Overview of the production background and treatment methods of waste photovoltaic modules

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Abstract. With the development of solar photovoltaic (PV) generation, a large number of waste PV appeared. The purpose of this paper is to discuss the background, causes and the main dealing method of waste photovoltaic (PV) modules. The large-scale research, popularization and application of solar energy are the fundamental reasons for the generation of waste PV modules. It is necessary to have a systematic cognize of the utilization of solar energy before expounding the issue of waste PV modules.

1. Introduction

1.1. The background of PV module
Solar power generation refers to the power generation method that directly converts light energy into electricity without thermal process. It includes PV power generation, photochemical power generation, photoinduction power generation and photobiological power generation. As the most important part, the PV power generation is the only method expounded in this paper.

PV power generation is a direct power generation method that uses solar energy level semiconductor electronic devices to effectively absorb solar radiation energy and convert it into electric energy. PV power generation system is mainly composed of solar cell, storage battery, controller and inverter. As the key part of the PV power generation systems, the quality and cost of solar panels will directly decide the quality and cost of the whole system. At present, the most widely used solar cells in the world are single crystal silicon solar cells, polycrystalline silicon solar cells, thin film solar cells and so on. Monocrystalline silicon solar cells and polycrystalline silicon solar cells are collectively called crystalline silicon solar cells, occupying more than 90% of the market share of PV power generation.

Monocrystalline silicon cells are based on high quality monocrystalline silicon materials and related processing technology. It has the highest conversion efficiency, the most mature technology, and is currently the most widely used solar power technology. Compared with 15 percent for mass-produced monocrystalline silicon solar cells, the highest conversion efficiency in laboratory is 23 percent. Typical examples of monocrystalline silicon efficient cells are backside contact batteries invented by Stanford university, passivated emission zone (PERL) batteries invented by the university of new south wales, and localized back-field batteries invented by the Fraunhofer solar research institute in Germany.

As mentioned above, the core component of PV power generation is solar cells, while a single solar cell cannot be used as power supply directly. A number of individual cells must be connected in series, in parallel and tightly encapsulated into components to be used as a power source. This component is
the photovoltaic module, which is the core part of the PV power generation system. However, the waste PV module is bound to become a new type of solid waste, causing serious damage to the environment recently. Therefore, the deal with the waste PV module has become a very urgent research topic. And because of the situation that crystalline silicon PV module occupies more than 90% of the PV market, the present study about disposal of PV module, including this study, refers to the study of waste crystalline silicon PV module.

1.2. The Structure Of Pv Module

PV module converts solar radiation energy into electricity directly or indirectly through photoelectric effect or photochemical effect by absorbing sunlight. The main component of PV module are semiconductor materials (mainly silicon) solid PV cells. A PV module is the combination of PV cells with organic glass, EVA (ethylene/vinyl acetate copolymer), the back, the aluminum alloy layer pressure, junction box, and silica gel. The details of these components are shown in figure 1-1. Their specific functions and characteristics are as follows:

1) Organic glass. The function of glass is to protect the main body of power generation (such as the battery plate), it is demanded to have high light transmittance (generally over 91%) and undergo ultra-white toughening treatment.

2) EVA. It is used to bond and fix the organic glass and the power generating body (battery plate). The quality of EVA material will directly affect the service life of the components. Once exposed to air the EVA will be easily aged and yellowed, which will affect the transmittance of the components and further affect the power generation efficiency of the PV module. In addition to the quality of EVA, the quality of laminating process also affects the service life of PV module seriously.

3) Cell. As described above, it is the core components of PV module. Being tightly encapsulated in the inside of PV module, the mechanical structure and performance of silicon slice always keep excellent when the other components are invalid.

4) The back. It plays the role of sealing, insulation and waterproof. TPT, TPE and other materials are generally used to ensure its performance of anti-aging, anti-corrosion, anti-ultraviolet radiation and anti-air permeability. The theoretical service life of the back is 25 years, which is the mainly restricted factor of the theoretical service life of PV module.

![Fig.1 Schematic representation of crystalline silicon PV module.](image-url)
5) Aluminum alloy. As the protective laminate, it plays a certain role of sealing and supporting.
6) The junction box. It protects the entire power generation system and acts as a current transfer station. If the component short-circuit, the junction box automatically disconnects the short-circuit battery string, prevents the whole system from burning out. The most important part of the junction box is the selection of diodes. The corresponding diodes are different according to the type of battery chip in the module.
7) Silica gel. It is used to seal the junction of components and aluminum alloy borders, components and junction boxes. [1]

2. Research of waste PV module

2.1. The production of waste PV module
Combined with the components of the PV module and its service life, a large amount of waste PV module will be generated as a new kind of garbage worldwide in the foreseeable ten years. According to the research of McDonald NC et al., the generation of 1MWp electricity will generate 70-80 tons of garbage. Bearing in mind that the next ten years will be an explosion period for the development and use of PV module, the coming waste PV module is even more difficult to estimate. Statistical evaluation data also confirm this point. The international renewable energy agency estimates that 1 million tons of waste PV module will be produced around 2030, and by 2050, the figure will reach 7.8 million tons [2]. In fact, the prevention and treatment of PV waste abroad has already begun, the European commission has decided to include PV module in the new WEEE catalogue [3]. These wastes contain cadmium and lead. When they enter the environment, they will infiltrate into the soil, causing serious soil pollution. Glass, aluminum, rare earth, brominated flame retardant (BFRs) and other harmful substances in PV module will also cause great damage to the environment [4].

