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RECENT TRENDS ON NANOSTRUCTURES BASED SOLAR ENERGY APPLICATIONS: A REVIEW

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Abstract. Nanostructure based solar energy is attracting significant attention as possible candidate for achieving drastic improvement in photovoltaic energy conversion efficiency. Although such solar energy expected to be more expensive, there is a growing need for the efficient and light-weight solar cells in aero-space and related industries. It is required to rule the energy sector when the breakeven of high performance is achieved and its cost becomes comparable with other energy sources. Various approaches have been intended to enhance the efficiency of solar cells. Applications of nanotechnology help us to solar devices more economically. Nanophotovoltaic cells are used to improve the efficiency to create effective systems for conversion cost, efficient solar energy storage systems or solar energy on a large scale. This paper reviews some of the current initiatives and critical issues on the improvement of solar cells based on nanostructures and nanodevices.

1. INTRODUCTION

The world's major energy sources are non-renewable and are faced with ever increasing demand, thus are not expected to last long. Besides being non-renewable, these sources includes mainly of fossil fuels, contribute tremendously to the perennial problem of global warming. The eminent depletion and pollution problems of the above energy sources make the international community focus attention on alternative sources of energy, especially solar energy appears highly promising. Solar energy is emitted from the sun primarily as electromagnetic radiation in the ultraviolet to infrared and radio spectral regions (0.2 to 3 μm). The sun has a reasonable constant life time with a projected constant radiative energy output of over 10 billions (1010) years [1]. A solar cell performs two major functions: photogeneration of charge carriers in a light absorbing material and separation of the charge carriers to a conductive contact that will transmit the electricity. Solar cells are electronic devices used for the direct conversion of solar energy to electricity, using the photovoltaic (PV) effect. Fundamental properties of nanostructured materials are currently extensively studied because of their potential application in numerous fields which includes electronic devices, opto electronics, optics, tribology, biotechnology, human medicine and others [2,3]. Nanostructured materials contain structures with dimensions in the nanometer length scale which includes polycrystalline materials with nanometer sized crystallites, materials with surface protrusions spatially separated by few nanometers granular or porous materials with grain sizes in the nanometer range or nanometer sized metallic clusters embedded in a dielectric matrix. The motivation for using nanostructured materials emerges from their specific physical and chemical properties. Enhancing the regular crystalline structure using nanocrystalline materials can increase the absorbance of all incident solar spectra in the form of thin films or multilayered solar cells. This increase

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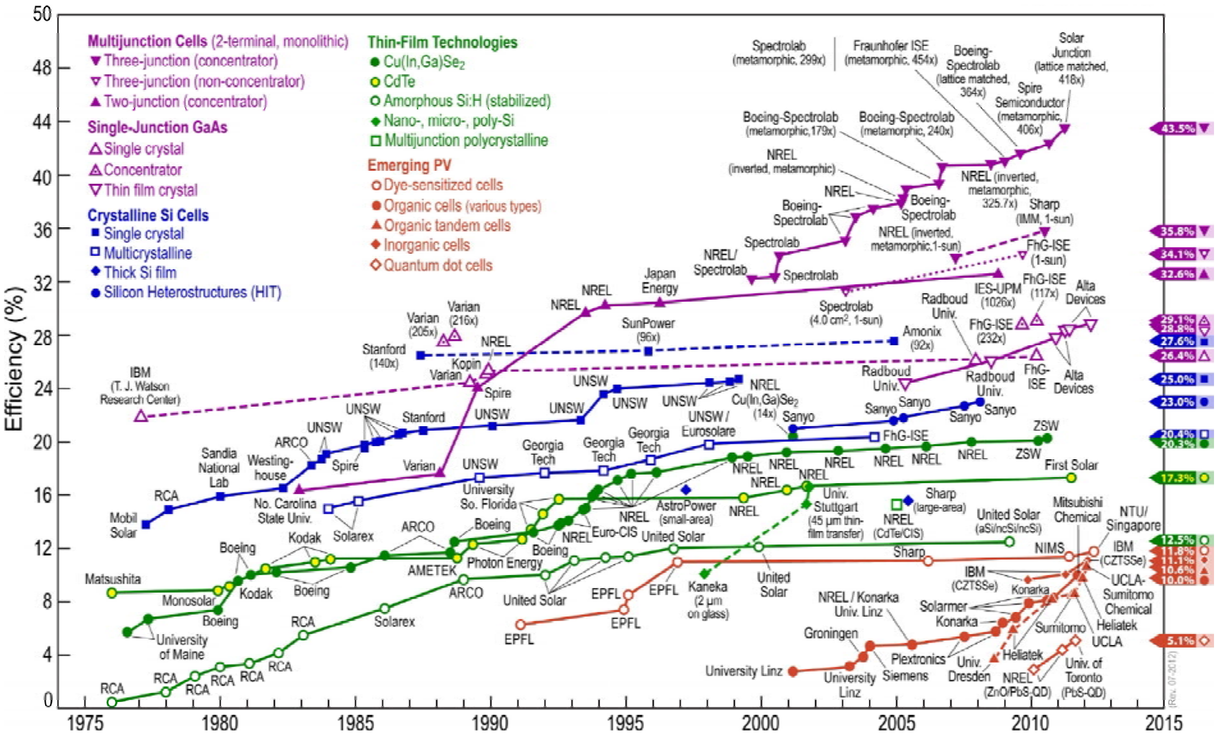

Fig. 1. Timeline of solar cell energy conversion efficiencies.

requires an electrolyte to transfer the charge from the photo-acceptor to the electrodes in dye-based and polymer solar cells, whereas in nanoparticle-based cells, the particles should be sufficiently close to one another to transfer the charge directly. Recently, significant progress has been made in improving the overall efficiencies of solar cell structures, including the incorporation of quantum dots (QDs) and nanocrystalline materials. A reported timeline of solar cell conversion efficiencies from 1975 to 2015 is shown in Fig. 1 [4]. The present investigation, deals with some potential applications towards the motivation for using nanostructured materials in solar energy conversion and to give an overview on current research topics in this field.

2. MOTIVATIONS FOR SOLAR ENERGY

Solar energy production is rapidly becoming a vital source of renewable energy being developed as an alternative to traditional fossil fuel-based sources of power. One of the primary challenges to the full-scale implementation of solar energy remains expensive associated with the construction of photovoltaic modules and also certain toxic elements presents in some of the thin film solar cells. For many decades, solar energy has been considered as a huge source of energy and also an economical source of energy because it is freely available. However, recently after years of research that technology has made it possible to harness solar energy. Some of the modern solar energy systems consist of magnifying glasses along with pipes filled with fluid. These systems consist of frontal glass that focuses the sun's light onto the pipes. The fluid present in the pipes heats up instantly. In addition, the pipes are painted black outside so as to absorb maximum amount of heat. The pipes have reflective silver surface on the backside that reflects the sunlight back, thus heating the pipes further and also helps in protecting everything present on the back of the solar panel. The heat thus produced can be used for heating up water in a tank, thus saving the large amount of gas or electricity required to heat the water.

