



Review Paper

TiO₂ Microstructure, Fabrication of thin Film Solar Cells and Introduction to Dye Sensitized Solar Cells

Dhonde Mahesh¹ and Jaiswal Rajesh²

¹Dept. of Engg. Physics Prestige Institute of Engineering and Science, Indore INDIA

²Dept. of Engg. Physics Prestige Institute of Engineering and Science, Indore INDIA

Available online at: www.isca.in

Received 30th October 2012, revised 08th February 2013, accepted 15th February 2013

Abstract

Various materials and technologies were developed such as use of single crystals, poly crystalline materials, thin film and nano particles deposition etc. To reduce the cost and spectral shift in the visible region methods of doping by nano particles of noble metal/ organometals this also enhances the conversion efficiency under different parametric variations. Different types of solar cells were developed in order to minimize the cost of dollars per watt and to maximize selectivity of the wavelength of solar spectrum in an effective manner. The objective of the present study is to review the progress in the solar cell technology along with problems associated with different solar cells utilized in the visible range of sunlight and the methods to optimize the efficiency and the cost.

Keywords: Solar cell, nano particles, thin film.

Introduction

In this age of technological revolution where saving energy and using renewable sources of energy are stressed, it is indeed possible to save energy if we use solar powered products. Not only they are environment friendly but they have many more advantages to them. All photovoltaic devices incorporate a p n junction in a semiconductor across which the photo voltage is developed¹.

Photovoltaic devices are based on the concept of charge separation at an interface of two materials of different conduction mechanism. To date this field has been dominated by solid-state junction devices, usually made of silicon, and profiting from the experience and material availability resulting from the semiconductor industry. The dominance of the photovoltaic field by inorganic solid-state junction devices is now being challenged by the emergence of a third generation of cells based, for example, on nanocrystalline and conducting polymers films. These offer the prospective of very low cost fabrication and present attractive features that facilitate market entry. It is now possible to depart completely from the classical solid-state junction device, by replacing the contacting phase to the semiconductor by an electrolyte, liquid, gel or solid, thereby forming a photo-electrochemical cell. The phenomenal progress realized recently in the fabrication and characterization of nanocrystalline materials has opened up vast new opportunities for these systems. Contrary to expectation, devices based on interpenetrating networks of microscopic semiconductors have shown strikingly high conversion efficiencies, which compete with those of conventional devices. The prototype of this family

of devices is the dye-sensitized solar cell, which realizes the optical absorption and the charge separation processes by the association of a sensitizer as light-absorbing material with a wide band gap semiconductor of nanocrystalline morphology².

Photovoltaic's, which by means of solid-state technology turn photon energy into electricity, can make a substantial contribution toward fulfilling these energy needs. Historically, the drawbacks to photovoltaic's have been cost and technological maturity³. From solid state physics we know that silicon is not the ideal material for photovoltaic conversion. For a 90% light absorption it takes only 1 mm of Ga As (a direct semiconductor) versus 100 mm of crystalline Si. It is not surprising, on the other hand, that a lot of effort has been going on and is still going into the search for new materials. Requirements for the ideal solar cell material are: i. band gap between 1.1 and 1.7 eV, ii. direct band structure, iii. consisting of readily available, non-toxic materials, iv. easy, reproducible deposition technique, suitable for large area production, v. good photovoltaic conversion efficiency; and vi. long-term stability. The progress has been going on to enhance the cost and conversion efficiency using nanotechnology in solar cells.

Brief History of the Solar Cell: In 1839, Becquerel reported the photovoltaic effect when he observed that when light was shined on a solid electrode immersed in an electrolyte solution an electrical current was produced.

The solar cell created by Charles Fritt's in 1883 only had a light to electricity conversion rate of about 1%. In 1941, Russell Ohl invented the silicon solar cell. With his discovery the efficiency of

solar cells began to increase. Bell Laboratory fabricated the first crystalline silicon solar cells in 1953, achieving 4.5% efficiency, followed in 1954 with devices with 6% efficiency⁴. In 1954, three American researchers, Gerald Pearson, Calvin Fuller and Daryl Chapin, discovered the use of silicon as a semiconductor and designed a silicon solar cell capable of achieving a conversion efficiency rate of 6%⁵.

These three inventors then developed the first solar panels. By 1956 the first commercial solar cells were made available to the public. They were extremely expensive (about \$300 per watt) and were used in radios and toys.

