

End-of-Life Management of Photovoltaic Panels: Trends in PV Module Recycling Technologies





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End-of-Life Management of Photovoltaic Panels: Trends in PV Module Recycling Technologies

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<Photos of cover: PV module recycling facility>

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Abbreviation	S
Ag	silver
AIST	National Institute of Advanced Industrial Science and Technology, Japan
Al	aluminium
ARC	anti-reflection coating
c-Si	crystalline silicon
CdTe	cadmium telluride
CENELEC	European Committee for Electrotechnical Standardization
CIS	copper indium selenide
CIGS	copper indium gallium (di)selenide
Cu	copper
EVA	ethylene-vinyl acetate
FAIS	Kitakyushu Foundation for the Advancement of Industry, Science and Technology, Japan
GW	gigawatts
IEA	International Energy Agency
IEA PVPS	International Energy Agency Photovoltaic Power System Programme
IRENA	International Renewable Energy Agency
ITRI	Industrial Technology Research Institute, Taiwan
KETI	Korea Electronics Technology Institute
KIER	Korea Institute of Energy Research
KRICT	Korea Research Institute of Chemical Technology
METI	Ministry of Economy, Trade and Industry, Japan
MOE	Ministry of Environment, Japan
MOTIE	Ministry of Trade, Industry and Energy, Republic of Korea
MW	megawatts
NEDO	New Energy and Industrial Technology Development Organization, Japan
OECD	Organisation for Economic Cooperation and Development
PCT	Patent Cooperation Treaty
PV	photovoltaic
PVF	polyvinyl fluoride
R&D	research and development
SEIA	Solar Energy Industries Association
TUAT	Tokyo University of Agriculture and Technology, Japan
WEEE	waste of electrical and electronic equipment
WIPS	Worldwide Intellectual Property Service

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Foreword

Photovoltaic (PV) technology is one of the most promising technologies for improving energy security and mitigating climate change. The PV market is growing rapidly, and further market expansion is expected all over the world. In addition to its positive impacts on energy security and climate change, PV technology is also among the most environmentally friendly technologies of all energy and electricity generation technologies, particularly when evaluated from a life-cycle viewpoint, including end-of-life management. This means that proper end-of-life management is an indispensable issue for "clean" energy technologies.

All technologies eventually degrade to where they enter their end-of-life stage, eventually requiring replacement. PV modules have a useful lifespan of approximately 30 years. With PV deployment increasing exponentially, the number of PV modules that reach the end of useful life will also greatly increase after the time lag of operation, accumulating proportionately as waste. A report published by International Energy Agency Photovoltaic Power Systems Programme (IEA PVPS) Task12 and the International Renewable Energy Agency (IRENA) in 2016¹ projected waste PV modules globally to amount to 1,7–8,0 million tons cumulatively by 2030 and to 60-78 million tons cumulatively by 2050.

Generally, sustainable waste management offers opportunities known as the 3Rs: reduce, reuse, and recycle. When a product cannot be repaired or reused, recycling is the next preferable option before disposing as waste. In anticipation of the large volume of waste PV modules, and to retain PV's position as a clean energy technology, PV module recycling has become an important emerging topic, and various discussions and activities have been conducted and developed by governments, organizations, and companies. (Discussions on the topic of PV module reuse are considered to be less mature.)

The EU Waste Electrical and Electronic Equipment (WEEE) Directive revised in 2012 (2012/19/EU) addresses the waste management of all electronics, including waste PV modules, in the EU member states. It requires 75%/65% (recovery/recycling rate) of waste PV modules by mass to be recycled through 2016, then increases to 80%/75% through 2018 and to 85%/80% thereafter. In addition to such a regulatory scheme, it is obvious that recycling technologies must be available to meet the increasing requirements of WEEE. Available recycling facilities that treat PV modules can meet current WEEE requirements; additional research and development (R&D) is required to meet subsequent WEEE requirements at reasonable cost.

This report aims to provide an international survey of trends related to the development of PV module recycling technology from the perspective of both the private and public sectors. For the private sector, we review patents, as patent filing has been increasing since 2011. For the public sector, we review R&D plans and investments made by many countries active in PV module recycling technology development.

Because it takes a long time to develop and commercialize new technologies, we hope that this report will accelerate technology development through transparent sharing of status and insight pertaining to the development of PV module recycling technologies. Managing end-of-life PV modules to recover valuable materials that can displace virgin ones is an important step toward meeting the challenge of sustainably.

¹ IEA PVPS Task12/IRENA: End-of-Life Management: Solar Photovoltaic Panels, June 2016

Executive Summary

While the recycling of waste photovoltaic (PV) modules has already begun to be commercialized, various technologies for PV module recycling are under development in order to improve process efficiency, economics, recovery and recycling rates, and environmental performance. To meet the needs for future recycling and recovery operations, further efforts including the acceleration of technology R&D, are expected.

In this report, an overview of trends in the development of PV module recycling technologies is given from the perspectives of patents and national R&D projects, and expected upcoming issues related to PV module recycling technologies are addressed.

