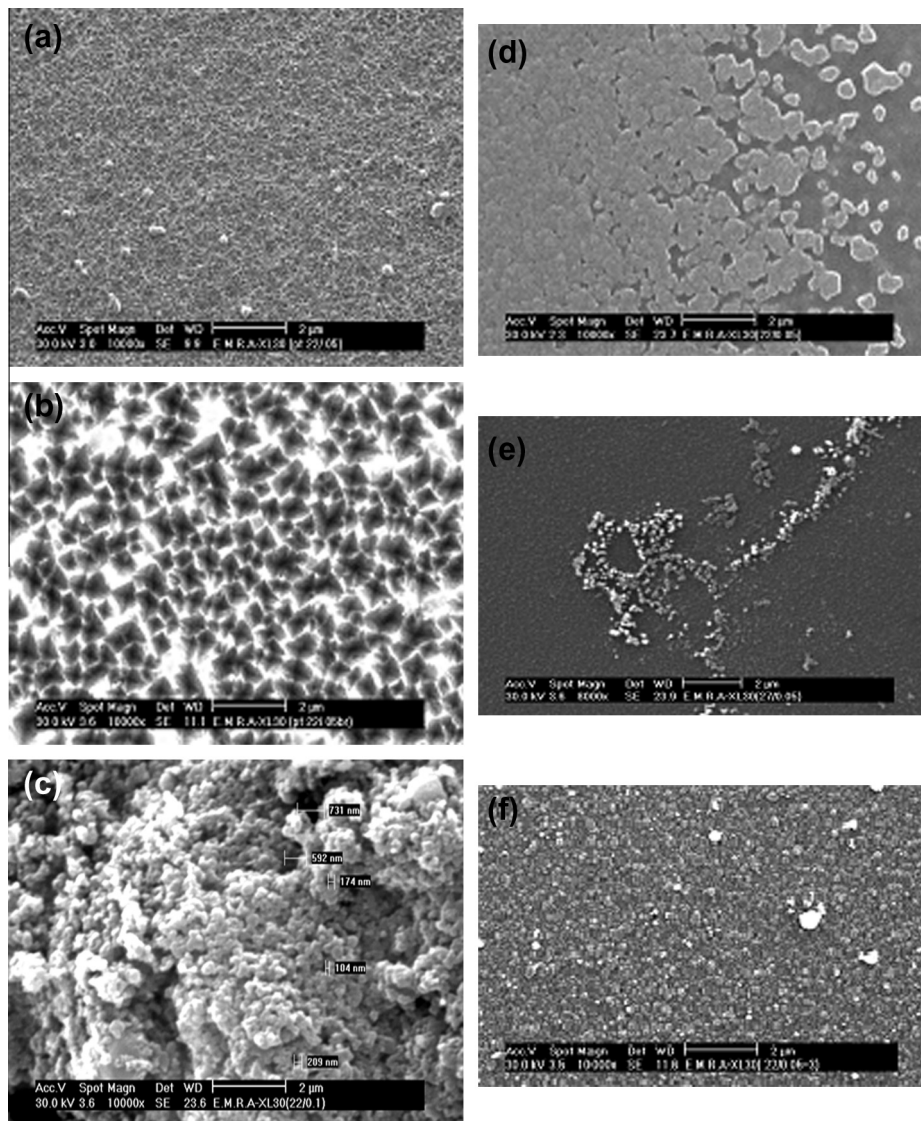


Fig. 11 SEM of p-Si in different solutions for different time intervals (a) SEM – p-Si etched in 22 M HF-0.05 M KIO_3 for 1 h, (b) SEM – p-Si etched in 22 M HF-0.05 M KBrO_3 for 1 h, (c) p-Si etched in 22 M HF-0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$ for 1 h, (d) p-Si etched in 22 M HF – 0.05 M $\text{K}_2\text{Cr}_2\text{O}_7$ for 1 h, (e) SEM- p-Si etched in 27 M HF – 0.05 M $\text{K}_2\text{Cr}_2\text{O}_7$ for 1 h, (f) p-Si etched in 22 M HF – 0.05 M $\text{K}_2\text{Cr}_2\text{O}_7$ for 3 h.

Table 2 Photoelectrochemical parameters of n-Si/oxide and n-Si/PSL/oxide photoelectrochemical cells under simulated solar spectrum at 298 K. The electrolyte consists of 0.05 M $K_3Fe(CN)_6$ /0.05 M $K_4Fe(CN)_6$ /0.5 M KNO_3 .

| Photoelectrochemical cell | J_{ph} (mA cm ⁻²) | V_{oc} (mV) | FF | η (%) |
|----------------------------------|---------------------------------|---------------|------|------------|
| n-Si/SnO ₂ /Elec. | 26 | 440 | 0.40 | 4.59 |
| n-Si/PSL/SnO ₂ /Elec. | 30.5 | 490 | 0.68 | 10.20 |
| n-Si/TiO ₂ /Elec. | 28.0 | 580 | 0.44 | 7.13 |
| n-Si/PSL/TiO ₂ /Elec. | 31.0 | 600 | 0.59 | 10.92 |

substrate because of its less-nobleness although it must be noted that the surface is subjected to oxidation.

Characteristics of metal deposition on silicon

Metal deposition on Si has some characteristic features. Si and the deposited metal usually show a weak interaction leading to the 3D island growth or Volmer–Weber mechanism. Electrochemical reaction on Si is generally sluggish. Once the surface receives metal deposition, electrochemical reaction is possible also on the deposit surface, where the reaction rate is faster than that on the uncovered Si surface. The relative deposition rates on the substrate and deposits determine the morphology of deposits. In Fig. 10, the morphology of metal deposit and pore structure is presented.

The porous structure and pore morphology and size depend on three important parameters. The first is the etching medium and its concentration. The second is the oxidizing agent and its concentration and the third is the time of etching. Some other parameters, such as the electro-less metal deposit, are influencing the formed nano- and/or micro-porous structures. The effect of such parameters on the surface morphology can be seen clearly on the scanning electron micrographs. These micrographs are presented in Fig. 11 which gives detailed pictures of these effects.

It is clear from Fig. 11b that the etching of p-Si in 22 M HF containing 0.05 M potassium bromate for one hour represent the best conditions for obtaining micro- and nano-porous film on p-Si [35,44].

The formation of porous film on the Si surface leads to an improvement in the solar conversion efficiency of the solar cells fabricated on this basis. Such improvement leads to more than 25% increase [35,84]. The improvement obtained in the solar conversion efficiency of photovoltaic and photoelectrochemical cells with and without PSL is presented in Tables 1 and 2.

Conclusions

Nano-crystal/nanowire architectures of semiconductors can develop solar energy converters that can, theoretically, convert more than 66% of the solar spectrum into electricity. They can produce more electricity than conventional solar cells and for practical applications; they can double the practically existing solar cell efficiencies by optimizing the charge collection.

Homogeneous nano-structures of PSL were prepared conveniently on the top of n-Si or p-Si. The PSL improves the solar conversion efficiency. The PSL has different applications not only in solar cell but also in optoelectronics. The oxidizing agent and its concentration play an important role on the nature and morphology of the formed porous layer. The time of etching and also the concentration of HF should be optimized.

Conflict of interest

The author has declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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