In 1962, Bell Telephone Laboratories launches Telstar, the first active telecommunications satellite. It's powered by solar cells that produce about 14 watts of electricity. i. The Energy Crisis in 1970 led to the dramatic drop in price (about \$20 per watt) of solar cells. ii. In 1969, Berman reduced cost from \$100/watt to about \$20/watt. iii. In 1998 Subhendu Guha leads a team that invents flexible solar shingles, a roofing material to converting sunlight to electricity. iv. The worldwide installed photovoltaic capacity reaches 1000 megawatts in 1999. v. The best laboratory efficiency for single crystal silicon is today 24.7%⁶. vi. In 2007, National Renewable Energy Laboratory and Boeing Spectrolab created the High-Efficiency Metamorphic Multijunction Concentrator Solar Cell (HEMM solar cell). It breaks the 40% conversion efficiency barrier, making it twice as efficient as a typical silicon cell.

Development of Solar Cells (Three Generations of Solar Cells): First generation cells consist of large-area, high quality and single junction devices. First Generation technologies involve high energy and labor inputs. Single junction silicon devices are approaching the theoretical limiting efficiency of 33% and achieve cost parity with fossil fuel energy generation after a payback period of 5-7 years.

Second generation materials make the use of thin film technology. The first considerations concerning thinner silicon wafers for solar cells were made by Wolf⁷ and Lofersky⁸, while simulating the ideal parameters for record high efficiencies. The most successful second generation materials have been cadmium telluride (CdTe), copper indium gallium selenide (CIGS), amorphous silicon and micro amorphous silicon. These materials are applied in a thin film to a supporting substrate such as glass or ceramics reducing material mass and also the cost.

Third generation technologies aim to enhance poor electrical performance of second generation (thin-film technologies) while maintaining very low production costs. In this generation solar cells the focus of study is to harness the plentiful visible portion of sunlight to achieve maximum conversion efficiency (light into electricity). Current research is targeting conversion efficiencies of 30-60% while retaining low cost materials and manufacturing techniques.

Thin Film Solar Cells: Nanotechnology-enhanced, thin-film solar cells are a promising and potentially important emerging technology. The mainstay at present is the silicon solar cell which accounted for 90% of the market in 2004. However these are costly to manufacture and have limited efficiency (around 14% in most production modules, and up to 25% in the lab). The cost per unit of power is at least several fold higher using silicon solar cells than that derived from fossil fuel combustion (The Institute of Nanotechnology, 2006). Component is applied as a thin coating. As a result much less material is required (as low as 1% compared with wafers) and costs are decreased. Most such cells utilize amorphous silicon, which, as its name suggests, does not have a crystalline structure and consequently has a much lower efficiency (8%), however it is much cheaper to manufacture.

Nanotechnology ("nano") incorporation into the films shows special promise to both enhance efficiency and lower total cost. Many nano-structured materials are now being investigated for their potential applications in photovoltaics.

Nano-structured layers in thin film solar cells offer three important advantages. First, due to multiple reflections, the effective optical path for absorption is much larger than the actual film thickness. Second, light generated electrons and holes need to travel over a much shorter path and thus recombination losses are greatly reduced. As a result, the absorber layer thickness in nano-structured solar cells can be as thin as 150 nm instead of several micrometers in the traditional thin film solar cells. Third, the energy band gap of various layers can be tailored to the desired design value by varying the size of nano-particles. This allows for more design flexibility in the absorber and window layers in the solar cells.

Doped TiO₂ semiconductor powders were synthesized using Al and W as photovoltaic property-enhancing impurities. Al-doped TiO₂ electrodes increased open-circuit voltage (Voc), but reduced short-circuit current (Isc).

Dye Sensitized Solar Cells

Historical background: The history of the sensitization of semiconductors to light of wavelength longer than that corresponding to the bandgap has been presented elsewhere^{9,10}.

The first panchromatic film, able to render the image of a scene realistically into black and white, followed on the work of Vogel in Berlin after 1873¹¹, in which he associated dyes with the halide semiconductor grains. The first sensitization of a photo-electrode followed shortly thereafter, using a similar chemistry¹². However, the clear recognition of the parallelism between the two procedures, a realization that the same dyes in principle can function in both¹³ and a verification that their operating mechanism is by injection of electrons from photo-excited dye molecules into the conduction band of the n-type semiconductor substrates¹⁴ date to the 1960s. In subsequent