Background on PV recycling approaches

For this report, the recycling of two main classifications of PV cell technologies are considered: crystalline silicon (c-Si), which is the dominant cell technology of existing and currently sold modules; and compound PV technology, which includes thin film modules like cadmium-telluride (CdTe) and copper-indium-gallium-selenium (CIGS).

Recycling technologies for c-Si PV modules and compound (CdTe and CIGS) PV modules have different characteristics owing to differences in the module structures and the metals contained in them. One important difference is that the objective of eliminating the encapsulant from the laminated structure of compound PV modules is to recover both the cover glass and the substrate glass which has the semiconductor layer, whereas the objectives for c-Si modules is separating and recovering glass, Si cells, and other metals.

Processes for c-Si PV module recycling can be roughly divided into those that eliminate the encapsulant from the laminated structure of the module and those that recover the metals from the Si cells. Eliminating the encapsulant from the laminated structure is one of the most difficult and some approaches such as thermal, mechanical, and chemical approaches are available. Recovering metals from Si cells can be achieved by chemical approaches such as etching; another viable method is a treatment in the metal refinery industry.

With regard to the recycling of compound PV modules, processes are roughly divided into those that eliminate the encapsulant from the laminated structures and those that recover the metals and substrate glass. To eliminate the encapsulant from laminated structures, three approaches such as thermal, mechanical, and optical approaches have been developed. To recover semiconductor metals and substrate glass, chemical approaches such as etching are effective. When a substrate is recovered without breakage, mechanical scraping may be an alternative process.

Patent trend for understanding PV recycling technology

Recycling technologies must be available to address future waste from end-of-life PV modules. Therefore, numerous R&D projects have been conducted to optimize recycling efficiency or improve performance. Analysis of trends in past and current PV recycling technologies can provide insight into the direction of future developments. Many resources are available for an analysis of trends in PV recycling technology, including books, technical papers, and internet resources. However, patents may be a particularly practical

resource for technology trend analyses because they are often seen as a pre-requisite for commercialization and represent evidence of private-sector investment in specific technology areas. Taking this into consideration, an analysis of trends in patents for PV recycling technologies is conducted to complement this report's review of existing technologies and publicly-funded R&D projects in the second main section of this report.

Patents were examined from 1976-2016 in the following countries; Europe, Germany, France, the UK, the U.S., China, Japan, and Korea including the patent cooperation treaty (PCT). Out of a total of 6 465 patents identified in the initial search, after screening to ensure relevance to recycling of PV modules (and not manufacturing waste), 178 patents were positively identified and included in the analysis herein. Detailed information such as patent title, filing year, country, filing number/date, patent number/date, assignee, and legal status on the patents is provided in the Appendix of this report. Also, the patent list will be included in the database of IRENA-INSPIRE², which is an on-line database of patents related to renewable energy technologies and will be expanded based on the research contained in this report to include patents for recycling of renewable energy technologies.

Of the total of 178 PV recycling patents, 128 pertained to c-Si modules and 44 for compound module types, the latter of which are classified here as cadmium telluride (CdTe) and copper indium (gallium) selenide (CI(G)S) modules. More patents for c-Si module than for compound module might have relevance to installation market trends, which demand for recycling technologies. At present, c-Si PV modules occupy most of the installation market. In c-Si module, starting with a patent filed in 1995, PV recycling patents increased to 26 in the peak year (2011). In compound module, PV recycling patents increased to 10 in the peak year (2012), starting with two patents filed in 1997.

In a patent trend analysis of c-Si module recycling technology, a drastic increase in patent filings occurred in China since 2011 (48% of 128 c-Si recycling patents), followed by Korea and Japan, much more so than for other countries examined. It is interesting to note that Asian countries are actively interested in PV recycling technologies. Analysis of which component of the PV module was targeted as the way to separate the module reveals that 45% of patents focus on separating module components by removing encapsulants (mostly ethylene-vinyl acetate [EVA]). A mechanical method, used mainly in China, accounts for 40% of the total. Analysis of recovered materials indicate that many patents have been filed for the recovery of components such as Al frames, glass, and solar cells through the method of module separation but not for that of individual materials such as Si, Ag, and Cu from c-Si modules.

With regard to compound PV module recycling technology, there has been no great increase since the first patent for a compound-based PV module recycling technology was filed in the United States in 1997. The largest number of filings took place in the United States, with 27% of the total of 44 patents, followed by Japan, China, and countries in Europe. Analysis of components targeted in recycling compound PV modules shows no major differences: 53% for EVAs and 47% for semiconductor materials. A combined method of more than two single methods account for 64% of the total, and it is followed by single methods: thermal, optical, mechanical, and chemical. Analysis of recovered materials shows that the recovery of

² http://inspire.irena.org/Pages/default.aspx

semiconductor materials is the more important than that of glass in compound PV module recycling technologies.