2.1. Importance of solar energy

Solar energy is already being successfully used in residential and industrial settings for cooking, heating, cooling, lighting, space technology and for communications among other uses. In fact, fossil fuels are also one form of solar energy stored in organic matter. With the fossil fuels making major impact on the environment and raising issues of pollution and global warming, solar energy has increased in its importance to industries and homes. While the reserves of fossil fuels are restricted, there is no limitation to the availability of solar energy.

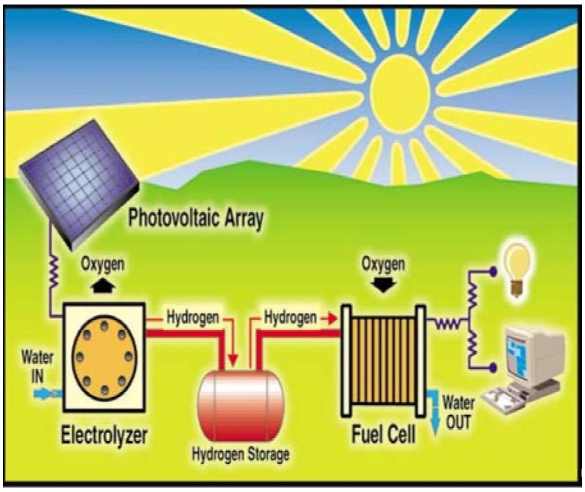

Fig. 2. Fossil fuels applications of solar energy.

With the improvement in solar energy technology and the increase in prices of fossil fuel, solar energy is gradually becoming more and more affordable. Hence, there is an additional cost in the form of importation and transportation required for oil, coal and gas. Fig. 2. depicts the application of the fossil fuels as a form of solar energy.

On the surface of the earth's orbit, normal to the sun, solar radiation hits at the rate of 1,366 watt per meter square. This is known as solar constant. While 19% of this energy gets absorbed in the atmosphere, 35% are reflected from the clouds. In the last few years, the costs of manufacturing the PV cells have gone down by a more than 5% in a year and thereby the percentages of government subsidies have gone up. This implies that every year, it is becoming more and more affordable to use Solar Energy. In 2004, the global solar cell production increased by 60%. The amount of energy released from a single kilo watt of solar energy unit is equivalent to burn as much as 76 kg of coal that releases over 135 kg of carbon dioxide. In recent years, the number of photovoltaic installations on homes connected to utility grid has been growing significantly. The demand is also extending due to the interest of households to get electricity from renewable, non-polluting and clean source. However, most of the users are interested in solar energy but they can pay only a limited premium for it. The returns on the initial high costs of installation are in the form of selling solar energy to the grid at premium rates and also in the form of long-term savings that can be maintained without paying any utility bills. The solar system that is connected to the utility grid supplies the regular generation of electricity to be used at home and the excess electricity is exported to the utility. Vacation homes or holiday homes that do not have an access to the grid can utilize the solar energy in a more cost-effective manner as compared to rely upon the grid for running wires to reach the remote location. The basic components required in the solar power system are solar panel, battery for storing all the energy gathered during daytime, a regulator and essential switches with wiring. These types of systems are commonly known as Solar Home Systems (SHS).

2.2. Solar energy and its economy

Solar energy is available free of cost and rather found in many parts around the world. This kind of energy source can be utilized in different ways: PV technology which directly converts light into electrical current, solar thermal systems used in solar collectors, artificial photo synthesis which produces either carbohydrates or hydrogen via water splitting, the so-called 'passive solar' technologies where the building design maximizes solar lighting and heating, and even biomass technology where

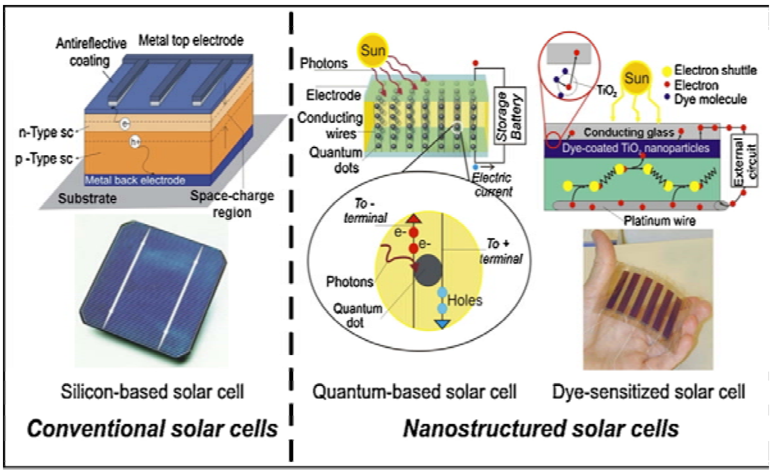

Fig. 3. Evolution of photovoltaic technology from conventional to nanostructured solar cells.

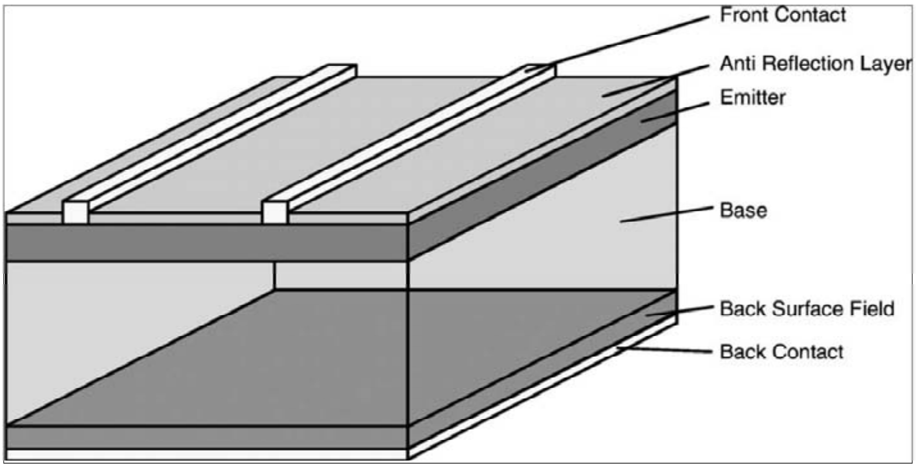

Fig. 4. Typical solar cell structure a cross-section.

plants use the solar radiation to drive chemical transformations and create complex carbohydrates which are used to produce electricity, steam or biofuels. All these energy-related processes and their applications are enclosed in the so-called solar economy (Fig. 3).

Biomass technologies are mostly based on the production of biofuels from agricultural and forest feed stocks specifically grown crops or organic wastes. These biofuels can be further used in fuel cells to obtain electricity. In comparison with solar PV, biomass shares a low energy density and relatively low conversion efficiency, but in contrast biomass has the advantage of being able to store solar energy for use on demand. Current research is much focused on the development of new photoactive materials that can be used to directly convert sunlight (or artificial light) into electricity. Also, solar thermal systems find interesting applications in self-cleaning devices like using the heat from solar radiation and storing it in a thermal store that is ready for use in heating and hot water applications. The evolution of nanostructured solar cells is given in Fig. 3.