years the idea developed that the dye could function most efficiently if chemisorbed on the surface of the semiconductor^{15,16}. The concept emerged to use dispersed particles to provide a sufficient interface¹⁷, then photo-electrodes were employed¹⁸. Titanium dioxide became the semiconductor of choice. The material has many advantages for sensitized photochemistry and photo-electrochemistry: it is a low cost, widely available, non-toxic and biocompatible material, and as such is even used in health care products as well as domestic applications such as paint pigmentation. The standard dye at the time was *tris* (2,2'-bipyridyl-4,4'-carboxylate) ruthenium(II), the function of the carboxylate being the attachment by chemisorption of the chromophore to the oxide substrate. Progress thereafter, until the announcement in 1991¹⁹ of the sensitized electrochemical photovoltaic device with a conversion efficiency at that time of 7.1% under solar illumination, was incremental, a synergy of structure, substrate roughness and morphology, dye photo physics²⁰ and electrolyte redox chemistry. That evolution has continued progressively since then, with certified efficiency now over 10%.

A DSSC is composed of a porous layer of titanium dioxide nanoparticles, covered with a molecular dye that absorbs sunlight. The titanium dioxide is immersed under an electrolyte solution, above which is a platinum-based catalyst. As in a conventional alkaline battery, an anode (the titanium dioxide) and a cathode (the platinum) are placed on either side of a liquid conductor (the electrolyte). In quantum efficiency terms, DSSC's are extremely efficient. Due to their "depth" in the nanostructure there is a very high chance that a photon will be absorbed, and the dyes are very effective at converting them to electrons. Most of the small losses that do exist in DSSC's are due to conduction losses in the TiO₂ and the clear electrode, or optical losses in the front electrode. The overall quantum efficiency for green light is about 90%, with the "lost" 10% being largely accounted for by the optical losses in top electrode. The quantum efficiency of traditional designs vary, depending on their thickness, but are about the same as the DSSC.

DSSC's degrade when exposed to ultraviolet radiation. The barrier layer may include UV stabilizers and/or UV absorbing luminescent chromophores (which emit at longer wavelengths) and antioxidants to protect and improve the efficiency of the cell. Principle of operation and energy level scheme of the dye-sensitized nanocrystalline solar cell.

The regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye. The iodide is regenerated in turn by the reduction of triiodide at the counter electrode the circuit being completed via electron migration through the external load. The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte.

Overall the device generates electric power from light without suffering any permanent chemical transformation.

In this part different microstructure and characterization of TiO₂ that has been worked on so far is reviewed chronologically.

DSSC's are mostly based on randomly nanocrystalline TiO₂ film produced by sol-gel method. There has been many efforts to develop ordered or one dimensional TiO₂ films in order to improve the electron transport. In this article for the first time ordered TiO₂ nanotubes array used as photoanode for ionic electrolyte in dye sensitized solar cells. the nano tubes were prepared by anodization of Ti foils and then immersed in TiCl₄ solution and rinsed following by sintering at 500°C for 3hr.

Construction

In the case of the original design, the cell has 3 primary parts. On top is a transparent anode made of fluoride-doped tin dioxide (SnO₂:F) deposited on the back of a (typically glass) plate. On the back of this conductive plate is a thin layer of titanium dioxide (TiO₂), which forms into a highly porous structure with an extremely high surface area. TiO₂ only absorbs a small fraction of the solar photons (those in the UV). The plate is then immersed in a mixture of a photosensitive ruthenium-polypyridine dye (also called molecular sensitizers) and a solvent. After soaking the film in the dye solution, a thin layer of the dye is left covalently bonded to the surface of the Ti. Other oxides has been investigated but so far TiO₂ shows the best response. S_nO₂ has also been considered for its faster charge transport, but its conduction band energy is 0.4V more positive than TiO₂.

Operation

Sunlight enters the cell through the transparent SnO₂:From top contact, striking the dye on the surface of the TiO₂. Photons striking the dye with enough energy to be absorbed create an excited state of the dye, from which an electron can be "injected" directly into the conduction band of the TiO₂. From there it moves by diffusion (as a result of an electron concentration gradient) to the clear anode on top.

Meanwhile, the dye molecule has lost an electron and the molecule will decompose if another electron is not provided. The dye strips one from iodide in electrolyte below the TiO₂, oxidizing it into triiodide. This reaction occurs quite quickly compared to the time that it takes for the injected electron to recombine with the oxidized dye molecule, preventing this recombination reaction that would effectively short-circuit the solar cell.

The triiodide then recovers its missing electron by mechanically diffusing to the bottom of the cell, where the counter electrode re-introduces the electrons after flowing through the external circuit.

