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Review Of Solar Cell Materials And Fabrication Technologies

D.D.O. Eya* and F.C. Eze
Department of Physics, Federal University of Technology, Owerri, Nigeria.

Abstract

Solar cell is a semiconductor device that converts solar energy to electrical energy by photovoltaic effect. The first solar cell was built in 1883 with conversion efficiency of 1%, however the first practical cell was produced in 1954 at Bell laboratories after it was discovered accidentally that doped silicon is very sensitive to light. The first generation solar cells were fabricated from high quality bulk, single crystal in form of wafer and single junction silicon devices achieving efficiencies of up to 16%. The second generation solar cells were developed to address energy requirements and production costs of solar cells. They involve thin film semiconductors. The first set of thin film materials employed in the fabrication include cadmium telluride (CdTe), Copper Indium Selenide (CIS), Copper Indium Gallium Selenide (CIGS), amorphous and microcrystalline silicon. The third generation of solar cells involves the use of multijunction photovoltaic cells. Concentrators, excess thermal generation and infrared spectrum to achieve higher efficiencies in excess of the Shockley-Queiser limit (i.e theoretical solar conversion efficiency limit of 31% for a single energy threshold material and 40.8% under maximal concentration of sunlight). With the present trend of research and materials, 30-60% efficiencies have been predicted. Presently, the range of efficiencies that have been achieved are in the 19.9 - 40.7% range, with the multijunction cells having the best performance.

Keywords: Solar, Cell, Conversion, Semiconductor, Energy and Technology.

1.0 Introduction

The lessons of the energy crises in the past, the rapid depletion of the existing conventional energy sources and the recognition of solar energy as the most potentially viable energy source which if properly harnessed will launch the world into an era of abundant and uninterrupted energy supply, have moved energy research to continue to search for most efficient and economic means of tapping the wasting solar insolation. Even though the sun is frequently labeled as an alternative energy source, it has in fact produced almost all of man's energy throughout history (Ehrenreich, and Martins, 1979). It has been estimated that in 40 days, we receive enough solar energy that can last for a century. Chopra and Das, (1983) in quoting Hayes (1978; 1977) states that no country uses as much energy as is contained in the sunlight that strikes just the buildings. Incidentally, the poor and less developed nations of the world especially Africa have this gift of nature more than the developed countries.

The amount of sun light reaching the ground is given by (http://en.wikipedia.org/wiki/sunlight).

$$E_{ext} = E_{sc}\left[\ 1+0.034Cos\left(\frac{d_n-3}{365}2\pi\right)\ \right]$$

where E_{ext} is extraterrestrial solar luminance, E_{sc}, the solar illuminance constant 128×10^3 Lx or $1366 Wm^{-2}$ and d_n, the day number of the year.

The estimated range of values is $1321\text{-}1413 Wm^{-2}$ (http://en.wikipedia.org/wiki/sunlight). The variation of the values being as a result of the elliptical nature of the earth.

The successful fabrication of solar cell in the early 1950s and the successful conversion of solar radiation to electric current using the semiconductor device opened a new chapter in energy research. In this paper, we review solar cell materials and its fabrication techniques

2.0 Solar Cells and Fabrication Techniques

Solar cell is a semiconductor device that converts solar energy to electrical energy by the photovoltaic

Corresponding Author's e-mail: eyadom2003@yahoo.com

effect. Solar cell was first built in 1883 by Charles Fritts with conversion efficiency of 1% using selenium coated with thin layer of gold. The first practical solar cell was produced in 1954 with conversion efficiency of 6% by Daryl Chapin, Calvin Fuller and Gerald Pearson of the Bell laboratories after they discovered accidentally that doped silicon is very sensitive to light.

Figure 1: Solar Cell

The process of the conversion involves the absorption of photon energy by the cell, generation of carriers (electrons and holes), separation of the carriers at the p-n junction and delivery of the generated current to the load. Absorption and carrier generation occur for most photons of energy greater than the band gap energy of the materials. Obviously for greater carrier generation and consequently higher photocurrent, the band gap energy should be small (Hayes, 1978; 1977). However the open circuit voltage that is available is determined by the band gap and is, for optically designed device, about half the band gap. For high efficiency solar cells, with high photocurrents and high open circuit voltage, the semiconductor band gap has to be matched with solar spectrum and it can be shown that the optimum band gap is in the range of 1.1 - 1.5 eV.