2.3. Technologies based on solar energy

Technologies and resources of solar energy refer to sources of energy that can be directly attributed to the light of the sun or the heat generated from the sun [5]. In contrast, active solar energy technology refers to the harnessing of solar energy to store it or convert it for other applications and can be broadly classified into two groups: (i) Photovoltaic and (ii) solar thermal. The PV technology converts radiant energy contained in light quanta into electrical energy when light falls upon a semiconductor material by causing electron excitation and strongly enhancing conductivity. Two types of PV technology are currently available in the market: (a) crystalline silicon-based PV cells and (b) thin film technologies made from a range of different semiconducting materials, including amorphous silicon, cadmium-telluride and copper indium gallium diseline. Solar thermal technology uses solar heat, which can be used directly for either thermal or heating application or electricity generation. Accordingly, it can be divided into two categories: (i) solar thermal non-electric and (ii) solar thermal electric. The former includes applications such as agricultural drying, solar water heaters, solar air heaters, solar cooling systems and solar cookers [6] and the latter refers to the use of solar heat to produce steam for electricity generation, also known as concentrated solar power (CSP).

2.4. Photovoltaic systems

PV systems use solar panels to convert sunlight into electricity. A PV system is made up of one or more solar panels, usually a controller or power converter, and the interconnections and mounting for the other components. A small PV system may provide energy to a single consumer, or to an isolated device like a lamp or a weather instrument. Large grid-connected PV systems can provide the energy required for many customers. Due to the low voltage of an individual solar cell (typically ca. 0.5 V), several cells are wired in series in the manufacturing of a “laminate”. The laminate is assembled into a protective weather proof enclosure, thus making a photovoltaic module or solar panel. The electricity generated thereby can be either stored or

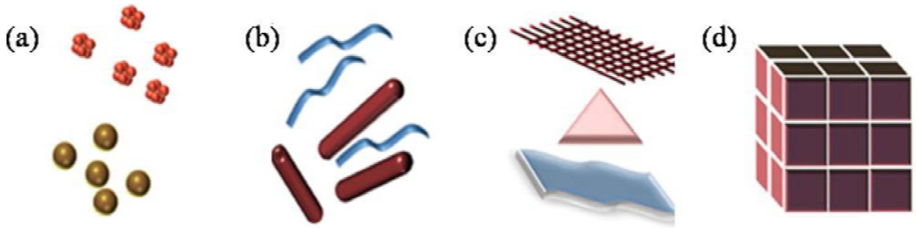

Fig. 5. Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers,wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

used directly (island/standalone plant), or fed into a large electricity grid powered by central generation plants (grid-connected/grid-tied plant) or combined with one or many domestic electricity generators to feed into a small grid (hybrid plant). Practically all PV devices incorporate a p-n-junction in a semiconductor across which the photovoltage is developed. These devices are also known as “solar cells”. A cross-section of a typical solar cell is shown in Fig. 4. The semiconductor material must be able to absorb a large part of the solar spectrum. Dependent on the absorption properties of the material the light is absorbed in a region more or less close to the surface. When a light quantum is absorbed, electron hole pairs are generated and if their recombination is prevented they can reach the junction where they are separated by an electric field. Even for weakly absorbing semiconductors like silicon most carriers are generated near the surface. The thin emitter layer above the junction has a relatively high resistance, which requires a well-designed contact grid as shown in the Fig. 4.

3. NANOSTRUCTURES AND DIFFERENT SYNTHESIS TECHNIQUES

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nm. A nanometer is one millionth of a millimetre that is approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials have extremely small size with at least one dimension of the order of 100 nm or less. Nanostructured materials can be nanoscale in zero dimension (e.g. Quantum dots), one dimension (eg. surface films), two dimensions (eg. strands or fibres), or three dimensions (eg. particles). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. Nanomaterials have the structural features in between those of atoms and the bulk materials. While most of microstructured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulk materials. This is mainly due to the nanometer size of the materials, which render them: (i) large fraction of surface atoms (ii) high surface energy (iii) spatial confinement and (iv) reduced imperfections cannot be seen exist in the corresponding bulk materials.

3.1. Classification of nanomaterials

Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, which makes a large number of surface or interfacial atoms, resulting in more “surface” dependent material properties. Nanomaterials can be classified depending on the dimensions such as (a) 0D spheres and clusters, (b) 1D nanofibers, nanowires, and nanorods, (c) 2D films, plates, and networks, (d) 3D nanomaterials as shown in Fig. 5. Especially, when the sizes of nanomaterials are comparable to length, the entire material will be affected by the surface properties of nanomaterials. This in turn, may enhance or modify the properties of the bulk materials. For example, metallic nanoparticles can be used as very active catalysts. Chemical sensors from nanoparticles and nanowires enhance the sensitivity and sensor selectivity. The nanometer feature sizes of nanomaterials also have spatial confinement effect on the materials, which bring the quantum effects. The energy band structure and charge carrier density in the materials can be modified quite differently from their bulk and in turn will modify the electronic and optical properties of the materials. Reduced imperfections are also an important factor in the determination of the properties of the nanomaterials. For example, the chemical stability for certain nanomaterials may be enhanced and the mechanical properties of nanomaterials will be better than the bulk materials. Nanomaterials

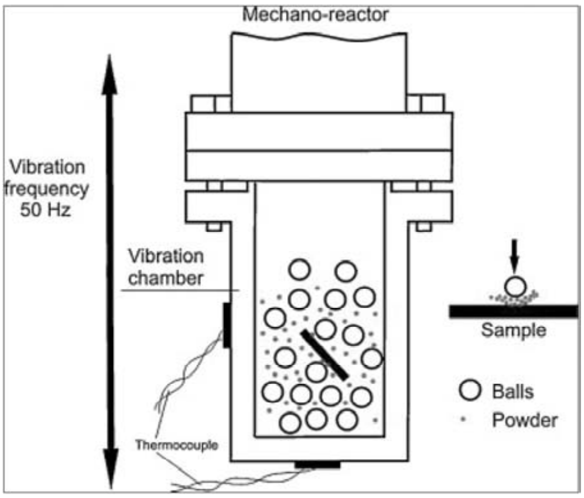

Fig. 6. Schematic representation of the principle of mechanical milling.

have applications in the field of nanotechnology and displays different physical chemical characteristics from normal chemicals (i.e., silver nano, carbon nanotube, fullerene, photocatalyst, carbon nano, silica).

3.2. Synthesis and processing of nanomaterials

Nanomaterials can be synthesized in deal both the 'bottom up' and the 'top down' approaches i.e. either to assemble atoms together or to disassemble (break, or dissociate) bulk solids into finer pieces until they are simplified to few atoms.

Mechanical attrition, a typical example of 'top down' method of synthesis of nanomaterials in which the material is prepared not by cluster assembly but by the structural decomposition of coarser-grained structures as the result of severe plastic deformation. This has become a popular method to make nanocrystalline materials because of its simplicity, the relatively inexpensive equipment needed and the applicability to essentially synthesize all classes of materials.