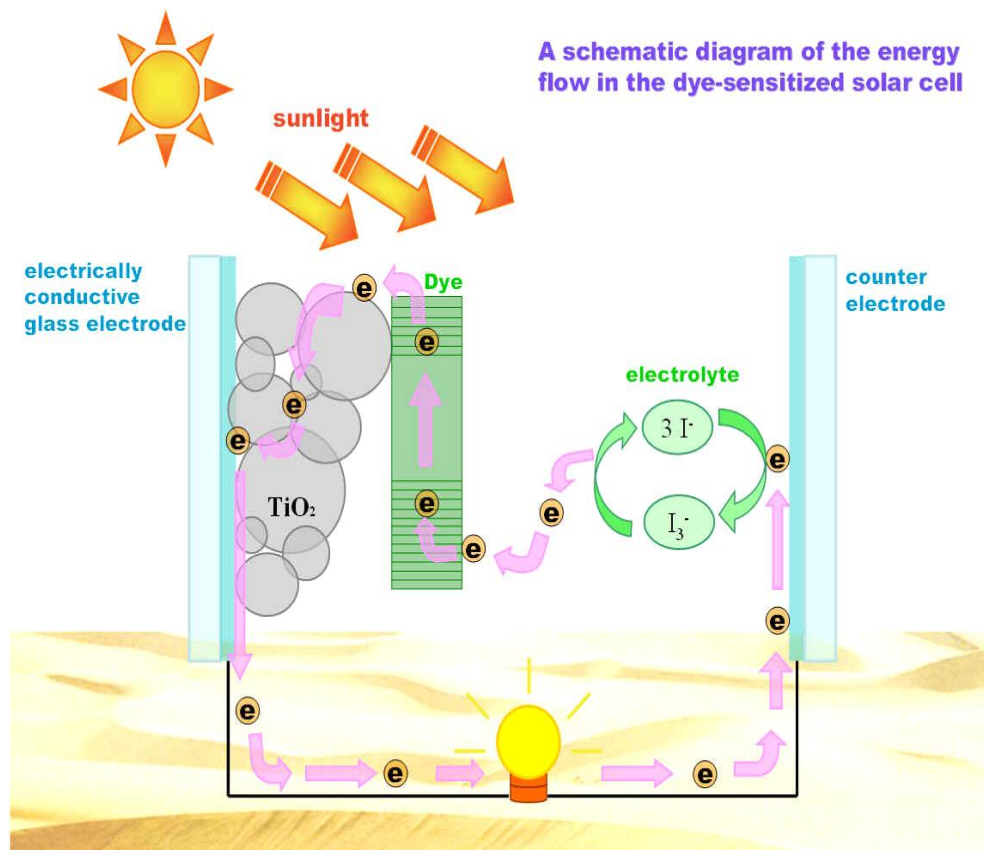


Figure-1
Energy Flow Diagram in Dye –Sensitized Solar Cell

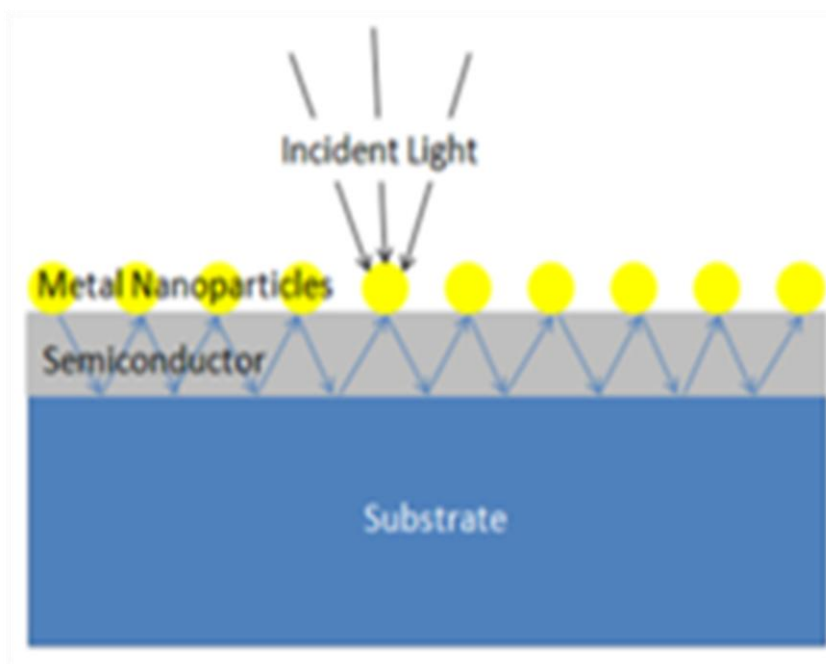


Figure-2
PSC using metal nanoparticles

Problems

The major disadvantage to the DSSC design is the use of the liquid electrolyte, which has temperature stability problems. At low temperatures the electrolyte can freeze, ending power production and potentially leading to physical damage. Higher temperatures cause the liquid to expand, making sealing the panels a serious problem. Another major drawback is the electrolyte solution, which contains volatile organic solvents and must be carefully sealed. This, along with the fact that the solvents permeate plastics, has precluded large-scale outdoor application and integration into flexible structure. Replacing the liquid electrolyte with a solid has been a major ongoing field of research. Recent experiments using solidified melted salts have shown some promise, but currently suffer from higher degradation during continued operation, and are not flexible.