There are some comparisons between the patents for recycling of c-Si and compound PV modules. The patent assignees for compound PV recycling are corporations in most countries (95% of the total of 44), which contrasts to the case of c-Si in which both corporations and public entities like research institutes and universities are split. This difference suggests that the patent technologies related to compound PV module recycling could be more likely to be commercialized. According to the analysis result of components targeted in compound PV recycling, the similar percentages between EVAs and semiconductor materials imply a trend toward high-value recycling (where higher fraction of the mass of PV modules are separated and recovered) rather than simple bulk separation (which leaves significant mass of materials mixed or unrecovered); patents for compound PV module recycling in many countries claim a "total-recycling" process that covers all recycling steps by combining methods, from module separation to material recovery. The recycling technologies that combine several methods to address compound PV take up 64% of the total, which is in contrast to c-Si recycling technologies with only 25% of the total represented by combination recycling technologies. Most patents for compound PV recycling address the total process without concentrating on any specific components or materials, whereas many patents related to c-Si were filed focusing on specific target components. A compound PV module is manufactured by the continuous deposition process, but a c-Si module is based on the assembly with various components such as glass, solar cell, and Cu ribbon. Due to a structural difference between the both modules, a single method with a focus on disassembly is not effective for recycling compound PV modules, even though the method can be effectively used for at least bulk material separation for c-Si modules. For instance, glass cannot be recovered from a compound PV module by the single method because semiconductor materials remain on the surface of glass after module separation. Therefore, an additional step is needed to remove the semiconductor materials, which is the reason that the combination method is preferred for recycling compound PV modules.

Technology R&D trend for upgrading PV recycling processes

To improve PV recycling processes, several technology R&D projects have been implemented. Recycling technologies for both types of modules have different aspects owing to the differences in module structures and the metals contained in them.

As for c-Si PV modules, a mechanical approach, e.g. crushing and sorting, is currently commercialised in Europe. Metals will be recovered from remaining and separated materials by additional processes. However, the capacity of the treatment of waste PV modules is not very large, and the glass recovered is recycled as a low-grade product. Preparing for future mass treatments, several technologies are under development to realize economical processes, achieve higher recovery/recycling rate, and improve the quality of recovered materials.

After pre-disassembly for removal of the metal frames and terminal boxes from the modules, processes for PV module recycling can be roughly divided into eliminating encapsulant from laminated structure and recovering metals from the Si cell. Eliminating the encapsulant from the laminated structure (i.e., delaminating) is the most difficult process and the most important target of recycling technology R&D.

As a process for eliminating the encapsulant from the laminated structures, thermal approaches, mechanical approaches and chemical approaches can be used. The thermal approach is a combustion process; the expected materials recovered are glass, Si cells, and electrode ribbons. Under certain conditions, glass and Si cells can be recovered without breakage, which is the benefits of this approach, as is the expected higher value of the recovered materials for recycling. If the cells have flaws such as edge chipping and/or micro-cracks they typically cannot be recycled into an intact wafer and would be allocated as Si raw materials. On the other hand, the thermal approach will require a mass treatment to increase its economy and efficiency. It was also found that higher energy consumption will be a critical issue; thus, processes that consume low energy, for instance, during the heat recovery step are required. When burning a fluoride-based backsheet with other structures, it becomes necessary to plan countermeasures for the generation of fluorine gas. Cutting the encapsulation layer, scribing non-glass layers, scribing glass, and crushing/grinding technologies are examined as a mechanical process. The first two technologies can recover glass without breakage and other technologies can recover broken glass, though Si cells cannot be recycled as Si wafers. For glass of a higher quality and recovery rate, processes that are without breakage are superior, and may extend to material other than glass. These mechanical technologies are basically combined with a post-treatment step, typically a chemical treatment, to separate Si chips and other metals from the remaining mixture. A mechanical process will consume less energy compared to a thermal process; but combinations that involve thermal processing consume more energy, and combinations with chemical processes may require improving the processing speed and treatment of waste chemicals. The chemical processes, such as the use of solvent treatments to eliminate the encapsulant from the laminated structures, will be technologically feasible and will enable the recovery of Si cells. However, such processes require long treatment times and require liquid waste treatment steps as well. Although they may not be suitable for mass treatment even if environmental issues are resolved, they may be suitable as on-site, small-scale treatment, akin to combinations of thermal and mechanical processes for the recovery of Si cells and metals.

Recovering metals from Si cells can be achieved by chemical approaches such as etching with acid or alkali hydroxide, for example, and a proper treatment for chemical waste (e.g., hydrofluoric acid) is indispensable. Another method is a direct treatment by a metal refinery company.

With regard to the recycling of compound semiconductors PV modules, a combination process involving mechanical (crushing) and chemical etching is in operation on a commercial scale. However, preparing for the future with regard to waste PV modules, several additional technologies are under development.

Processes are roughly divided into those that eliminate encapsulant from laminated structures and those that recover metals and substrate glass, after the pre-disassembly process. An important difference with reference to c-Si modules is that the objective of eliminating the encapsulant from the laminated structure is to recover both the cover glass and the substrate glass with the semiconductor layer, while separating and recovering glass, Si cells, and other metals form the objectives for c-Si modules. After eliminating the encapsulant from the laminated structure, the metals and substrate glass can be separated and recovered effectively during the next step of the process.