Mechanical milling is typically achieved using high-energy shaker, planetary ball, or tumbler mills as shown in Fig. 6. Nanoparticles are produced here by the shear action during grinding. Milling in cryogenic liquids can greatly increase the brittleness of the powders influencing the fracture process. This method of synthesis is suitable for producing amorphous or nanocrystalline alloy particles, elemental or compound powders. In principle, we can classify the wet chemical synthesis of nanomaterials into two broad groups: (i) The top down method in which single crystals are etched in an aqueous solution for producing nanomaterials, For example, the synthesis of porous silicon by electrochemical etching can be done. (ii)The bottom up method that consists of sol-gel method, precipitation, etc., where materials containing the desired precursors are mixed in a controlled fashion to form a colloidal solution.

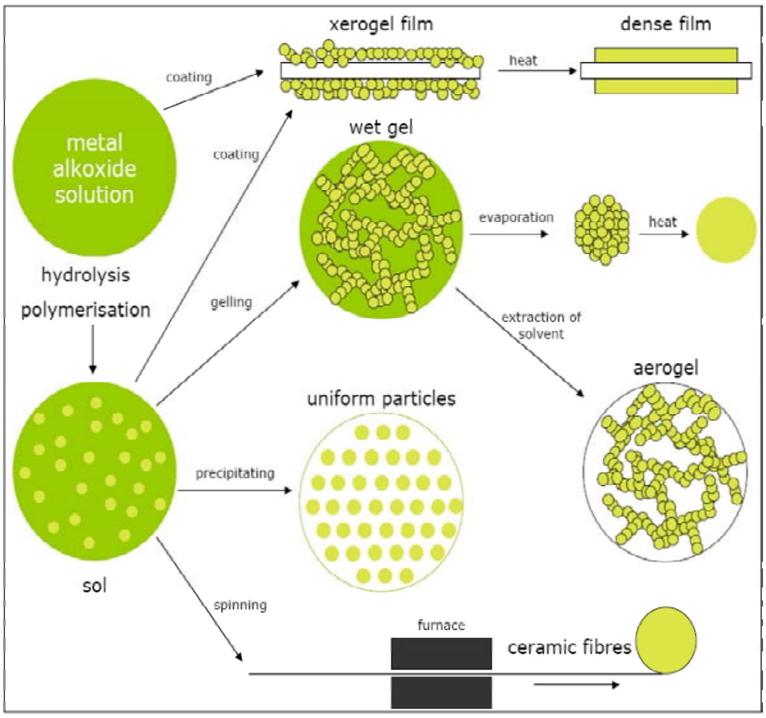

Fig. 7. Schematic representation of sol-gel process of synthesis of nanomaterials.

The sol-gel process involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. The removal of the liquid from the sol yields the gel and then the sol/gel transition controls the particle size and shape. Sol-gel method of synthesizing nanomaterials is very popular among the chemists and is widely employed to prepare oxide materials. The sol-gel process can be characterized by a series of distinct steps as depicted in Fig. 7.

4. NANOMATERIALS FOR SOLAR CELLS APPLICATIONS

The surface chemistry and dopant chemistry of the transition metal compounds are determined by coordination chemistry which renders the required scientific approach that is different from that of classical materials such as Si, gallium arsenide (GaAs) and cadmium telluride (CdTe). For any photosensitive material to be developed in the future, the quality control capable of achieving homogeneous photo activity is expected to be a key factor. The materials are classified as thin films, such as inorganic layers, organic dyes, and organic polymers that are deposited on supporting substrates. The third group that uses QDs embedded in a supporting matrix by a ''bottom-up'' approach is configured as nanocrystals. Si is the only material that is well researched in both bulk and thin film forms. There are many new alternatives to Si photocells, such as copper indium gallium selenide (CIGS), CdTe, dye-sensitized solar cells (DSSCs) and organic solar cells [7,8]. Most of them are directed at printing onto low-cost flexible polymer films and ultimately on common packaging materials. Among these new materials, semiconducting polymers are gaining much attention because of their large parameter space and inherent simplicity of device fabrication, and thus warrant further investigations [9]. Given that, the solar cells are intended for use under prolonged exposure to sunlight and another major challenge is their degradation with time. For instance, thin film materials especially chalcogenides used in solar cells must be protected carefully against oxidation.

Nanomaterials and nanostructures hold promising potency to enhance the performance of solar cells by improving both light trapping and photocarrier collection. Meanwhile, these new materials and structures can be fabricated in a low-cost fashion, enabling cost-effective production of photovoltaics. As the family of nanomaterials has great diversity number of representative materials and structures, nanowires, nanopillars, nanocones, nanodomes, nanoparticles, etc. As a photoelectric device in nature, performance of a PV device largely relies on both photon absorption and photocarrier collection. Therefore, in design of a PV device with decent energy conversion efficiency, both factors have to be optimized. Nevertheless, there requirements in optimizing optical absorption and carrier collection can be in conflict. For example, in a planar structured solar cell thicker materials are needed in order to achieve sufficient optical absorption; however, it will lower carrier collection probability due to the increased minority carrier diffusion path length, and vice versa. In fact, recent studies have shown that 3-D nanostructures not only improve light absorption utilizing the light trapping effect but also facilitate the photocarrier collection via orthogonalizing the directions of light propagation and carrier collection.

4.1. CdTe, CdSe and CdS thin film PV devices

The nanoparticles are so small, a large percentage of their atoms reside on their surfaces rather than in their interiors and this means that the surface interactions dominate nanoparticle behavior. And, for this reason, they often have different characteristics and properties than larger chunks of the same material. Nanostructured 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 nanostructured 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 made to the desired design value by varying the size of nano particles. This allows for more design flexibility in the absorber of solar cells.

Thin film is a more cost-effective solution and uses a cheap support onto which the active 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 of such

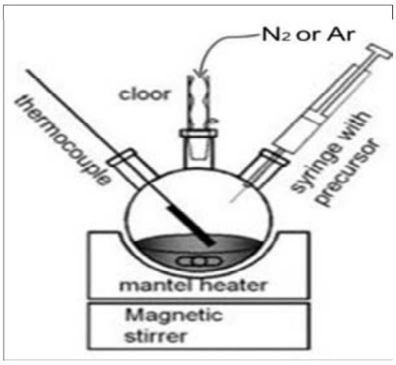

Fig. 8. Air-free hot-injection technique

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. Electrodeposition and chemical bath deposition of semiconducting materials in aqueous medium is an easy way of preparing cheap and large areas of polycrystalline semiconductors for various applications in particular for the conversion of solar energy in PV and Photoelectro chemical cells (PEC) [10-12]. Thin films of Polycrystalline CdTe, CdSe and Cds have been reported as the most promising photovoltaic materials for thin film solar cells [13,14].

