Recent Developments in Fabrication and Performance of Solar Cell

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Abstract—Solar cell is a kind of energy conversion device that converts solar energy directly into electric energy and has received a lot of attention in the past decades. Here, we summarize the latest progress in the field of solar cells. Firstly, the working principle and device structure of solar cells are introduced. Then it introduces the four most representative solar cells, which are silicon-based solar cells, copper indium gallium selenium thin film solar cells, organic solar cells, perovskite solar cells, and summarizes the advantages and challenges of these four types of solar cells. Finally, we summarized the preparation method of solar cells. We hope that we can help people to understand this field and invest in the research and development of solar cell materials and devices.

1. INTRODUCTION
There are a lot of global problems caused by traditional fossil fuel, such as environmental pollution and energy shortage in recent years. In that case, finding a kind of clean, abundant, and reliable energy is one of the key tasks that all countries are endeavoring to achieve. Fortunately, solar energy can satisfy all the prerequisites mentioned above, and we use a structure named solar cell to contain solar energy now. As shown in Fig.1, we can know about the history and development of all kinds of solar cell efficiency from 1975 to 2021. The first piece of solar cell was actually produced by W.G.Adams and R.E.Day in A.D 1877, and its basic theory was proposed by Charles Britts in A.D 1883, which is based on Se with low efficiency. Up to now, the development of solar cell has experienced three generations since it was invented.

The first generation solar cell is based on silicon, which has the longest history and maturest fabrication process, so it has occupied the largest market share and has the best commercial prospect. However, as shown in Fig.1, its efficiency is in the medium (about 27.6% highest in A.D 2021), and growth rate is quite low during history, both of them may limit its future development. The second generation solar cell is based on a thin membrane substrate, which consumes less materials but higher efficiency and stability than those solar cells in the first generation. Though it is easier to produce this
kind of solar cell in a large scale, the rare elements included in its materials will cost too much to fabricate it in a large scale in reality.

Figure 1. The development and category of solar cell [1]

The exact concept of the third generation solar cell is still in debate but there are some requirements the third generation solar cell must be satisfied with. The third generation solar cell must have thin film and a high efficiency at first. Besides, its material should be rich in nature or easy to produce in the factory and be non-toxic. In recent years, the scientific community of various countries has focused on the research of laminated thin film solar cells. Compared with the previous two generations, the battery has stronger advantages and application prospects. The solar cell in this generation has the highest efficiency, as shown in Fig.1 but still has a long way to go to sell in the market rather than just do research in the laboratory. Nowadays, since decreasing the efficiency of the first generation solar cell based on silicon is too difficult, people pay more attention to how to lower the fabrication cost. Most scientists are now focused on the research of the second & third generation solar cell because they can achieve higher efficiency theoretically, but there are still many difficulties remaining to overcome before they can be fabricated on a large scale. Here, we will give a comprehensive introduction to the structure and working principle of solar cells and summarize the latest progress of four kinds of solar cells.

2. Basic Structure and Theory of Solar Cell
A typical structure of solar cell can be seen in Fig.2(a), which includes an electrode on the top (TE), an electrode on the bottom (BE), a piece of hole transport layer (HTL) under TE, a piece of electron transport layer (ETL) above the BE and a piece of light-absorbing layer between HTL and ETL. Fig.2(b) shows the process of how photocurrent can be generated in the solar cell. Firstly, when light penetrates the surface of the structure and to the perovskite area, its energy will be absorbed in this area so that electron-hole pairs will be generated. Secondly, by Imaging the perovskite area as an intrinsic area, we will gain a PIN junction, and the holes and electrons will also move in the opposite direction because of the influence of the built-in electric field in both HTL and ETL. Thirdly, both electrons and holes will enter the electrode in each side and then get in outer circuit, which can generate a photocurrent eventually.
Figure 2. The structure and working theory of solar cell. a) Typical sandwich-type structure b) Schematic diagram of photocurrent generation

Figure 3. Diagram of spectral irradiation under AM1.5 [2].

