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## INTRODUCTION

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## 1.1 General

Energy is the major factor in the development of mankind. Only a nation which generates energy many times more than the muscular power can attain the higher level of industrial and agricultural growth. National income is directly proportional to the per capita energy consumption.

Up to the end of $20^{th}$ century fossil fuels i.e. coal, oil and gas would remain main sources of energy. But due to their extensive use these fossil fuels are getting exhausted very rapidly and hence becoming more and more costly. At the same time there is a hazard of environmental pollution in the large scale use of fossil fuels. Therefore to overcome these difficulties we have to find some alternative sources for energy. The new sources should be abundant, easily available, inexhaustible and non-pollutent. Solar energy with its inexhaustible source, easy availability, freedom from environmental pollution and safety from hazard, may become one of the best alternative to the fossil fuels.

As solar energy is one of the most dilute and intermittent forms of energy, it requires the methods of utilization which are different than those used for conventional forms of energy. Again solar energy is most promising for the large scale utilization because of its abundance and minimal adverse environmental effects of its conversion[1-4]. The prospects for solar energy as a source of massive energy supply were substantially improved during seventies, particularly in 1971-72[5-6].

It is strongly believed that if the world had diverted all the money that was spent on space research to solar energy, by this time solar energy would have become supplementary source to the fossil fuels and main energy source by the end of $20^{th}$ century.

## 1.2 Solar Cells and Solar Energy Materials

### 1.2.1 Solar Cells

The devices in which solar energy is converted into either electric or chemical energy through a phenomenon of the photovoltaic effect are called as solar cells. The photovoltaic effect is the generation of an electromotive force by the absorption of ionizing radiations/7/.

The key parameter involved in the operation of solar cell is the existance of the local field or the built-in potential, needed to separate the electrons and holes generated due to photons incident on a semiconductor. This built in potential can be generated by making a junction. When a semiconductor junction is formed, the transport of charges takes place across it to set up the equilibrium i.e. to make the Fermi levels on par on both sides of the junction. During this process electrons and holes recombine and a depletion region is formed around the junction, leaving acceptors and donors ionized. This gives rise to a local field, also called as built in potential. When the light of energy $h\nu > E_g$ is made incident within this interface layer, the pairs of electron and hole are generated. If this excess of photogenerated electron-hole pairs are separated by the local electric field, an electromotive force is developed. If these electrons are

allowed to pass through the external circuit a photocurrent will flow. The generation of electron-hole pairs inside the semiconductor is possible only when the energy of incident photon is greater than the band-gap energy of the semiconductor.

In a solar cell built in potential is due to the formation of the junction. According to the nature of junction, solar cells can be grouped mainly into the following four categories, namely :

i) Semiconductor - Semiconductor junction Cells

ii) Semiconductor - Metal junction Cells

iii) Semiconductor - Liquid junction Cells and

iv) MIS and SIS Cells.

Photovoltaic devices or solar cells are simple in construction, extremely reliable and easy to handle.

### 1.2.2 Solar Cell Materials

There are a large number of materials with the help of which solar cells have been fabricated. The merits and demerits of these materials are as follows :

i) Silicon Solar Cells

Historically Silicon Solar Cell has been the first to be fabricated and then used in spacecraft application /1/. Lateron a fullfledged crystalline silicon solar cell technology got developed for terrestrial use. However, amorphous silicon solar cell technology is overtaking the traditional single crystal technology for terrestrial applications. Remarkable progress has been seen in both physics and

technology of a-Si ( hydrogenated amorphous silicon ) as a new electronic material due to its significant properties such as excellent photoconductivity with high optical absorption coefficient for visible light, the ability to produce a non-epitaxial growth on any foreign substrates and large area fabrication.

The average efficiency of present silicon solar cells is about 11 percent for space and 14 percent for terrestrial applications. Silicon solar cells up to the efficiencies 22 percent have been reported. The major problem with silicon solar cells is about the price. As the production cost of silicon cells is high, the electrical energy obtained with their use is 100 times more costly than that from the traditional sources. Therefore, before silicon solar cells can be used for production of bulk power, their prices must come down by a factor of about 100 from the present level.

ii) III-V Compounds

Semiconductors made up of elements from III$^{rd}$ and V$^{th}$ groups, such as gallium arsenide, indium phosphide, gallium phosphide, aluminum-gallium arsenide have very interesting properties for photovoltaic energy conversion. They all have band-gaps in the proper range for efficient solar energy conversion. In fact, GaAs with a band-gap of 1.35 eV is very close to the theoretically optimum material.