4.2. Nanoparticles/quantum dot solar cells and PV devices

As another major class of nanomaterials, QDs have also been extensively studied for PV applications. The motivations of the related research is based on (i) small nanoparticles, or quantum dots(QD) with unique physical properties such as size dependent band-gap [15–17], multiple-exciton-generation (MEG) [18], which enables new PV mechanism to potentially break current thermodynamic limit and (ii) most of the QD synthesis are compatible with solution-based processes, therefore, PV fabrication based on these nanoparticles can potentially utilize high through-put, low temperature and low cost processes, such as ink-jetprinting [19]. In this section, progress on both of these two interesting aspects will be reviewed. The most common approach to synthesize colloidal QDs is the controlled nucleation and growth of particles in a solution of chemical precursors containing inorganic salts or organometallic compounds. In the so-called hot-injection technique, the precursors are rapidly injected into a hot and vigorously stirred solvent containing organic surfactant molecules that can coordinate with the surface of the precipitated QD particles. This method is usually employed to synthesize II–VI and I–VI semiconductor colloidal QDs [20]. The organic surfactant molecules play the key role in tuning the kinetics of nucleation and growth by preventing or limiting particle growth via Ostwald ripening [21]. Following the similar growth process, a number of nanocrystals have been synthesized, including CdS [22], CdTe [23], CdSe [17], Copper–Indium–Selenide [24,25], etc. And these nanocrystals have been fabricated into PV devices [22,23]. The nanocrystals used in PV devices are rod-shaped CdSe and CdTe nanocrystals prepared by air-free hot-injection techniques as shown in Fig. 8.

4.3. Iron disulfide pyrite, $CuInS_2$, and Cu_2ZnSnS_4

Iron disulfide pyrite is an interesting material for solar energy conversion devices in photoelectro chemical and PV solar cells (PECS) [26,27] as well as for solid state solar cells [28] due to its favorable solid state properties [29-31]. Considerable progress has been made since Wohler [32] first prepared artificial pyrite by the reaction of Fe_2O_3 with liquid sulfur and NH_4Cl in an open system in the last century and succeeded in obtaining small brass yellow octahedron. Many different methods have been developed for the preparation of pyrite thin films and single-crystals, such as through iron pent carbonyl and sulfur or hydrogen sulfide in an organic solvent [33] or by metal organic chemical vapor deposition (MOCVD) [34]. Recently, 1D nanocrystalline materials such as semiconductor fibers or nanorods have become the main focus and are of much considerable interests [35] and their morphology control has been demonstrated [36,37].

At present, thin film solar cells based on the absorber material $CuInS_2$ are prepared either by co-evaporation [38] or by a sequential process consisting of the deposition of metal precursors (copper-rich) followed by annealing in a sulfur atmosphere [39,40]. For a future mass production of such cells, a direct deposition by magnetron sputtering would be advantageous since this technique can be easily scaled up to large areas. Furthermore, magnetron sputtering is currently used for the deposition of the molybdenum back contact and of the ZnO/ZnO: Al window and contact layer offers the opportunity to develop a continuous vacuum process for the cell preparation. In the last decade, only few papers in the literature dealt with the deposition of ternary compound semiconductors by magnetron sputtering [41,42]. However, in the 1980s a big effort was undertaken at the University of Illinois (Urbana) by Thornton et al. to prepare $CuInSe_2$-thin film solar cells by reactive magnetron [43-45]. Obviously, the low efficiencies achieved for solar cells [46] with sputtered absorbers led to the idea that sputtering is not suited for absorbers of good quality. The thin film deposition using reactive magnetron sputtering is a well established method for the deposition of oxides, nitrides and carbides, which are used as optical films, for surface protection and for hard coatings [47]. Plastic solar cells [48] provide the possibility of easy and cheap production of large area PV devices on low cost polymer substrates. Based on interconnected networks of p-type polymers with percolating electron conducting C_{60} derivatives, recently achieved more than 2.5 % solar efficiency in devices of less than 100 nm thickness of the absorber layer in which only a small portion of the solar light is absorbed [49]. Copper indium disulfide (CIS) nanocrystals are found to be one of the best solar absorbers for photovoltaic applications.

Iron disulfide (FeS_2) with a pyrite structure, has significant scientific interest and technological applications [50-52]. On the application side, FeS_2 is the major sulfur mineral in coal and has demonstrated a significant increase in photoelectrochemical activities [53]. Owing to their large potential capacities for solar cell applications, iron-based materials have been extensively studied as possible alternatives for commercially available silicon or gallium arsenide solar cells [54]. Compared with other multicomposition PV materials such as Cu_2ZnSnS_4 [55,56] binary FeS_2 nanocrystals allow solution-processed solar cells. Recent efforts on research and development of pyrite FeS_2 nanocrystals have been driven remarkable improvement in performance of low cost solar cells to meet ever-increasing energy demands [57]. However, the main drawback of this system is stemming from oxidation and due to the orthorhombic metastable marcasite structure that is detrimental to PV properties [58].

4.4. Organic solar cells and nanowire solar cells

Organic solar cells consist of either two organic layers or a homogeneous mixture of two organic materials [59,60]. One of the organic materials either an organic dye or a semiconducting polymer that gives the electrons and the other component is used as the electron acceptor. In these devices, indium tin oxide (ITO) coated substrates is usually used as the transparent anode. Other transparent conductive oxide (TCO) films such as aluminium doped zinc oxide (ZnO: Al) have been probed, but low device efficiencies were achieved when they are used as the anode [61,62].

The solar cell research and nanowire research have become hot topics within the science and engineering technology [63–68]. The need for higher solar cell efficiencies at lower cost has become apparent, and at the same time, synthetic control in nanoscience has been improved that makes the existence of high-performance electronic devices possible [69-72].Functioning nanowire PV have been fabricated using a wide variety of materials including silicon, germanium, zinc oxide, zinc sulfide, cadmium telluride, cadmium selenide, copper oxide, titanium oxide, gallium nitride, indium gallium nitride, gallium arsenide, indium arsenide, and many polymer/nanowire combinations [73-86]. Output efficiencies have been steadily increased so that most of the material systems achieved efficiencies higher than 1% with some close to 10% but a number of unresolved questions must be answered before such materials can be used in commercial devices.

4.5. Polycrystalline thin-film solar cells

Polycrystalline thin-film solar cells such as $CuInSe_2$ (CIS), Cu (In, Ga) Se_2 (CIGS), and CdTe compound semiconductors are important for terrestrial solar applications because of their high efficiency, long-term stable performance and potential for low-cost production. Because of the high absorption coefficient (~10^5 cm^{-1}), a thin layer of ~ 2 mm is sufficient to absorb the useful part of the spectrum. Highest record efficiencies of 19.2% for CIGS [87] and 16.5% for CdTe [88] have been achieved. Many groups across the world have developed CIGS solar cells with efficiencies in the range of 15–19%, depending on different growth procedures. Glass is the most commonly used substrate, but recently some effort has been made to develop flexible solar cells on polyimide and metal foils. Highest efficiencies of 12.8% and 17.6% have been reported for CIGS cells on polyimide [89] and metal foil [90] respectively. Similarly, CdTe solar cells having the efficiency in the range of 10–16%, depending on the deposition process, have been developed on glass substrates, while flexible cells with efficiency of 7.8% on metal, [91] and 11% on polyimide have been achieved. Currently, these polycrystalline compound semiconductors solar cells are attracting considerable interest for space applications because proton and electron irradiation tests of CIGS and CdTe solar cells have proven that their stability