Figure 4. The voltage-current curve of solar cell under illumination and some corresponding parameters [3].
Fig. 3 shows how the spectral irradiance of light changes as the wavelength of light changes. The material we use in the light-absorbing layer should have good performance under the wavelengths of light whose spectral irradiance are high. There are several parameters that can be used to weigh the performance of a solar cell. Firstly, short-circuit current ($J_{sc}$), the current through the solar cell when the voltage across the solar cell is zero. We can calculate the value of it by:

$$I_{sc} = qG(L_n + L_p)$$  \hspace{1cm} (1)

($L_n$ is the diffusion length of electron and $L_p$ is the diffusion length of hole)

We can also measure the current at the cell terminals when the resistance of the load is zero. Secondly, open-circuit voltage, the maximum voltage when the current is zero in a solar cell. We can also measure the value of it in two ways:

1. Using the formula:

$$V_{oc} = \frac{nkT}{q} \ln \left( \frac{I_L}{I_0} + 1 \right)$$  \hspace{1cm} (2)

($I_L$ is the photocurrent generated in solar cell and $I_0$ is the saturation current of PN junction)

2. Measuring the voltage at the cell terminals when there is no load.

Besides, by testing the performance of the realistic solar cell, we can gain an IV curve similar with that is shown in Fig. 4. The curve we gain here looks like the IV curve of the PN junction, but it will be higher than the PN junctions because of the generation of photocurrent. We can gain the value of fill factor (FF) from Fig. 4, which can be modeled by:

$$P_{MP} = I_{MP}V_{MP}$$  \hspace{1cm} (3)

$$FF = \frac{P_{MP}}{V_{oc}I_{sc}}$$  \hspace{1cm} (4)

(MP means maximum power in both equations)

We can also work out the photoelectric conversion efficiency (PCE) of a solar cell according to its IV curve and the formula below:

$$\eta = \frac{V_{oc}I_{sc}FF}{P_{IN}}$$  \hspace{1cm} (5)

($\eta$ means PCE, $P_{IN}$ means input power of solar cell).

3. Different Kinds of Solar Cells
As said in the introduction, the solar cell has undergone three generations up to now and has many different cell structures in each generation. Here we will talk about crystalline Si cell, perovskite cell, organic cell, and CIGS cell because all of them have representative characteristics. Besides, crystalline Si cell has the largest market now, and others all have great developing potential in the future.

3.1 Crystalline Si Cells
As shown in Fig. 5, the structure of the crystalline Si cell is a little different from the structure we have mentioned above, because the light-absorbing layer is changed to an antireflection coat whose position is on the top of ETL and function is to reduce reflected light by designing the thickness of it.
Figure 5. Several schematics about crystalline Si cell. a) A typical structure of crystalline Si cell [4].

Figure 6. Changing the angle of incidence (AOI) on the surface of solar cell during a day.

Figure 7. The nano inverted cone surface structure fabricated through RIE [5].
Using silicon as source material has lots of advantages, such as stable quality, great thermal resistance, and long life, in that case, crystalline Si cell is applied widest in reality now and is also named traditional solar cell. However, the material properties of crystalline Si cell also limit its development to be light and flexible, which is not conducive to large-scale application in the future [7]. Nowadays, the quality of this cell is becoming better, and its price is becoming lower, which benefits from the successive improvement of the fabrication process. As shown in Fig.1, though the recent improvement of the highest conversion efficiency of crystalline silicon solar cells is not obvious, the PCE of various types of crystalline silicon solar cells are constantly improving. Since decreasing the efficiency of crystalline Si cell is too difficult, people pay more attention to how to lower the fabrication cost. One way is to promote the fabrication process such as using diamond wire sawn technology rather than slurry wire sawn technology. Besides, as we know, we can divide crystalline Si cell into two groups: monocrystalline silicon solar cell and polysilicon solar cell. Monocrystalline silicon solar cells have occupied most of the market share of crystalline silicon solar cells now, because it cost less and has higher PCE and better quality than polysilicon solar cell's.

3.2 CuInGaSe solar cells
In the 1970s, Wagner et al. at Bell Laboratories used the CdS/CuInSe2 heterojunction in light detectors. By measuring its quantum efficiency spectrum, they found that CuInSe2 is an excellent material for solar cells. Then, in 1975, the same team prepared a CdS/CuInSe2 heterojunction solar cell with an efficiency of 12% using CuInSe2 single crystal, which was the first report on CIGS solar cells. In the first preparation, the efficiency of CIGS thin film solar cells had already improved to ten percent after a short time, and later through continuous development, gradually improved to the present level.
Copper indium gallium selenium solar cell (Cu(In, Ga)Se₂, CIGS) is the solid solution of CuInSe₂ (CIS) and CuGaSe₂ (CGS), which belongs to the I, II, and VI groups of compounds. It has a chalcopyrite structure at room temperature. CIGS is developed from the ternary compound CIS, in which part of the CIS is replaced by the homologous Ga. The structure of chalcopyrite can be derived from the sphalerite structure of the II-VI compounds ZnS or ZnSe. The CIS chalcopyrite crystal cells can be obtained by cross-replacing the Zn atoms in the two sphalerite primary cells with Cu or In atoms. In the structure of CIS chalcopyrite, the valent Cu atom and the trivalent In atom form four bonds with the four nearby Se atoms respectively, and each Se atom also forms four bonds with the two nearby Cu and In atoms.