In addition to the already proven crushing technology, combustion as a thermal approach, cutting the encapsulation layer as a mechanical approach, and a laser treatment as an optical approach have been

developed to eliminate the encapsulant from the laminated structures. These processes will enable the separation of double-glass structures and recovery of cover glass components without any damage or contamination. Under certain conditions, substrate glass with the semiconductor layer will be recovered while also maintaining the shape. Considering the treatment speed and yield during the next step for the recovery of metals from substrates, crushing the substrate will also be an effective approach. However, non-damaged glass and glass cullet components with a larger particle size are attractive, as they offer the potential to improve the recovery/recycling rates. These new approaches will have technical aspects similar to the technologies used with c-Si modules, because separating laminated structures as cover glass components, and other layers with them, will enable the recovery of Si cells. Indeed, one combustion technology is feasible for use with c-Si, thin-film Si, and CIGS. On the other hand, although crushing/grinding processes are also suitable for c-Si PV module, Si cells cannot be recycled as Si wafers.

With regard to recovering semiconductor metals from substrates, chemical approaches such as etching are promising, and substrate glass can be recovered and recycled as well. However, treatments that generate exhaust gases and waste liquids are critical issues. If a substrate is recovered without breakage, mechanical scraping may be an alternative process.

The way forward: Expected issues related to PV module recycling technology

In preparation for the significantly greater number of PV modules expected to reach end-of-life and requiring treatment in the future, and the opportunities for materials recovery therein, further technical innovations will be necessary in terms of developing recycling technologies that can both recover all valuable materials at high rates and low cost. These and other issues related to developing a viable module recycling private industry are identified in Box EX-1 as considerations at the early stages of industry formation.

Box EX-1 Opportunities for increased performance and benefits

- Technical innovation
 - > Higher recovery/recycling rate: close to 100% of module mass
 - ♦ Current target by WEEE* should be the minimum level.
 - ♦ Recovery rates of 90-95% are already achievable.
 - > More economical and environmentally-friendly processes
 - ♦ The value of the recovered materials should be carefully evaluated.
 - Prioritizing R&D towards identifying and commercializing promising lab-scale technologies that improve the environmental performance of future PV recycling operations at low cost.
 - > Higher quality and value of materials recovered
 - \diamond Methods by which to recover glass and Si cells at high purity levels will be key issues.
 - Recovered materials should be recycled into products for which the quality and value are equal to or higher than the original materials.
 - > Recycled materials recovered for use in PV modules
 - Ideally, the materials recovered should be used in PV modules as much as possible to promote circular economy.
- PV module recycling businesses
 - Scaling up: from laboratory to demonstration and commercial-scale operations
 - Among current R&D projects, only a few are in the pilot and demonstration stages at present.
 - ♦ Scaling-up will lead to further technical requirements.
 - Capacities and capabilities appropriate for a sustainable business model, including masstreatment and on-site processing
 - In general, a centralized facility with a large capacity for recycling treatment will contribute to effective and economical operations.
 - Smaller-scale, on-site recycling technologies are also promising pathways to service dispersed installations.
 - > Operational aspects regarding the use of recycling technologies
 - ♦ Securing a certain amount of waste PV modules is essential for viable operations.
 - In addition to collection networks, active collaboration with entities that use recovered/recycled materials from the technologies developed should be sought.

* Annual recovery/recycling target by revised WEEE Directive (2012/19/EU): up to 2016 - 75%/65%

(recovery/recycling rate), from 2016 to 2018 – 80%/75%, from 2018 and beyond – 85%/80%

1. Background and Recent Status of End-of-Life Management of PV Modules

1.1 Trends and forecast of PV installation

The deployment of PV technology has grown drastically in recent years. Globally, newly installed capacity reached 50 GW/year in 2015 [1] and 75 GW/year in 2016 [2], leading to a cumulative capacity of 227 GW by 2015 [1] and 303 GW by 2016 [2]. The leading PV markets today are Europe, China, Japan, and the United States (see Fig. 1-1 and Fig. 1-2). However, markets in other regions have been rapidly expanding in recent years as well.







Given that PV is becoming one of the most economically and environmentally competitive electricity generation technologies globally, and therefore offers a viable solution for the necessary decarbonisation of energy systems [3-6], it can be foreseen that PV deployment will continue to expand around the world.

For example, Fig. 1-3 shows the forecast of PV electricity by region to 2050 according to the International Energy Agency [IEA] [3]. The forecasted cumulative PV capacity globally will be 1 720 GW by 2030 and 4 675 GW by 2050. In addition to current PV market leaders, increased deployments in India, Africa, the Middle East, and other non-OECD regions are expected.



Fig. 1-3 Forecast of PV electricity production, according to the IEA PV technology roadmap [3]

1.2 Waste PV modules projections

The expansion of the PV market means an increase in waste PV modules in the future. As PV technology offers economic and environmentally friendly electricity production, stakeholders for PV deployment should implement environmental processes and policies, including responsible end-of-life management strategies. A framework supporting the early development of end-of-life strategies will foster good progress towards comprehensive policies. A better understanding of projections of future waste amounts and waste composition helps to establish the basis of such a framework.

PV modules have a typical lifespan of 30 years. However, it has been observed in the market that some PV modules have appeared in the waste stream earlier than expected due to damage during the transportation and installation stages, initial failures after start-up operations, technical and physical failures during operation caused by severe environmental conditions, and unexpected external factors including natural disasters.