Conclusion

TFSCs are attractive devices, which offer the possibility of reducing the active material requirement significantly. Even if expensive and/or not available in abundance, a number of semiconductors are well suited in thin-film form for reasonably efficient solar cell devices to be manufactured on a large scale. The performance of all thin-film solar cells being studied presently is improving steadily, owing to increasingly better understanding of the unique and wide range of structural, chemical and optoelectronic characteristics of thin-film materials, and effective exploitation of some properties for such functions as passivation, activation, photon scattering/recycling, generation of surface electric fields, graded bandgaps, etc. Further progress is expected in closing the gap between the achieved efficiencies and the theoretically expected ones, with more detailed understanding of the electronic role of interfaces in the layered structure of the devices and with more precisely audited account of photons and excited carriers in the device.

Moreover DSSC-Dye-sensitized TiO₂ solar cells efficiently convert solar energy into electricity using low cost and easy-to-make materials, becoming a promising alternative to classical photovoltaic devices based on inorganic semiconductor technology. In addition to practical interest as an effective alternative energy source, these devices are also very fascinating systems from a scientific point of view, in which electrical energy is obtained from an elegant excitation-charge injection-redox process. This is a result of a successful combination of materials, usually consisting of a dyesensitized nanocrystalline TiO₂ film, an electrolyte with a redox couple and a counter-electrode.

The overall efficiency in energy conversion depends critically on the individual properties of the constituents of the cell and

their successful interactions. The recent introduction of polymer materials in DSSC opens up an interesting research field with a high potential. Polymeric materials are less expensive, lighter and consume less energy for their large scale production, making these cells more environmental friendly.

References

1. Goetzberger et al. / Solar Energy Materials & Solar Cells 74 1-11 Solar cells: past, present, future (2002)
2. J. Moser, Monatsh. Chem., 8 (1887)
3. Science 21, 244(4902), 297-304 (1989)
4. Pearson G.L., 18th IEEE Photovoltaic Specialists Conference, PV founders award luncheon (1985)
5. Fuller C.S., Pearson G.L., *J.Appl.Phys.*, 25, 676 (1954)
6. Green M.A., et al., *Prog. Photovoltaics Res. Appl.*, 9 (2001)
7. Wolf M., Proceedings of the 14th IEEE Photovoltaic Specialists Conference, San Diego (1980)
8. Spitzer M., Shewchun J., Vera E.S., Loferski J.J., Proceedings of the 14th IEEE Photovoltaic Specialists Conference, San Diego (1980)
9. McEvoy A.J. and Grätzel M., *Solar Energy Mater.*, 32 (1994)
10. Regan B.O., Grätzel M., *Nature* 335 (1991) 737;(b) M. Grätzel, *Nature* 414 (2001)
11. West W., *Proc. Vogel Centennial Symp. Photogr. Sci. Eng.*, 18 (1874)
12. Hagfeldt M. Grätzel, *Acc. Chem. Res.*, 33, 269-277 (2000)
13. Namba S. and Hishiki Y., *J. Phys. Chem.*, 69 (1965)
14. Gerischer H. and Tributsch H., *Ber. Bunsenges. Phys. Chem.*, 72 (1968)
15. Dare-Edwards M.P., Goodenough J.B., Hammett A., Seddon K.R. and Wright R.D., *Faraday Disc., Chem. Soc.*, 70 J.B. H. Tsubomura, M. Matsumura, Y. Noyamura, T. Amamiya, *Nature* 261 (1976)
16. Duonghong D., Serpone N. and Grätzel M., *Helv. Chim. Acta*, 67 (1984)
17. DeSilvestro J., Grätzel M., Kavan L., Moser J. and Augustynski J., *J. Am. Chem. Soc.*, 107 (1985)
18. Regan O., Grätzel M., *Nature*, 335 (1991)
19. Amadelli R., Argazzi R., Bignozzi C.A. and Scandola F., *J. Am. Chem. Soc.*, 112 (1990)