The valence band top (VBM) of CIGS is mainly determined by the d orbital of Cu and the p orbital of Se, while the conductivity band bottom (CBM) is mainly determined by the s orbital of Ga/In and the sp orbital of Se [9]. Adjusting the ratio of Ga to In CIGS (Ga/(Ga+In), GGI) can adjust the band gap between 1.04 eV and 1.68 eV. CIGS thin film solar cells are considered to be the most promising solar cells to compete with silicon cells. Compared with crystalline silicon cells, CIGS thin film solar cells have the following characteristics [8], [10]: (1) CIGS is a direct bandgap semiconductor material with high light absorption coefficient; (2) The band gap can be adjusted by adjusting the content of Ga in CuIn1-xGaxSe2 between 1.04 eV and 1.68 eV. (3) The purity of the material is low; CIGS has a high tolerance to impurities and defects, the preparation process and environmental requirements are relatively low, the production cost and energy consumption are low; Less materials are used, and the material cost is low, so the cost of CIGS photovoltaic power generation is lower than that of crystalline silicon cells. In addition, CIGS has good stability, excellent performance under diversified scattered light and high temperature conditions, good low light performance, flexibility, light weight, so it can be used...
in a wide range of scenarios, not only for large-scale ground cluster power generation, but also as a building material and used in consumer electronic products.

Although the highest efficiency of CIGS thin film solar cells has reached 23.35% [11], it has many advantages and has been industrialized. Market share is still low. The major factor limiting the size of the market is that the current efficient and commercial CIGS cells are prepared by vacuum method, which cannot fully exploit the cost advantages of thin-film solar cells. It is very important to find a low-cost film preparation technology to replace the vacuum method for realizing the large-scale application of CIGS.

3.3 Organic Solar cells

![Figure 10. Structures of Different Organic Solar Cell: a). Some structures of fullerene molecules in fullerene solar cells. b). Structure of high-efficiency fullerene solar cell. c). Structure of polymer donor molecules. d). Structure of a typical A-D-A acceptor and the photovoltaic performance of it [12].](image)

Before 2015, most organic solar cells are based on the fullerene system because of the isotropic conductivity of the fullerene acceptor and the ease of isolate fullerene material from solutions. The best efficiency achieved by the fullerene solar cell is over 10% [13]. However, the fullerene solar cell still has some major weaknesses that block its further development. One important point is that fullerene solar cells have relatively low light absorption, and the active layer is unstable. To avoid those weaknesses, some non-fullerene materials have become another popular part of the solar cell fields recently to avoid those weaknesses.

To introduce organic solar cells specifically, details about fullerene solar cells and non-fullerene solar cells are needed. Consider fullerene solar cells first. Fullerene solar cells have fullerene material as the acceptor and have donor molecules, including small molecule donors and polymer donors. Fullerene is a series of spherical carbon molecules. Based on the carbon atoms in the sphere, they can be divided into C_{60}, C_{70}, C_{84}, C_{90} and so on. The donors in the fullerene system need to meet many requirements to overcome fullerene's weaknesses. For example, the donor should have a wide absorption spectrum of visible light to overcome the weak absorption of fullerene material, and it also needs to have a proper energy level to form excitons that can dissociate effectively. The structure of organic solar cells has no big difference from traditional solar cells. The most difference is the
material of active layers. A typical example of fullerene solar cell from A. J. Hegger's group is a solar cell taking PC61BM as the acceptor and polymer MEH-PPV as the donor to form a complex net structure from solutions [14]. The active layer's net structure extends the surface area of the acceptor, so the amount of excitons increases rapidly. Research shows that fullerene solar cells have approached their theory limit, so the development of non-fullerene solar cells needs to be done. There are many different types of non-fullerene solar cells, but based on the materials, they can be divided into all-polymer solar cells, all-small-molecule solar cells, small molecule acceptor and polymer donor solar cells, and small molecule donor and polymer acceptor solar cells. All-polymer solar cells use polymer acceptors and polymer donors to form an active layer. The polymer solar cells usually better thermal stability and morphological stability because of the bonds formed between polymers. Also, the all-polymer solar cells are usually very flexible due to those bonds. A problem of all-polymer solar cell was that there was no good polymer acceptor to form an efficient active layer. Recent research shows that some polymer acceptors like DCNBT can bring high efficiency to the all-polymer solar cells due to the cyano group that can lower the energy level. The polymer DCNBT-IDT formed by the copolymerization of DCNBT and IDT has a low energy level and narrow band gap, so it can be a good kind of polymer acceptor [15]. All-small-molecule solar cells utilize small molecule donors and small molecule acceptors to form an active layer. Those small molecule materials usually have a certain structure and thus high purity. However, the all-small-molecule solar cell faced the same problem as the all-polymer solar cell—the lack of acceptors. Recently, A-D-A type and D-A-D-A-D type small molecule acceptors have been proved to be much more efficient than other small-molecule acceptors.