If we examine the available materials with an appropriate band gap, absorption coefficient, minority carrier life time or minority carrier diffusion length and surface recombination velocity, the choice is limited to such materials as silicon, Si (E_g=1.12eV), Gallium Arsenide, GaAs (E_g=1.42eV), Cadmium Telluride, CdTe (E_g =1.44eV) , Copper Sulphide (Cu_xS), Zinc phosphide (ZnP), Indium phosphide (InP) and Copper- Indium Selenide, CuInSe (E_g =1.05eV) in their thin film forms (http://en.wikipedia.org/wiki/solar_cell_).

Three key elements in a solar cell form the basis of their manufacturing technology. The first is the semiconductor which absorbs light and creates electron-hole pairs. The second is the semiconductor junction (p–n junction) which separates the photogenerated carriers and the third is the contacts on the front and back of the cell that allow the current to flow to the external circuit (http://en.wikipedia.org/wiki/solar_cell_). Because of the low level of output of a single cell (of the order 0.5V) a number of cells are connected in series to form solar or photovoltaic panel or module in order to obtain reasonable output. Manufacturers usually include a laser scribing sequence that enables the front and back of the adjacent cells to be directly interconnected in series. They are laminated to produce a weather resistant and environmentally robust module.

Although thin film solar cells are less efficient, they are potentially cheaper than crystalline silicon(c-Si) cell because of their lower material cost, energy cost and large substrate size.

Several large photovoltaic power plants with different capacities have been completed in various countries. For instance, Parque Fotovoltacco Olmedilla de Alarcon of capacity 60MW (Spain), Parque fotovoltaico Moura Alentejo, 46MW (Portugal), SinAn photovoltaic power plant, 19.6MW (South Korea), Nellis solar power plant, 14MW (U.S.A), etc (http://en.wikipedia.org/wiki/photovoltaics).

In 1970, the first highly effective GaAs hetero-structure solar cells were created by Zhores Alferov and his team in the USSR. GaAs solar cells with conversion efficiencies up to 17% were produced in quantities in the USA in 1988. Dual junction cell was accidentally produced in quantity in 1989 as a result of change from GaAs on GaAs substrate to GaAs on Ge substrate. This eventually led to the fabrication of cell with higher open-circuit voltage and higher conversion efficiency, 19% in 1993. The efficiency eventually increased to 22%. Triple junction solar cells have also been produced with conversion efficiencies of 24% in the year 2000, 26% in 2002, 28% in 2005 and 30% in 2007 (http://en.wikipedia.org/wiki/solar_cell).

Figure 2: Solar Power station.

2.1 First Generation Solar Cells

Solar cell was first produced as a single junction crystalline silicon cell having a theoretical efficiency of 33% and no prospect of reduction in production cost. Historically crystalline silicon(c-Si) has been used as the light-absorbing semiconductor in most solar cells, even though it is a relatively poor absorber of light and requires a considerable thickness (several hundred microns) of materials. Nevertheless, it has proved convenient because it yields stable solar cells with good efficiencies (11-16%, half to two thirds of the theoretical maximum) and uses process technology developed from the huge knowledge base of the microelectronics industry. For Silicon solar cell production either poly-crystalline or monocrystalline material is used. Poly-crystalline silicon for photo-voltaic applications is normally produced by casting methods while monocrystalline silicon is prepared in a Czochralski growth process (http://www.crystec.com/crysolae olae.htm). For both mono- and multicrystalline Si, a semiconductor homojunction is formed by diffusing phosphorus (an n-type dopant) into the top surface of the boron doped (p-type) Si wafer. Screen printed contacts are applied to the front and rear of the cell with the front contact pattern specially designed to allow the maximum light exposure of the Si materials with minimum electrical losses in the cell. Each c-Si cell generates about 0.5V, so 36 cells are usually soldered together in series to produce a module with an output to charge a 12V battery.

The cells are hermetically sealed under toughened high transmission glass to produce highly reliable weather resistant module that may be warrantied for up to 25 years (http://www.solarbuzz.com).

Nanocrystalline Silicon is an allotropic form of Si with polycrystalline structure. It has amorphous phase which makes it similar to a-Si. Nanocrystalline Si has small grains of crystalline Si within the amorphous phase in contrast to polycrystalline Si (poly-Si) which consists solely of crystalline Si grains separated by grain boundaries.

nc-Si has higher electron mobility than a-Si (due to the presence of Si crystallite), increased absorption in the red and infrared wave length and increased stability (lower concentration of hydrogen).

2.2 Second Generation of Solar Cells.

The high cost of crystalline Si wafers has led the solar cell industry to look for cheaper materials to make solar cells. Solar cells suffer from significant degradation in their power output when exposed to the sun. The mechanism of degradation is called the Staebler – Wronski effect. Better stability requires the use of thinner layers in order to increase the electric field strength across the material. However, this reduces light absorption and hence cell efficiency. Amorphous Si is the most well developed thin film technology to-date and has an interesting avenue of further development through the use of micro-crystalline silicon.