Considering this early appearance of waste PV modules, a previous analysis by IEA PVPS Task12 and the International Renewable Energy Agency (IRENA) [7] estimated the future amount of waste PV modules. The projection of cumulative PV waste volumes to 2050 was based on IRENA (2030) and IEA (2030-2050) PV system deployment trajectories, converted through a Weibull distribution that incorporated statistical data on early failure modes of historic PV modules. The conversion ratio between weight and power (W) for historic and projected future PV modules was fitted by an exponential curve based on the trend from the past to today.

Fig. 1-4 shows the estimated cumulative waste volumes of end-of-life PV modules around the world. In the regular-loss scenario, PV module waste amounts to 43 500 tons by 2016 with an increase projected to 1,7 million tons by 2030. An even more drastic rise to approximately 60 million tons can be expected by 2050. The early-loss scenario projection estimates much higher total PV waste streams, with 250 000 tons alone by the end of 2016. This estimate would rise to 8 million tons by 2030 and a total of 78 million tons by 2050, as the early-loss scenario assumes a higher percentage of early PV module failures than the regular-loss scenario.



Fig. 1-4 Estimated cumulative global waste volumes of end-of-life PV modules, by IRENA/Task12 [7]

1.3 Recent approaches for the end-of-life management of waste PV modules in some regions

Both regulatory and technological approaches are needed to optimize end-of-life management plans and they should be well integrated. A range of potential options exist for end-of-life PV module management and should be adapted to the unique conditions of each country or region.

The European Union (EU) has adopted PV-specific waste regulations. In other parts of the world, little specific legislation for handling end-of-life PV panels yet exists, and PV waste is typically handled under each country's legislative and regulatory framework for general waste treatment and disposal. However, policy approaches for accelerating PV end-of-life management, including supporting technology R&D, have been developed.

Recent approaches in selected regions are summarized below.

(1) Europe

PV module recycling was mandated starting in 2012 through the Waste Electrical and Electronic Equipment (WEEE) Directive [8], which includes collection, recovery, and recycling targets for waste from electrical and electronic equipment, including photovoltaic panels. Since 2012, all EU member states have transposed the PV requirements into national law, requiring all producers that put PV panels on the market within the European Union to either operate their own take-back and recycling systems or join what are known as producer compliance schemes.

Corresponding to the WEEE Directive, a number of European R&D initiatives are driving the improvement of recycling technologies for the different PV technology families. These initiatives aim to decrease recycling costs and increase the potential revenue streams from the secondary raw materials recovered through the recycling process.

The European Commission also asked the European Committee for Electrotechnical Standardization (CENELEC) to develop specific PV treatment standards for different fractions of module the waste stream to support a high-value recycling approach (see Box 1-1). A supplementary standard and technical specification for PV module collection and treatment are under development within the Working Group 6 of the Technical Committee 111X "Environment" of CENELEC. The findings are due to be released in 2017 and also may be incorporated into future revisions of the WEEE Directive.

Box 1-1 Outline of the requirements developed by CENELEC

The European Committee for Electrotechnical Standardization (CENELEC) has been mandated by the European Commission (Commission Mandate M518) to develop requirements for the collection, logistics and treatment of waste electronic and electrical equipment in form of harmonized standards and technical specifications.

The general standard (EN50625-1 [9]) specifying general treatment requirements has been published and will be complemented with a series of Part 2 standards, which identify specific requirements for the collection, logistics and treatment of specific fractions of the WEEE stream.

EN50625-2-4 [10] covers the waste fraction of end-of-life photovoltaic panels and aims to assist organisations in achieving effective and efficient treatment of waste photovoltaic panels in order to

- Prevent pollution and minimize emissions
- Promote increased material recycling
- Promote high quality recovery operations
- Prevent the inappropriate disposal of photovoltaic panels and fractions thereof, assuring the protection of human health and safety, and the environment
- Prevent shipments of waste photovoltaic panels to operators whose operations fail to comply with this standard or a comparable set of requirements.

The standard follows the structure of the Part 1 standard for the general treatment requirements for WEEE. In addition to adjusting the scope and the applicable terms and definitions, the standard specifies the following administrative, organizational, and technical requirements for waste photovoltaic panels:

1. Administrative and organizational requirements

- Infrastructure shall be suitable for PV recycling operations
- A dedicated risk management process shall be maintained

2. Technical requirements

- During the handling and storage of waste PV modules, attention shall be given, but not limited, to the prevention of injuries from broken glass and electrocution
- A system to identify non-silicon based PV panels shall be established
- If a mixed treatment of non-silicon-based PV panels and silicon-based PV panels is applied, regular batch testing for compliance with the depollution requirements is required
- The treatment of all PV panels shall use technologies that allow the removal of metallic lead or lead solder to achieve specified depollution requirements
- The treatment of non-silicon-based PV panels shall use technologies that allow the removal of hazardous substances in the semiconductor layer, including contacts, to achieve the specified depollution requirements
- If it is uncertain whether a PV panel is silicon- or non-silicon-based, treatment procedures shall follow the requirements for non-silicon-based PV panels
- Fractions containing hazardous substances shall not be diluted or mixed with other fractions or materials for the purpose of reducing their concentrations
- The content of hazardous substances in output glass fractions shall not exceed the following defined limit values:
 - 1 mg/kg (dry matter) cadmium (Si-based PV) / 10 mg/kg (dry matter) cadmium (non-Si-based PV)
 - 1 mg/kg (dry matter) selenium (Si-based PV) / 10 mg/kg (dry matter) selenium (non-Si-based PV)
 - 100 mg/kg (dry matter) lead

Furthermore, the standard provides details on monitoring, sampling, and reporting requirements as well as storage requirements generally applicable to WEEE storage.