3.4 Perovskite solar cells

Perovskite cell is the representative of the third-generation solar cell, whose light-absorbing layer is made of perovskite. Many scientists are focused on its research now, because it has low cost, high PCE, and we can use multiply feasible ways to fabricate this cell. Besides, perovskite cell is much lighter and more flexible than crystalline Si cell, so it is quite conducive to large-scale application.

![Figure 11. several schematics about perovskite cell. a) A typical ABX₃ perovskite structure [16]. b) A schematic diagram about the one-step solution processing method [17]. c) The SEM images of perovskite film with NH₄Cl addictive [18]. d) A J-V curve from forward and reverse scan based on a L-NiOx transport layer](image-url)
Perovskite is a kind of crystal material with a calcium titanate mineral structure, whose chemical expression is ABX3. In the chemical expression of perovskite, A is a univalent cation (e.g., $\text{FA}^+$ and $\text{MA}^+$), B is a divalent metal cation (e.g., $\text{Pb}^{2+}$ and $\text{Sn}^{2+}$), and X is a negative trivalent halogen anion (e.g., $\text{Cl}^-$ and $\text{Br}^-$). Its cell structure is shown in Fig. 11(a). Normally, the structure of the perovskite cell is a sandwich type, as shown in Fig. 2(a). It can absorb the energy of the photon and then generate electron-hole pairs in its light-absorbing layer.

The reason why we choose perovskite as the material of the light-absorbing layer is that it has a lot of advantages in the photoelectric field. First, its light-absorbing capacity is better than any material in the first or second generation, which means that when comparing with older devices that have similar performance, it can cost less material but perform at the same level. Second, perovskite can achieve bipolar transport, because both of its top of valence band and bottom of conduction band are quite separative, which means that the velocity of electrons in the conduction band and holes in the valence band are almost equal, and both of them are quite high. Third, the diffusion length of its carriers is long, which can decrease its recombination rate, so that perovskite cell can have higher efficiency.

We usually use quasi-2D perovskite as the material of the light-absorbing layer, because the binding energy of excitons of quasi-2D perovskite is between 2-D and 3-D perovskite's, in that case, it will have better photoelectric performance when being the material of light-absorbing layer, such as higher extinction coefficient, higher absorbance in the range of uv-nir spectroscopy, and higher carrier mobility [19].

Similarly, we can choose SnO2 or TiO2 as the material of ETL, because they can transport electrons well meanwhile prevent holes from passing ETL as much as possible. Based on this choice, we can use poly [bis (4-phenyl) (2,4,6-trimethylphenyl) amine] (PTAA) and nickel oxide (NiOx) as the material of HTL because they can transport holes well meanwhile prevent electrons from passing HTL as much as possible [20].

The J-V curve shown in Fig.11(d) from a perovskite cell shows that the efficiency of a perovskite cell whose transport layer is made of L-NiOx is about 18.7% while its FF is about 77.2%, both of them are relatively high nowadays.

Nowadays, the highest efficiency of single-junction perovskite cell is about 25.2%. However, it is difficult for researchers to increase this figure a lot now for many reasons. That is why some researchers are focused in multi-junction structure now to pursue higher efficiency.

Besides, there are two difficulties perovskite cell should overcome in fabricating a light-absorbing layer. The first one is its stability, up to now the operation life of it is only about one year, which means it is impossible to sell it in market. Besides, it is still difficult to fabricate perovskite cell in a large scale though it is theoretically possible.

### 3.5 Fabrication Process of Some Types of Solar Cell

#### 3.5.1 The fabrication process of crystalline Si cell

1. **Growing Ingot:** We should melt a large piece of silicon in a crystal growing furnace at the temperature that is higher than the melting point of Si and cool the ingot down slowly, so that we can gain very large grains.