Cadmium telluride (CdTe), Copper Indium Selenide ($CuInSe_2$), Copper Indium Gallium selenide ($CuInGaSe_2$), Amorphous and micromorphous silicon thin films have been involved in the fabrication of solar cell with the aim of reducing cost but the efficiency achieved so far is not appreciable. CdTe has a band gap of 1.44eV (Boisio, *et al.*,2005). Thin film CdTe-based solar cells with area of 1cm^2 have been made with efficiencies over 15% and modules have been made with efficiencies over 10% in addition. CdTe solar cells with efficiencies over 11% have been made by a variety of deposition methods and several of these methods have been adapted to module manufacturing (Birkumire and Meyers, 2006). Recently energy conversion efficiency of 16.5% was reported for CdTe (Boisio, *et al.*,2005; Wu, 2001). In 2002, the highest reported efficiency for solar cells based on thin firms of CdTe is 18% by the research group of Prof. I.M. Dharmadasa at Sheffield Hallam University, UK.

Copper Indium Diselenide ($CuInSe_2$ or CIS) has a band gap of 1.05eV (Boisio, *et al.*,2005). The use of Gallium to substitute some Indium in the compound increases the optical band gap of CIGS layer as compared to pure CIS, thus, increasing the open circuit voltage, but decreasing the short circuit current. For instance, CIGS with 7% Gallium has band gap of 1.15eV. Those that have higher amount of Ga have lower efficiency.

Recently energy conversion efficiency of 19.2% was reported for $CulnGaSe_2$ (Boisio, *et al.*,2005; Romero et al./ 2003). The United States National Renewable Energy Research Laboratories, NREL achieved an efficiency of 19.9% for the solar cells based on copper Indium Gallium Selenide thin films, also known as CIGS (http://en.wikipedia.org/wiki/solar_cell).

Amorphous silicon (a-Si) thin film has a band gap of 1.7eV while crystalline and nanocrystalline silicon (nc-Si) has 1.1eV. Nanocrystalline and a-Si can advantageously be combined in thin layers, creating a layered cell called a tandem cell. The top cell in a-Si absorbs the visible light and leaves the infra –red part of the spectrum for the bottom cell in nc-Si.

2.3 Third Generation of Solar Cells

Developing multijunction photovoltaic cells and the use of concentrators are steps being evolved to achieve high efficiencies. Other steps may include the use of excess thermal generation and infrared spectrum (to produce electricity at night). In order to achieve the objectives, the following technologies should be put to use;

i. Silicon nanostructures,
ii. UP/Down converters,
iii. Hot-carrier cells, and
v. Thermoelectric cells. The highest efficiency ever reported for silicon solar cell is 24.7% by University of New South Wales (UNSW), Australia in 1994 using monocrystalline silicon and has developed silicon solar cell to achieve 25% efficiency.

Although University of Delaware, Fraunhofer Institute and NREL claim to have achieved 42.8, 41.1 and 40.8 % efficiencies, respectively using multiple junction solar cells, the records are still disputed.

GaAs based multijunction devices are the most efficient solar cells to date reaching a record high 40.7% efficiency under solar concentration and laboratory conditions. These multijunction cells consist of multiple thin films (produced using metal organic vapour phase epitaxy). A triple- junction cell may consist of the GaAs, Ge and $GaInP_2$. The semiconductors have their characteristic band gap energies and are carefully chosen to absorb nearly the entire solar spectrum, thus generating electricity from as much of the solar energy as possible. The Dutch Radbond University Nijmegen set the record for thin film solar cell efficiency using single junction GaAs to 25.8% in August, 2008 employing only 4µm thick GaAs layer which can be transferred from a wafer base to glass or plastic film.

For organic/ polymer solar cells, the highest reported efficiency is 6.5% and are beneficial for some applications where mechanical flexibility and disposability are important.

Various techniques are involved in the deposition of the materials for these solar cells. The two main growth techniques for III – V solar cells are the bulk growth methods, as Czochralski and Bridgman methods and epitaxial growth methods as liquid phase epitaxy (LPE), chemical vapour deposition (CVD) which could be atmospheric pressure chemical vapour deposition (APCVD), low pressure chemical vapour deposition (LPCVD) or more preferably Plasma Enhanced Chemical Vapour Deposition (PECVD); metal organic chemical vapour deposition (MOCVD), or molecular beam epitaxy (MBE). The precision of the growth method allows for a high mobility of carriers, ensuring they can reach the junction before any recombination process takes place (Romero, *et al.*, 2003). The components for this group are GaAs and InP which can be alloyed with other materials as Al, Sb to give rise to ternary or quaternary compounds like $Al_xGa_{1-x}As$ or $In_xGa_{1-x}As_yP_{1-y}$. Elements used as n-type dopants are S, Se, Te, Sn, Si, C, Ge and p-type dopants are Zn, Be, Mg, Cd, Si, C, Ge.