(2) United States of America

No federal regulations currently exist in the United States regarding the collection and recycling of endof-life PV modules; therefore, the country's general waste regulations apply.

California is in the process of developing a regulation for the management of end-of-life PV modules within its borders, though several steps remain before this regulation is implemented. In California's 2014-2015 legislative session, Senate Bill 489 was proposed [11], which authorises the California Department of Toxic Substances Control to change the classification of end-of-life PV modules identified as hazardous waste to universal waste. The bill is now law in California. A public notice on rulemaking will be made in fall 2017, and the rule will become effective within one year [12].

In July 2017, the state of Washington passed Senate Bill 5939, which modifies state renewable energy system tax incentives and requires a takeback and recycling program for end-of-life PV modules [13]. The law requires manufacturers to prepare product stewardship plans that describe how they will finance the takeback and recycling program and provide for takeback of PV modules at locations within the state. In lieu of preparing a stewardship plan, a manufacturer may participate in a national program if its intent is substantially equivalent to that of the state program. The Washington State Department of Ecology will develop guidance for the state program. The stewardship requirement states that manufacturers who sell solar units in the state of Washington after July 1, 2017, are responsible for financing and providing a recycling program for their units. Manufacturers who do not provide a recycling program cannot sell solar modules after January 1, 2021.

The voluntary collection and recycling of end-of-life PV modules has been provided by several PV industry stakeholders. For example, the company First Solar operates commercial-scale recycling facilities in Ohio for its own thin-film cadmium telluride (CdTe) PV products, as well as in Germany and Malaysia. The U.S. Solar Energy Industries Association (SEIA) has maintained a corporate social responsibility committee that reviews developments related to PV recycling and announced the launch of a National PV Recycling Program in September 2016 [14], as outlined in Box 1-2.

Box 1-2 Outline of SEIA's National PV Recycling Program [14]

PV Recycling Working Group within the SEIA

- Members: First Solar, SunPower, Flex, JinkoSolar, Panasonic, SolarCity and Trina Solar
- Building an end-of-life solution to ensure that clean energy solutions do not pose a waste burden for future generations
- Committed to responsible end-of-life management
- Proactively developing collection and recycling processes

SEIA's national PV recycling program

- Identify and recommend recyclers who can manage PV waste while striving to avoid landfill options
- Provide SEIA members with specific account management and members-only pricing
- Establish new and innovative processes
- Track waste over time and ensure that timely solutions and channels are available when waste volumes increase

By creating this program that aggregates the services offered by recycling vendors and PV manufacturers, SEIA and its members are making it easier for consumers to select a cost-effective and environmentally responsible end-of-life management solution for their PV products. SEIA's PV Recycling Working Group will choose Preferred Recycling Partners who offer specific benefits only to SEIA members; however, their general services will be available to all interested parties [15].

Further, SEIA is planning proactive waste management strategies in an effort to make the entire industry landfill-free. This includes the national recycling network program, which will provide a portal so that system owners and consumers know how to recycle their PV systems responsibly, and invest in research and development leading to better recycling technologies. With the goal of creating a long-term global circular economy, SEIA is thinking about how to repurpose its components into new products for a better future and plans to invest the cost savings from effective waste management into research and development of PV's "new life" after decades of service producing clean, renewable energy [15].

(3) Japan

Japan has no specific regulations for end-of-life PV panels, which, therefore, must be treated under the general regulatory framework for waste management (the Waste Management and Public Cleansing Act). The act defines wastes, industrial waste generator and handler responsibilities, and industrial waste management aspects, including landfill disposal.

Ministry of Economy, Trade and Industry (METI) and Ministry of Environment (MOE) have jointly assessed how to handle end-of-life renewable energy equipment such as PV, solar water heaters and wind turbines. In June 2015, a roadmap for promoting a scheme for collection, recycling and proper treatment was developed [16], covering the promotion of technology R&D, environmentally friendly designs, guidelines for dismantling equipment, transportation, and treatment, and publicity to users. On the basis of this roadmap, the first edition of a guideline promoting proper end-of-life treatment for PV modules including recycling was published in April 2016 [17]. The guideline covers basic information such as relevant laws and regulations on decommissioning, transportation, reuse, recycling, and industrial waste disposal (see Box 1-3). It is expected that the roadmap and the guideline will lead to further consideration of policies pertaining to the end-of-life management of waste PV modules.

In parallel with this policy approach, various technical R&D projects have been conducted (see Appendix B). The objective of these R&D projects is to develop practical approaches for PV recycling. This will be achieved by establishing low-cost recycling technology and investigating optimal removal, collection, and sorting methods.