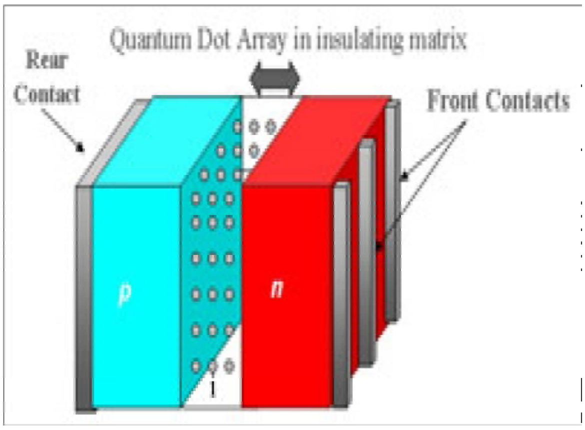

Fig. 9. Typical quantum dot cell.

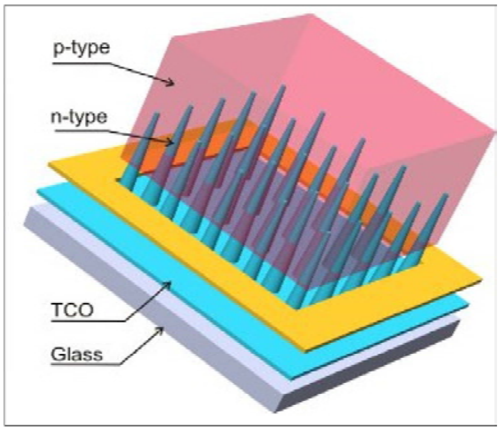

Fig. 10. Nanocones for solar cell applications.

against particle irradiation is superior to Si or III–V solar cells [92]. Moreover, lightweight and flexible solar cells can yield a high specific power (W/kg) and open numerous possibilities for a variety of applications. The super state configuration facilitates low-cost encapsulation of solar modules. This configuration is also important for the development of high-efficiency tandem solar cells effectively utilizing the complete solar spectrum for photovoltaic power conversion [93]. The emphasis is placed on various aspects of solar cell development and most of the efficiencies reported are related to small-area cells (≤1 cm^2).

5. ADVANCED NANOSTRUCTURES FOR TECHNOLOGICAL APPLICATIONS

The use of photovoltaic power has been an instrumental tool in the human exploration and development of space. In order to meet future PV space power requirements, it will be necessary to move toward innovative device design and ultimately new material systems. The device efficiencies are improved by reducing weight and maintaining structural integrity, we propose a next-generation approach to device design that involves the use of nanostructured materials in PV cells. In the near term, this approach will allow us to improve the currently available best space solar cells in terms of their efficiency and materials properties that play a significant role for space utilization. The use of nanomaterials will allow us to develop viable thin film solar arrays for space and ultimately make these arrays out of light weight, flexible, polymer-based materials [94-98]. Quantum dot cell is shown in Fig. 9.

In the solar cell community, scientists are increasingly focusing on polymer or plastic, devices. Most of the attention is focussed on hybrid approaches in which photoactive nanomaterials are introduced into polymer-based thin-film PV devices. In these hybrid solar cells, inorganic semiconducting nanomaterials get dispersed in an organic-polymer matrix. This approach provides efficient, light-weight, robust, flexible, and potentially inexpensive energy from the sun. Many of the nanomaterials that are being investigated for use in these polymeric-photovoltaic devices are capable of serving multiple roles. Non-hybrid polymer devices must rely solely on the conversion of solar photons with energies above the conducting polymer-energy bandgap (typically greater than 2 eV, which is not well suited to our solar spectrum). The nanomaterials used in the hybrid approaches generally exhibit optical absorption below the conducting-polymer bandgap and therefore allow these composite devices to absorb a much larger portion of the solar spectrum. Hybrid solar cells might also exploit some of the other results of quantum confinement that have been demonstrated in some semiconducting quantum dot systems. Finally, various semiconducting QDs produce a nanomaterial additive that can address many of the short-comings associated with the basic polymeric solar cells [99,100].

5.1. Nanocones used as inexpensive solar cells

The hybrid solar cells make use of nanoscale texturing has two advantages; it improves light absorption and reduces the amount of silicon material needed. Previous nanoscale texturing of solar cells has involved nanowires, nanodomes, and other structures. Recently, the researchers found that a nanocone structure with an aspect ratio (height/diameter of a nanocone) of approximately one provides an optimal shape for light absorption enhance-

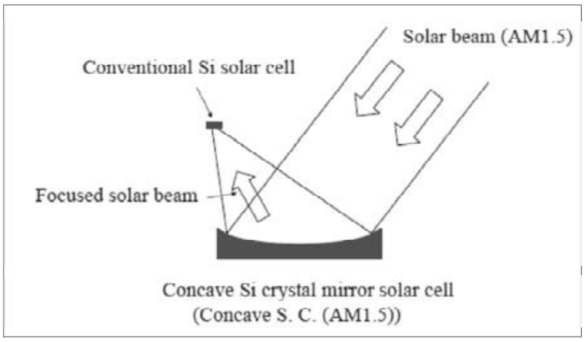

Fig. 11. Pictorial representation of Concave-mirror solar cell made of Si crystal.

ment because it enables both good anti-reflection (for short wavelengths of light) and light scattering (for long wavelengths). In nanoscale texturing, the space between structures has normally been too small to be filled with polymer so that a full second layer is required. The tapered nanocone structure demonstrated here allows the polymer to be coated in the open spaces eliminating the need for other materials. In the formation of the nanocone/polymer hybrid structure shown in Fig. 10 with a simple and low-temperature method, processing costs can also be reduced. After testing the solar cell and making some improvements, the researchers produced a device with an efficiency of 11.1%, which is the highest among hybrid silicon/organic solar cells to date. In addition, the short-circuit current density which indicates the largest current that the solar cell can generate is slightly lower than the world record for a monocrystalline silicon solar cell and very close to the theoretical limit. Due to the good performance and inexpensive processing of hybrid silicon nanocone-polymer solar cells, the researchers predict that they could be used as economically viable PV devices in the near future.

5.2. Core/shell nanoparticles towards PV applications

The size dependent properties of semiconducting and magnetic nanocrystals are demanding in the field of information technology and microelectronics. The instability of the smaller sized nanoparticles because of the high surface tension leads to Ostwald ripening in which smaller particles larger sized particles. Hence, core-shell nanoparticles are needed for encapsulating the nanoparticles by means of an organic ligand in order to prevent the particles aggregation. The growing field is hybrid solar cells in which the core/shell nanoparticles or inorganic nanoparticles are blended in a semiconducting polymer matrix as a photovoltaic layer. Recently, researches are going on in the thin film solar cells that use $CuInS_2$ and $CuInSe_2$ core/shell system due to their bandgap and adsorption coefficient and were realized with conversion efficiency of 18.8% [101-103]. For the design of tandem solar cells, one can tune the bandgap in which one particular compound is altered to get various bandgap. The important criteria in forming organic/inorganic hybrid solar cells is the formation of interpenetrating heterojunction network resulting from blending the inorganic nanoparticles in acpolymer matrix [104].