GaAs and other III – V semiconductors present high quality properties: a direct bandgap with high absorption, relatively insensitive to temperature, and radiation resistance. These properties make them suitable for three major applications; thermo-photovoltaics (TPV), concentrator systems and space applications (Roman, 2004).

The deposition technique adopted and the size of the cell affect the efficiency achievable with the material. For instance, the report of the United States of America Department of Energy on CdTe (Birkumire, 2006) shows the percentage conversion efficiencies achieved when the following deposition techniques were used to deposit CdTe.

Compound sublimation	5.8%
Closed –space sublimation	8.4%
Screen printing	8.1 – 12.8%
Molecular beam epitaxy	10.5%
Sputtering	10.4%
Electrodeposition	14.2%

Antireflection coatings, which increase the amount of light coupled into the solar cell are applied over the surface of the cell. Silicon nitride for the past decade has gradually replaced titanium dioxide as the antireflection coating of choice because of its excellent surface passivation qualities (i.e prevents carrier recombination at the surface of the solar cell). It is applied as a layer on the surface using plasma enhanced chemical vapour deposition (PECVD)

2.3.1 Dye Sensitized Solar Cell

A dye-sensitized solar cell (DSSc, DSC or DYSC) also known as Gratzel cell is a low cost thin film solar cell that is based on semiconductor formed between a photo sensitized anode and an electrolyte, a photoelectrochemical system. It was invented by Michael Gratzel and Brain O'Regan at the Ecole Polytechnic que Federale de Lausanne in 1991 (Wu, *et al.*, 2001).

This cell is extremely promising because it is made of low-cost materials and does not need elaborate apparatus to manufacture. In bulk it should be significantly less expensive than older solid-state cell designs. It can be engineered into flexible sheets and is mechanically robust requiring no protection from minor events like hail or tree strikes. Although its conversion efficiency is less than the best thin-film cells, its price performance ratio (kWh/m^2/annum/dollar) should be high enough to allow them to compete with fossil fuel electrical generation (grid parity) (http://en.wekipedia.org/kiki/Dye-sensitized-solar_cell).

In the traditional semiconductor solar cell design, silicon for instance, acts as both the source of photoelectron as well as providing the electric field to separate the charges and create a current but in dye-sensitized cell, the bulk of the semiconductor is used solely for charge transport, the photoelectrons are provided from a separate photosensitive dye while charge separation occurs at the surface between the dye, semiconductor and electrolyte.

The dye molecule is quite small (nanometer size). In order to capture a reasonable amount of incident light, the layer of dye molecules needs to be fairly thick, much thicker than the molecules themselves. As a solution, a nanomaterial is used as a scaffold to hold large number of the dye-molecules in a 3-Dimatrix, increasing the number of molecules for any given surface area of cell. In the present design, the scaffold is provided by the semiconductor material.

Construction: The original Gratzel design has three primary parts, a transparent anode made of fluorine doped tin oxide ($Sn0_2$:F) on top, a thin layer of titanium dioxide ($Ti0_2$) which forms into a highly porous structure with extremely high surface area on the back of the conductive plate and a mixture of a photosensitive ruthenium polypyridine dye (also called molecular sensitizers) and a solvent in which the plate is immersed.

After the film has been soaked in the dye solution, a thin layer of the dye is left covalently bonded to the surface of the $Ti0_2$. A separate backing is made with a thin layer of the iodide electrolyte spread over a conductive sheet, typically platinum metal. The front and back parts are then joined and sealed together to prevent the electrolyte from leaking.

Operation: Sunlight enters the cell through the transparent SnO_2:F top contact, striking the dye on the surface of the TiO_2. Photons striking the dye with enough energy to be absorbed will create an excited state of the dye, from which an electron can be injected directly into the conduction band of the TiO_2, and from there it moves by diffusion to the clear anode on top.

The dye molecule having lost an electron will decompose if another electron is not provided. The dye strips one from iodide in electrolyte below the TiO_2, oxidizing it into triiodide. The reaction occurs more rapidly than 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.