Box 1-3 Contents of a guideline for proper end-of-life management of PV waste, in Japan [17]

Background and objectives

Parts from PV modules installed in the past already have been disposed of and it is forecasted that the amount of waste from PV modules will increase at an accelerated pace in the future. In order to support further deployment of PV technology, it is necessary to develop a framework of end-of-life management such as reuse, recycling, and proper treatment.

Although waste PV modules are properly treated under the Waste Management and Public Cleansing Act, it is important to prepare for a significant increase in PV waste modules to be disposed in the future.

The guideline summarizes existing laws and points of concerns for each stage of handling waste PV modules to inform PV owners and relevant industries.

Stages covered by the guideline

- Dismantlement
- Collection and transportation
- Reuse
- Recycling and disposal

Target audiences

 PV owners and operators, PV equipment manufacturers, installers, home builders, construction and decommissioning companies, insurance companies, reuse businesses, recycling and disposal system operators, operators of collection and transportation systems, and local governments.

(4) China

China currently has no specific regulations for end-of-life PV modules. However, related technology research has begun, and the National High-tech R&D Programme for PV Recycling and Safety Disposal Research under the Twelfth 5-Year Plan [18] has provided suggestions for policy and technology R&D.

On the policy side, the suggestions include the need for special laws and regulations for end-of-life PV panel recycling, targets for recycling rates and the creation of necessary financial frameworks. On the technology and R&D side, recommendations concentrate on developing and demonstrating high-efficiency, low-cost and low-energy-consumption recycling technologies and processes for c-Si and thin-film PV panels.

In the Thirteenth 5-Year Plan for 2016-2020, directions for accelerating the end-of-life management of waste PV modules will be given. Although this plan has not yet been published, expected directions are shown in Box 1-4.

Box 1-4 Directions for EOL management of PV modules proposed for China's 13th 5-Year Plan [19]

- Thin-film PV module recycling technology

 CdTe
 ClGS

 Empirical demonstration and key equipment development of efficient, low-cost, low-energy large-scale recycling of crystalline silicon PV module

 100MW demonstration line
 Different technologies and key equipment R&D for recycling
 Recycled material reuse

 Mobile platform development for the on-site recycling of MW-scale crystalline
- silicon PV modules
- Focus on the large PV plants in China
- Pre-treatment platform for on-site recycling to reduce the transport cost

Recycling standard specifications and policy

(5) Korea

There are no specific regulations governing the end-of-life management of waste PV modules. However, the report of "2015 energy information and policy support projects" [20] from Ministry of Trade, Industry and Energy (MOTIE) proposed the addition of a regulation mandating the reporting of PV waste disposal to the existing "Act on the Promotion of the Development, Use and Diffusion of New and Renewable Energy" as a measure to increase PV recycling. According to the report [20], it would be more efficient to add regulations covering PV waste to the existing law on renewable energy rather than create a new law specifically about PV waste. The report also recommends that a public organization should be selected to handle the registration and procedures related to reporting of PV module waste disposal, as there currently is no organization in charge of reporting of PV waste disposal.

In 2016, two new projects for PV module recycling were launched. One is an R&D project for demonstrating recycling technology by developing a recycling facility with a capacity of 2 tons per day, with a project target to reclaim unbroken wafers from PV waste modules with a yield of >70% to reduce the electricity consumption for manufacturing new PV modules. The other project [21] is non-R&D for the establishment of a PV recycling center in Korea for the management of PV waste modules. It will take five years to achieve the five missions (Box 1-5) set forth for this recycling center. This non-R&D project was awarded to the local government of Chungcheongbuk-do, which serves as the lead organization, with six other non-profit organizations collaborating: Chungbuk Technopark, KIER (Korea Institute of Energy Research), KTL (Korea Testing Laboratory), KCL (Korea Conformity Laboratories), KLRI (Korea Legislation Research Institute), and GEI (Green Energy Institute). A portion of the recycling technologies developed in the R&D project will be used for the non-R&D project to increase the capacity of the recycling center.

Box 1-5 Expected achievements of the project entitled "PV recycling center in Korea" [21]

- 1. Build a center for the recycling of c-Si and thin-film Si PV module
- 2. Establish the technology, process, and facilities for the recycling of PV modules (capacity of 3 600 tons/year)
- 3. Establish a system for the declaration, collection, and transportation of PV waste
- 4. Support a governmental announcement of the management of end-of-life PV modules
- 5. Prepare a plan to test the operation and growth of the PV recycling center

1.4 'Recycling' as a means of end-of-life management

PV modules have long service lives (the average is 30 years) and in most countries have been installed primarily in large scale systems (> 1 MW), particularly since the middle of the 2000s. It has been predicted that significant amounts of PV module waste will be generated by 2030 as these long-lived PV systems age, as shown above.

The end-of-life management of waste PV modules offers opportunities related to each of the three Rs of sustainable waste management, as elaborated in Box 1-6.

Among the 3Rs, recycling systems and their concomitant regulatory schemes to deal with PV end-of-life management have only recently emerged.