5.3. Silicon PV devices

In present days, Si PV technology is of more importance and amorphous silicon alloys are demanding for large area low-cost PV. Si is a promising candidate in photovoltaics not only for space related applications but also in terrestrial technology and they offer an energy source even in remote areas. Recently, Si PV industry is blooming to meet the energy requirements of people in both developed and developing countries [105]. The higher conversion efficiency poses a major problem in Si PV and can be controlled by lowering the impurities, stress and defects in the Si crystals. The indirect band gap semiconductor such as silicon in the form of thick layers are applied in solar cells and inversely in the case of thin film solar cells, strongly absorbing direct band gap semiconductors can be used. The minority carrier diffusion length plays a major role in the transport properties of a semiconductor. Nowadays, Hybrid solar cells, a thin film solar cell arranged on a low-cost μc-Si solar cell seems to be a good material for the fabrication of high efficiency and low-cost solar cells [106].Si single crystals or multi crystals are commonly used in solar cells [107]. Nakajima et al. proposed concave-Si-crystal mirror obtained from Si single crystal wafer polished mechanically and explained that there is an increase in total conversion efficiency [108]. The conventional solar cells together with the focussed solar cell system through the lens constitute the focused mirror solar cell system which is able to attain high efficiency by efficiently making use of the photons reflected from the cell and is shown in Fig. 11[109] the development of the first Si p/n solar cells at Bell Labs, USA occurred in 1954 with 6% efficiency [110]. In 1958, the Soviet satellite Sputnik 3 and the US Vanguard successfully initiated the first solar cells application where n-type Si with p type boron as dopant having efficiency of 8% was used. Due to the increasing use of Si solar cells, extensive research has been carried out to achieve lighter modules and enhanced radiation resistant devices by improving their reliability and efficiency [111]. The world's first PV human installation was done in Papago Indian Reservation in Arizona to distribute electricity for 15 houses using 3.5 KWp systems [112].

5.4 III-V semiconductors

GaAs and InGaP are realized for high efficiency solar cells due to their high reliability and direct band gap and hence used as power sources for space satellites having an overall efficiency of 30%. III-V semiconductors based on GaAs grown on GaAs substrates finds application in photovoltaics because of their improved efficiency rate with respect to Si and enhanced physical properties [105]. In recent days, Silicon is almost replaced by solar devices based on III-V semiconductors due to their less weight, enhanced radiation resistance and better efficiency to be used in flat PV modules for space applications. GaAs employed in high efficiency solar cells is a III-V compound having the direct bandgap of 1.42 eV with high electron mobility and high electron saturation velocity operating at frequencies above 250 GHz. As compared to Si devices, high frequency GaAs make less noise perhaps work at high power due to high breakdown voltage than the equivalent Si device and its electronic properties are comparatively superior to Si [112].

Compared to single-junction solar cells, multi-junction solar cells are more adequate due to the fact that there exists tuning of each junction to the wavelength of the light collected. The complex heterostructures with phosphides and arsenides multi-junction solar cells on germanium substrates have been realized for satellite power sources with improved efficiency of 20%. With the help of InGaP/GaAs/Ge triple junction device, efficiency rate of 30% was attained by the year 2000. GaInP/GaAs/Ge with high-efficiency currently finds application in terrestrial concentrators and also in space applications [113]. The three- and four-junction solar cells designed from appropriate bandgap materials with higher efficiencies are needed. In order to reduce the strain-induced defects that causes degradation in the performance of solar cells, III-V semiconductors having bandgap comparably lower than that of GaAs are preferred that could be lattice matched with GaAs. Materials such as GaNAs with anomalous large bandgap bowing [114] and GaInNAs [115-119] having preferable lattice matching to GaAs were used for high efficiency solar cell applications

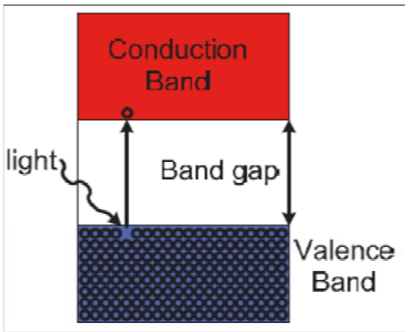

Fig. 12. Light conversion process in a solar cell.

and were found to exhibit short minority carrier diffusion lengths [120, 121]. As the solar cells need long diffusion lengths in the effective collection of the photogenerated carriers, short diffusion length of III-N-V semiconductors have to be taken into account for further improvement.

6. THEORY AND FUTURE TRENDS IN SOLAR CELLS

Electromagnetic radiation (primarily in the visible and near-infrared regions of the spectrum) is emitted from the sun and absorbed by the solar cell. A photon will then excite a negatively charged electron from the valence band (low energy state) to the conduction band (a higher energy state) leaving behind a positively charged vacancy, called a hole. For this energy transfer to create any usable energy, the photon must have energy greater than the bandgap of the material, or else the electron will immediately relax down and recombine with the hole and the energy will be lost as heat. Upon excitation above the bandgap the photon creates an electron and a hole which are now free to move throughout the semiconductor crystal. These acts as charge carriers which transport the energy to the electrical contacts, which results in a measurable external current and these processes are shown in Fig. 12.

The materials and structure of the solar cell are very important in light conversion process. A solar cell is made out of semiconductor material which facilitates the creation and motion of charge carriers. Current solar cells cannot convert all the incoming light into usable energy because some of the light can escape back out of the cell into the air. Additionally, sunlight comes in a variety of colors and the cell might be more efficient at converting bluish light while being less efficient at converting reddish light. Higher energy light does excite electrons to the conduction band, but any energy beyond the band gap energy is lost as heat. If these

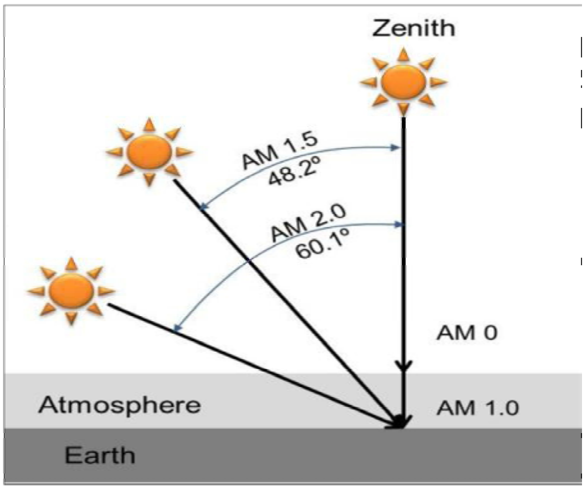

Fig. 13. The path length in units of Air Mass.

excited electrons are not captured and redirected, they will spontaneously recombine with the created holes, and the energy will be lost as heat or light. In conventional solar cells, ultraviolet light is either filtered out or absorbed by the silicon and converted into potentially damaging heat, not electricity. Ultraviolet light could efficiently couple to particular sized nanoparticles and produce electricity. Integrating a high-quality film of silicon nanoparticles 1 nanometer in size directly onto silicon solar cells improves power performance by 60 percent in the ultraviolet range of the spectrum.