Efficiency: DSSc's are currently ranked among the most efficient third-generation solar technology available. The overall peak power production of DSSc is about 11% but in terms of quantum efficiency, (chances that one photon of a given energy will create one electron) DSSC is highly efficient. This makes them attractive as replacement in low-density applications like rooftop solar collectors where mechanical robustness and light weight of the glass-less collector is a major advantage. Also the injection process is not like the traditional cell where an excited electron could recombine with an already existing hole. It can withstand long exposure to light and heat compared with the traditional Si based solar cell. The major disadvantage of DSSC is the use of liquid electrolyte which has temperature stability problems. Problems associated with the state of the electrolyte at various temperatures like freezing; expansion, etc. are serious challenging problems.

3.0 Solar Concentrator

Solar cells usually operate more efficiently under concentrated light. The range of approaches adopted include using mirrors or lenses to focus light on to specially designed cells and use heat sinks or active cooling of the cells to dissipate the large amount of heat that is generated. Concentrator systems require direct sunlight (clear sky) and will not operate under cloudy conditions; they generally follow the sun's path through the sky during the day using single-axis tracking. However for all season tracking, two-axis tracking is sometimes used.

Figure 3: Solar Energy concentrators.

At present, concentrators are more widely used in solar thermal electricity generation technologies where the generated heat is used to power a turbine. Solar concentrators of all varieties may be used, and these are often mounted on a solar tracker in order to keep the focal point upon the cell as the sun moved across the sky. Cooling of the cell is achieved with passive heat sinks. Concentrating photovoltaic (CPV) system operates most effectively in sunny weather since clouds and overcast condition create diffuse light which essentially cannot be concentrated. The CPV system is graded as low concentration (2-10 suns), medium concentration (10-100 suns) and high concentration (200 suns and above).

4.0 Current Research Efforts

Even though the present level of efficiencies achieved for various generations of solar cells are relatively low, the situation is highly promising in view of the level of work that has been done and associated expectations. Apart from the research activities geared towards a more comprehensive development of polycrystalline and multijunction solar cells, there are a number of other research activities going on at various parts of the world aimed at fabricating highly efficient solar cell.

Starsolar is a new technology that aims at more efficient capture and use of photons that ordinarily pass through solar cells without generating electricity. The design could make it possible to cut the cost of solar cells in half while maintaining high efficiency. The process uses a type of material called a Photonic Crystal which according to J. Joannopoules of MIT (Massachusetts Institute of Technology) has the ability to do things with light that have never been done before (Bullis, 2007). Even though the primary objective of silicon solar cell for instance is to absorb incoming light and convert it to electricity, it is known that if the silicon is made thinner, it may still retain its ability to convert the photons it absorbs into electricity but fewer photons will be absorbed, decreasing the efficiency of the cells. This is the problem starsolar intends to solve.

MIT researchers developed sophisticated computer simulations to understand how thin layers of photonic crystal could be engineered to capture and recycle the photons that slip through thin layers of silicon. They found that by creating a specific pattern of microscopic spheres of glass within a precisely designed photonic crystal and then applying this pattern in a thin layer at the back of a solar cell, they could redirect unabsorbed photons back into the silicon. Photonic crystal reflects more light than aluminum which is used to back conventional cells especially when the aluminum oxidizes. Some of the light that passes through the cell is diffracted by the photonic crystal so that it reenters the cell at low angle. The low angle prevents the light from escaping the cell and instead bounces around inside, increasing the chances of the light being absorbed and converted into electricity.

Researchers at the University of California have designed a new cell which will be far cheaper than conventional silicon cells. The cell consists of a range of 550nm-high cadmium sulphide pillars embedded in a film of cadmium telluride. The cells are implanted upright in aluminum foil. They become bendable when enclosed in polymer. Presently the efficiency is 6% (See http://solarfeeds.com/sc/7863-cheaper-more-efficient-solar-cells-under-development.html). Day4Energyis is another new technology based in Burnaby and British Columbia; designed to boast the efficiency of solar panels. The company has developed a new electrode that, together with a redesigned solar cell structure, allows solar panels to absorb more light and operate at higher voltage. This increases the efficiency of multicrystalline silicon solar panels from an industrial standard of about 14% to nearly 17% http://www.technologyreview.com/Energy/21255/.

5.0 Conclusion

A good number of deposition techniques have been used in depositing thin films of various semiconductor materials in search of suitable materials for the production of high efficient solar cells. At present the high profile thin film materials for the fabrication of solar cells include Si, GaAs, CdTe, $CulnGaSe_{2,}$ Cu_xS, ZnP and InP.

Various conversion efficiencies have been achieved for various materials with a record high of 40.7% for GaAs heterojunction cell being the highest so far.

The conversion efficiency achieved for a solar cell is affected by the fabrication technique adopted in the production process of the solar cell.

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