One of the problems with a direct band-gap material such as GaAs is that the surface recombination is very high and because the carriers are generated so close to the surface that a great many of them are lost. In comparision with silicon very little is known about

surface properties of III-V compounds. However, it should be possible to improve the surface considerably. One idea is to grow epitaxially an indirect band-gap material such as AlAs on a GaAs substrate. The AlAs has the wide band-gap that allows the light to penetrate and to generate carriers at the GaAs p-n junction, now unaffected by a surface that is relatively far away.

Gallium-arsenide solar cells are considerably more expensive than the silicon cells and the production cost would probably be a factor of 10 more because of the cost of gallium.

One advantage of gallium-arsenide and other large band-gap semiconductors is their ability to operate at higher temperature than silicon. This is important where space mission to venus, mercury or the Sun are under consideration or where the use of sunlight concentrators is contemplated.

iii) II-VI Compounds

These are the materials such as Cadmium Sulfide and Cadmium telluride made up of elements in $II^{nd}$ and $VI^{th}$ groups. Solar cells made from these materials commonly involve heterojunctions and barrier layer. Efficiencies in single crystal cells have been reported to be about 8 percent in CdS and CdTe. These materials are important to thin film polycrystalline solar cells. Because of the high degree of ionicity in II-VI compounds, many of the single crystal properties are preserved even when the material is microcrystalline, as it is in thin films. Such cells have shown efficiencies of 6 to 8 percent in large areas about 60 sq. cm. Such cells are light weight and show

promise of high power-to-weight ratio suitable for space applications. Also, because single crystal material is not required, the cell shows promise of low cost and it is hoped to be 100 times less than the cost of present silicon cell. Thus, in order to reduce the cost of solar cells, the efforts are directed from single crystals /8/, Press Pallets /9/ to polycrystalline films /10-12/ with a view to use large area for terrestrial applications.

$CdS/Cu_2S$ solar cells are proposed to be used because of the possibility to adapt the current technology to relatively inexpensive mass production method. Using typical steps of the Clevite / Gould Fabrication process, modified by certain doping and proprietary treatment procedures, thin $CdS/Cu_2S$ layers can be fabricated, which are expected to have life time in excess of ten years for terrestrial applications, when properly encapsulated. $CdS/Cu_2S$ solar cell hardware is presently available with up to 8 percent conversion efficiency at 25 $^{o}C$.

A major problem in the CdS cell is that of reliability. In the presence of humidity these cells have been known to degrade by more than 50 percent. Light and voltage cause degradation due to ion motion in the CdS.

iv) Organic Materials for Solar Cells

Many organic compounds have been investigated and found to have properties of interest to solar energy conversion. In particular, many of them have band-gap in the range of interest i.e. 0.5 eV to 2 eV. While p-n junction photovoltaic devices have not been fabricated from

these materials, some Schottky barrier cells have been made. Open circuit voltage of 0.5 V to 1 V have been observed. These are in the same range as semiconductor devices. However, the currents are much too small to provide efficient energy conversion. This is largely due to the high resistivity of the organic materials. Improvements in resistance and current by a factor of over a million are required before such materials will be of interest for solar cells.

Organic semiconductors do not promise a short-term solution to the photovoltaic solar energy problems, but their long-term low-cost potential continues to make them attractive. There is some question about the availability of Ga, In, perhaps even Cd for large-scale ( a few thousand squere miles of cells ) systems.

v) Photosynthetic Materials

Photochemical systems in plant may be more interesting. These systems based on chlorophyll compare well with the better organic photovoltaic devices, although they are a long way off from high efficiency devices. Some photovoltaic concepts, like the separation of the charges by the potential barrier should be applied to the photosynthetic process.

Other materials are inorganic materials like BiS, $P_{b\ 1-x}\ Cd_x S$, $CuInS_2$ and $CuInSe_2$ and the organic semiconductors like tetracen, pyrene and photosynthetic pigment. There are probably yet other materials which are possible candidates for solar energy conversion.

A review of literature on solar cell materials revealed that all the solar cell devices suffered from inherent limitations i.e.

photocorosion, poor sunlight absorption and effieiency. In view of this it is important to choose a semiconductor material which is more resistive, non-destructible and is capable of using the greater part of the incident radiations. In this respect many semiconductor materials Such as Si/13/, GaP/14/, CdS/15-16/, $SnO_2$/17/, $TiO_2$/18-19/, $SrTiO_3$/20/, $KTaO_3$/21/, $BaTiO_3$/22/ and $\alpha$- $Fe_2O_3$/23/ have been used in the solar cells.