Actually, there possible will be more waste PV modules than the predictive data. In the process of actual use, because of the aging recession of some components, a large amount of PV modules get ineffective before the theoretical service life, while the silicon wafer, as the core component, maintains a complete mechanical structure and excellent photoelectric performance. Therefore, the waste PV module is not only a new type of solid waste which is difficult to deal with. In fact, it is also a kind of resource with high recycling value.

2.2. The disposal of waste PV module
Abandoned PV module cause serious harm to the environment and waste of resources. The abandoned glass, metal, silicon and so on is valuable for recycling. In particular, the silicon wafer, which is not only the most core part of the PV module, but also the most expensive component. The high cost is the most important factor restricting the development and spread of PV power generation. If the waste PV modules can be properly disposed, it can not only avoid environmental pollution, but also recycle valuable materials and resources. Recycle of silicon wafer is significant to reduce the cost of PV module. Once accomplished, it can promote the popularization of PV power generation a lot, eventually, make contribution to environmental protection and sustainable development of human society.

Since EVA acts as the binder among silicon wafer with back plate and glass, the treatment of PV module usually begins with the removal of EV. There are many corresponding methods, and the purpose of these methods is to recycle high-purity silicon, glass, and metals such as silver, copper and aluminum [5]. Generally speaking, the main separation methods are heat treatment, chemical treatment and physical treatment. Several major processing techniques are described below.

Frisson et al. used the conveyor belt furnace and fluidized bed reactor to pyrolyze the waste PV modules in 2000, and then etched the crystalline silicon cell with 15% HF, 4:1 H2SO4.H2O and 40% HNO3 solutions, and finally accomplished the recovery of silicon [6].

In 2010, Radziemaska and Ostrowski achieved the removal of aluminum metal coatings with 30% KOH, followed by 250ml HNO3 (65%), 150ml HF(40%), 150ml acetic acid (99.5%) and 3ml Br2 in a mixture to remove Ag coatings, AR coatings and flame retardants. Eventually, silicon was achieved [7].
Kang et al. successfully used organic solvent to separate and recycle glass in 2012, and then used pyrolysis method to remove the adhesive layer (EVA), so as to obtain the semiconductor material in the waste PV module. Further, the recovered battery plate was soaked in a mixture of etch solution and surfactant. Finally, silicon with a purity of more than 99.99% was achieved. [8]

In 2012, Wang et al. completed the layered separation of PV modules by two-step heat treatment, recovered the glass, and gradually recovered the silicon and copper by acid etching [9].

2.3. Description of two treatment methods
Among these methods, the research of Radziemska & Ostrowski and Kang et al. is especially remarkable. This paper tend to make a more concrete elaboration. In the research of Radziemska & Ostrowski, The universal recycling procedure for silicon solar cells is divided into two main steps:

i. Using 30% KOH for removing Al metal coatings (temperature 60 – 80°C, time 2 – 3 min)

ii. Etching, using the mixture: 250 ml HNO3 (65%): 150 ml HF (40%): 150 ml CH3COOH (99.5%) +3 ml Br2 for removing Ag coatings, AR coatings and n-p junctions (temperature 40°C, time 9 s).

During their research, they found that the standard acid etching mixtures contain high amounts of toxic nitrogen oxides, fluorides and different silicon species, which required expensive disposal measures. Moreover, autocatalysing reactivity effects complicate the controllability of these processes, which leads to losses of silicon and increased costs. The compositions of etching solutions were adjusted individually for different silicon cell types. Despite they made efforts to formulate a universal etching solution composition, the results showed that solutions need to be modified according to the type of waste PV modules. Finally, they made a practical suggestion about the application of their research, The most valuable recycled materials, silicon, can be recycled from the PV modules that do not meet the quality requirements, spent cells or cells damaged as a result of improper transport conditions, faulty assembly or misuse.

Kang et al. divided the process for recovering silicon and glass into three steps. The first step was the recovery of the glass from waste PV modules by using organic solvents, which caused the expansion of the EVA. In the next step, the EVA was removed by thermal decomposition. Through the two steps, the PV cell, which contained metal impurities including metal electrodes, AR coating, and a p-n junction layer was obtained. The final step aims at the recovery of silicon by using the chemical etching. The highest yield of recovered silicon they achieved was 86% when the PV cell was immersed in the chemical etching solution for 20 min, together with the surfactant which accounted for 20% of total weight of the solution at room temperature. The purity of recovered silicon is 99.999%. Generally, this method achieved the recovery of glass and high purity of silicon in an ideal yield.

3. Conclusion
The dramatic development of the photovoltaic (PV) module market will inevitably result in a remarkable production of considerable waste and pollution in the near future. The corresponding treatment method has also come out for this new kind of solid waste. They are making great efforts on alleviating the problem of environmental pollution and resource waste. However, current mainstream treatment methods, such as heat treatment, chemical treatment and physical treatment methods all require rigorous reaction conditions, high energy consumption and complex process. Due to the use of organic solvent, the treatment process produces a large number of toxic and harmful effluent. Above all, the most valuable and expensive material, crystalline silicon in PV modules cannot be recycled in the form of complete silicon wafer, which can be directly reused in the assembly of new photovoltaic modules.

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