2. **Wafer Slicing:** We should use a wire saw to slice up the ingots we have got in the last step into very slim wafers.

3. **Wafer Cleaning:** We can use a kind of membrane consisting of glass fiber to filter large particles and absorb small particles, so that we can gain quite pure air to prevent the pollution from particles in nature air. Then, we should Use HF to remove the oxide layer and HCl to remove metal impurities on the silicon wafer surface.
3.5.1.4 Texturing: One simple way to achieve texturing is alkaline etching. Firstly, we should make the wafer textured in a dilute solution of NaOH with isopropanol as a wetting agent. Secondly, we should use acid to neutralize NaOH. Thirdly, we should put the wafer into a centrifuge for a final rinse and spin dry. We often use this way to gain pyramid structure. Another way we often use to achieve texturing is reactive ion etching (RIE): Firstly, we should build high frequency electric field in the reaction chamber to transform reactive gas into plasma. Then, plasma will be accelerated to bombard the substrate materials and react with them by the electric field, which will eventually achieve etching. We often use this way to gain pyramidal structure and nano inverted cone structure, a picture of nano inverted cone structure is shown in Fig.7.

3.5.1.5 Doping: Firstly, we should use SOG (spin-on glass) to form a doped oxide layer on the surface of the wafer by the gravity and centrifugal force generated when the spin processor rotates. Secondly, let the p-type material diffuse to the interior of the wafer at high temperature. Thirdly, let n-type material diffuse when the base is the p-type area to create a PN junction at high temperature. Then, we can use anneal furnace to diffuse n-type material to the bottom of the emitter when the emitter is the n-type area to form an n++ area to generate ohm contact that can decrease surface recombination at about 1000°C for about 5-20 minutes and finally remove SOG by HF dip. Edge Isolation: We should remove the diffusion around the edge of the device to ensure the emitter can be isolated from the rear by stacking the wafers and then etch them by using CF4 and O2.

3.5.1.6 Producing Antireflection Coatings: We can decrease the reflection of light on the solar cell surface by producing Antireflection Coatings (AR coatings). The way we use to product AR coatings is chemical vapor deposition process (CVD), whose basic theory is using one or several gaseous compounds or elemental elements containing thin film elements to react on the surface of the substrate to generate a thin film. During the CVD process, we can use TiCl4, O2, and CH4 to react to produce TiO2 and the temperature of the reaction is normally from about 850°C to about 1100°C. As shown in Fig.6, it is a key point for the efficiency of solar to decrease reflection under different kinds of light, because the angle of incidence (AOI) is changing during day and night. In that case, we can deposit three layers of AR coatings successively, and each layer has a different refractive index to achieve better performance under different AOI, as shown in Fig.8.

3.5.1.7 Screen Print Front & Rear Silver: Firstly, we should use simulation tools to design the metal mask. Secondly, we should use a screen printer to force the silver paste to form a metal pattern according to the design we have finished before on the top and bottom of the device. Then, we should put the wafer in a machine to evaporate off organic remnants in the paste at the temperature of about 200°C. During this step, we can use RTA (Rapid Thermal Anneal) to heat the wafer up to the set temperature and hold it for a period of time, whose length depends on the material and size of wafer, and finally cool the wafer down.

3.5.2 The fabrication process of Perovskite Cell

3.5.2.1 CVD process: Firstly, we should load the substrates and MAI into two separate temperature control zones of a furnace. Then, we should seal the furnace, pump down to a certain pressure and purge with inert gas [21]. However, the cells fabricated in this process always perform badly, so the fabrication process still needs to be promoted.

3.5.2.2 One-step solution processing method: As shown in Fig.11(b). In brief, we can deposit the PbI2 film by using a thermal evaporation system firstly. Then, we should place the film onto a layer of CH3NH3I powder. Upon a heat treatment at 150°C for 20 min, perovskite is formed. During the process of membrane growth, we can take some measures to gain a membrane with high quality. For example, we can add NH4Cl to the standard precursor mixed with PbI2 and MAI without any heat-
treatment. In that case, we can gain a very flat and dense membrane like what is shown in Fig.11(c) [22].

4. CONCLUSION
In this article, we introduced the developing status of solar cell firstly. Then, we talked about four kinds of solar cell and each basic structures and theories, besides we also discussed their advantages, disadvantages and the development trend of each of them. Finally, we introduced the fabrication process of two specific kinds of solar cell.

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