6.1. Theoretical formulation of solar cell

Once the photons enter the atmosphere, the continuous solar spectrum will become into spectral bands due to absorption and scattering of water, carbon dioxide and other substances. In the spectrum of solar radiation, 99% of energy concentrates between 276 nm and 4960 nm (Fig. 13).

When the vertical irradiation of sunlight outside the atmosphere, AM is 0; when the angle between incident sunlight and the ground is 90º, AM is 1, as shown in Fig. 13. The zenith angle θ is the angle between the connection line of any point of sea level with the sun and sea level. The relationship between θ and AM is expressed as follows:

$$AM = 1/\sin\theta. \tag{1}$$

The performances of solar devices are estimated under simulated solar illumination of AM 1.5 with an intensity of 1000 kW/m^2. The generated photocurrent in a solar cell under illumination at short circuit is dependent on the incident light wavelength and intensity. The short circuit current can be expressed by Eq. (1)

$$J_{sc} = q\int b_s(E)QE(E)\,\mathrm{d}E, \tag{2}$$

where *QE(E)* is the quantum efficiency, the probability that an incident photon of energy E will deliver one electron to external circuit and $b_s(E)$ is the incident spectral photon flux density. The number of photons of energy in the range E to $E+dE$ which are incident on unit area in unit time and q is the electronic charge. Quantum efficient is dependent on the absorption coefficient of the material, the efficiency of charge separation and collection. As we know that, for an ideal diode the dark current density J_{dark} *(V)* is defined as

$$J_{dark}(V) = J_0\left(e^{qv/k_BT} - 1\right), \tag{3}$$

where J_0 is a constant, k_B is Boltzmann's constant and T is the absolute temperature. The overall current of a solar cell under illumination can be approximated as the sum of short circuit current and dark current, which can be expressed as Eq. (3)

$$J_V = J_{SC} - J_{dark}(V). \tag{4}$$

When the cell is isolated, the potential difference will reach its maximum, the open circuit voltage, under a certain level of illumination. This is corresponding to the equivalent condition that the short circuit current is exactly equal to the dark current

$$V_{0c} = \frac{k_BT}{q}\ln\left(\frac{J_{SC}}{J_0} + 1\right). \tag{5}$$

The solar cell delivers power in the bias range from 0 to V_{oc}. The output power of a cell reaches its maximum at the optimum operating point. This occurs at some voltage V_m with a corresponding cur-

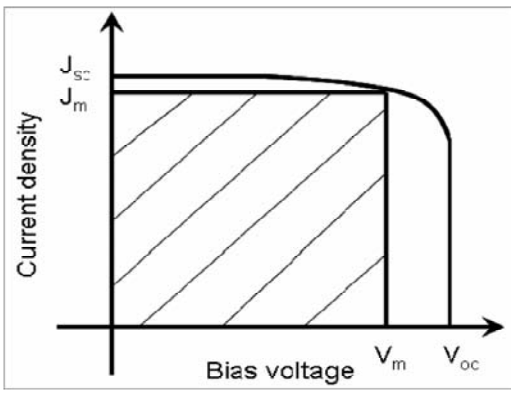

Fig. 14. Current-voltage characteristics of an ideal solar cell.

rent J_m as shown in Fig. 14. The fill factor is defined as the ratio of maximum power to the product of open circuit voltage and short circuit current

$$FF = \frac{J_m V_m}{J_m V_{OC}}. \tag{6}$$

The cell efficiency is the power density delivered at operating point as a fraction of the total incident light power density, *Ps*.

$$\eta = \frac{FF.J_{SC}.V_{OC}}{P_s}. \tag{7}$$

All the above mentioned four quantities, *Voc, Jsc, FF,* η, are essential parameters for solar cell characterization [122].

6.2. The third generation solar cells

Semiconductor nanocrystals are regarded as useful materials for building hybrid organic–inorganic so-called third-generation solar cells. This utility is due to the fact that their optical band can be tuned by both material selection and quantum confinement and because advances in synthesis allow control over nanocrystal size and shape to optimize performance. Solar cells may be formed using a p-n junction, a Schottky barrier, or a metal insulator semiconductor structure based on various semiconductor materials, such as crystalline silicon, amorphous silicon, germanium, III-V compounds, quantum wells and quantum dots structure. III-V compound semiconductor such as gallium arsenide and indium phosphide have near optimum direct energy band gaps, high optical absorption coefficients and good values of minority carrier lifetimes and mobilities making them better materials than silicon for making high efficiency solar cells. Despite the low optical absorption coefficient resulting from the indirect bandgap of silicon, the mature of crystal growth and fabrication process of silicon semiconductors ensures well control on minimizing defect density, thus minority carriers generated by photons can diffuse into depletion region without excessive losses due to non-radiative recombination. Solar cells can also be made of III-V compound semiconductors, e.g., gallium arsenide (GaAs) and indium phosphide (InP). The materials have high optical absorption coefficient due to their direct bandgaps and near optimal bandgap ~1.4 eV for solar energy conversion. The third generation solar cells, novel solar concepts are proposed to further increase the power conversion efficiency using the low-dimensional structures including hot carriers cell, tandem cell, multiple quantum wells (MQW) cell and intermediate band solar cell. III-V quantum dot superlattice based solar cells are proposed because of their promising potentials in high power conversion efficiency application. The intermediate band solar cell (IBSC) pursues the enhancement of efficiency through the absorption of below bandgap energy photons and production of additional corresponding photocurrent without degrading its output voltage.

7.CONCLUSION

The growing interest in applying nanoscale materials for solving the problems in solar energy conversion technology can be enhanced by the introduction of new materials such as quantum dots, multilayer of ultrathin nanocrystalline materials and the availability of sufficient quantities of raw materials. The inexpensive purification or synthesis of nanomaterials, deposition methods for the fabrication of thin film structures and easy process control in order to achieve a large-area production within acceptable performance tolerances and high life time expectancy are still the main challenges for the realization (fabrication) of solar cells. Therefore in attaining the main objectives of photovoltaics, the efficiency of solar cells should be improved without any compromise on the processing cost of these devices. Nanotechnology incorporation into the films shows special promise in enhancing the efficiency of solar energy conservation and also reducing the manufacturing cost. Its efficiency can be improved by increasing the absorption efficiency of the light as well as the overall radiation-to-electricity. This would help to preserve the environment, decrease soldiers carrying loads, provide electricity for rural areas and have a wide array of commercial applications due to its wireless capabilities. The solar energy, a boon to the mankind has to be properly channelized to meet the energy demand in the developing countries and solar cell industry can reach greater heights by the incorporation of third generation solar cell devices and panels based on nanostructures.

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