## 1.3 Oxide Semiconductors

Transition metal oxides of the general formulas MO, $MO_2$, $M_2O_3$, $M_2O_5$, $MnO_{2n-1}$ and $MnO_{2n+1}$ are known to exist. A study of the properties of these transition metal oxides not only serves as an excellent introduction to solid state chemistry and material science, but also provides a rich source of fascinating research problems for experimental and theoretical investigations. These oxides have novel properties which distinguish them from metals and insulators. These properties arise due to 'd' electrons of the outer unfilled shell of transition metal atom. The transport phenomena in these oxides are quite different from those in normal semiconducting materials. The nature of bonding in these oxides varies from ionic to covalent and to metallic. However, crystal structures of transition metal oxides vary from cubic to triclinic symmetry. Some of the oxides show interesting magnetic phase transitions from one crystal structure to another accompanied by changes in magnetic, electrical and other properties.

Amongst these transition metal oxides Ferric-Oxide ($Fe_2O_3$) is found to be the most interesting material due to its application

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in chemical energy conversion. It can be easily prepared, resists photodecomposition and possesses a flat band potential close to the hydrogen evolution. Band-gap energy is found to vary from 1.4 eV to 2.2 eV. Therefore $Fe_2O_3$ is an attractive semiconductor electrode material. It is also known as iron sesqui oxide or hematite. It exists in several forms such as $\alpha$- $Fe_2O_3$, $\beta$ - $Fe_2O_3$, $\gamma$ - $Fe_2O_3$, $\delta$ - $Fe_2O_3$ and E - $Fe_2O_3$. Among all the above modifications, $\alpha$-$Fe_2O_3$ is found to be the stable form and it posses a corundum structure. The corundum structure belongs to a trigonal system and resembles the rhombohedrally distorted NaCl structure. It is anti-ferromagnetic with high Neel Point ( $T_N$ = 960 $^oK$ ). It has a specially interesting character that it goes through the morin transition ( magnetic transition ). Previous study on electrical conductivity has shown that $Fe_2O_3$ is a semiconductor in the temperature range 200 $^oK$ - 1600 $^oK$.

$\alpha$ - $Fe_2O_3$ has been considered as useful material for the splitting of water with sunlight /24-27/. $\alpha$ - $Fe_2O_3$ is an intrinsic and a metal excess oxide semiconductor/28-33/. It is n-type with relatively low energy band-gap. Hardee and Bard have studied the photoelectrochemistry of polycrystaline $\alpha$ - $Fe_2O_3$ electrode prepared by chemical vapour deposition ( C V D ) of iron oxide on Ti and Pt substrates. The interest in this material is also due to its relatively low band-gap ( 2.2 eV) /34-37/ and the stability of its contact with solutions/24-27, 38-40/.

## 1.4 Statement of the Problem

In recent years oxide semiconductors have attracted attention due to their applications in solar energy conversion, particu-

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larly in the photoassisted decomposition of water. Many transition metal oxide semiconductors such as $TiO_2$, $SrTiO_3$, $BaTiO_3$, ZnO, etc. are found to be stable and useful in the photoelectrolysis of water. However, their high band-gap energies make them transparent for a large portion of the solar spectrum. For commercial applications the electrode material should be stable, have a good spectral response and should be inexpensive. In view of all these requirements it is forecasted that among all semiconducting oxide materials $Fe_2O_3$ may be the best candidate because of its smaller band-gap in comparision with other oxide semiconductors.

Thin films of semiconducting materials are usually deposited using vacuum evaporation, spray pyrolysis, chemical bath deposition and dip and dry technique. However, areas of the films grown, using these techniques, are restricted owing to the geometry of the experimental set up involving the substrate and the source material. Therefore, a novel technique for the growth of uniform large area films has been developed in our laboratory. Basically the method consists of the formation of a thin film of semiconducting material at the interface of solution and gas. The solution contains cations and the gas contains anions and required semiconducting film is formed by a simple chemical reaction at the interface.

In view of the above it is proposed to investigate the deposition of uniform large area films of $Fe_2O_3$ by the said solution-gas interface technique. Therefore, a process giving $Fe^{+++}$ and $O^{--}$ at the interface is required. Thus, the following studies were planned in the present dissertation work.

1) To carry out the reaction of $FeCl_3$, placed in a shallow container, in the atmosphere of $NH_3$ to obtain $Fe_2(OH)_3$ film at the interface.

2) To lift and support this film on glass substrate and to convert it to $Fe_2O_3$ film.

3) To study the microstructure, optical absorption and electrical properties of the films of $Fe_2O_3$.

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