End-of-life management with material recovery is preferable to disposal in terms of environmental impacts and resource efficiency as a way to manage end-of-life PV systems [22]. When recycling processes themselves are efficient, recycling not only reduces waste and waste-related emissions but also offers the potential for reducing the energy use and emissions related to virgin-material production. This could be particularly significant for raw materials with high levels of impurities (e.g., semiconductor precursor material), which often require an energy-intensive pre-treatment to achieve required purity levels. Recycling is also important for the long-term management of resource-constrained metals used in PV modules.

PV module recycling technologies have been studied and developed to a considerable extent over the past decade, yet are not entirely commercialized nor have they achieved high levels of material recovery, at least for the dominant PV technology family on the market c-Si PV. Support for technological R&D can improve technology performance levels and produce greater value from recycling. In addition to material recovery from waste PV modules, how the recovered materials can be recycled as materials is significant. Material recycling often lacks the quality levels needed to achieve the maximum potential value. However, success in technological R&D could help close this gap and enable the improved and efficient recovery of raw materials and components.

Box 1-6 Opportunities related to sustainable waste management: the 3Rs

Reduce

As R&D and technological advances continue with a maturing industry, the composition of a typical PV module is expected to require fewer raw materials. In addition, hazardous materials are typically subject to rigorous treatment requirements with specific classifications, depending on the jurisdiction. Given current trends in relation to R&D and module efficiency, the raw material inputs and toxicity for both c-Si and thin-film technologies could be reduced significantly.

Reuse

Rapid global PV growth may result in an associated secondary market for panel components and materials. Early failures in the lifetime of a module present repair and reuse opportunities. Potentially, repaired PV modules can be resold on the world market at a reduced market price. Even operational but underperforming panels by standards of the first owner may meet expectations of a second owner. However, it should be noted there are several concerns that complicate secondary markets, such as product safety, voiding of warranties, future liability, voiding of feed-in-tariff agreements, and balance-of-system costs.

Recycle

As current PV installations reach the final decommissioning stage, recycling and material recovery will be preferable to module disposal. The nascent PV recycling industry typically treats end-of-life PV modules through separate batch runs within existing plants that were built to recycle one of the main materials of a PV modules, e.g., glass or metal. This allows for material recovery of major components and meets current regulatory requirements (i.e., in Europe). In the long term, however, dedicated module recycling plants can increase treatment capacities and maximise revenues owing to better output quality levels and the ability to recover a greater fraction of embodied materials.

This report will provide an overview of trends in the area of PV module recycling technology.

In order to understand the trends in past and current photovoltaic module recycling technologies and to predict future technological trends, an analysis of trends in patents in the field of photovoltaic recycling technology is initially conducted. Second, recent technologies associated with PV module recycling under national R&D projects are summarized.

Based on the results, the expected directions toward the accelerated technological R&D on PV module recycling as well as end-of-life management will be discussed.

2. Analysis of trends in patents for PV recycling technology

2.1 Overview of patent trends analysis

Analysis of patent trends in PV recycling technology was conducted in order to understand the trends in development and commercialization of past and current PV module recycling technologies and to predict future technological trends. The scope of this section covers published³ patents related to PV module recycling technologies in Europe (EP), Germany (DE), France (FR), the UK (GB), the U.S. (US), China (CN), Japan (JP), Korea (KR), and the PCT⁴ (patent cooperation treaty) during the period between January 6, 1976 and December 9, 2016. The search database used in this section was the online WIPS⁵ (worldwide intellectual property service) system. The scope of this search was limited to the title of the opened patent, the summary, and independent claims (those that stand on their own). If classification was not clear using only independent claims dependent claims (those that depend on a single claim or on several claims and generally express particular embodiments as fall-back positions) were also considered to create a database for analysis.

For this analysis, the technologies were classified according to PV module types: "c-Si PV modules," "compound PV modules," and "other PV modules (e.g., organic solar cells, dye-sensitized solar cells, thinfilm silicon solar cells)." Patents identified for each of these three classes of PV technologies were then analyzed in depth according to the analysis categories of the targeted components, the processing method, and the recovered materials. Although targeted components limit the scope of the recovered materials, the recovered materials were treated as an independent minor classification, the scope of which is not limited by the targeted components. This explains why there are some patents that deal with encapsulants as a targeted component for module separation to obtain glass, cells, and copper (Cu) ribbon as recovered materials from the modules. For processing methods, patents were categorized according to which of six recycling process methods, and not according to cell types, such as single-crystalline and multi-crystalline cells in the case of c-Si PV modules. It was possible for each patent to be counted multiple times in these analyses. For example, if a single patented technology was applied to three recovered materials, such as Si, silver (Ag), and Cu, it was counted as contributing to each of these three categories. The classification of technologies is presented in Table 2-1.

The search keywords used to find related patents according to PV module type and the initial search results are reported in Table 2-2.

³ Patent filing is generally published 18 months after the priority date, i.e., after the first filing date; filing is a request pending at a patent office for the grant of a patent for the invention described and claimed by the application. The examiner may either grant the patent filing without amendments, may change the scope of the claims to reflect the known prior art, or may refuse the filing.

⁴ PCT assists applicants in seeking patent protection internationally for their inventions, helps patent offices with their patent granting decisions, and facilitates public access to a wealth of technical information relating to those inventions. By filing one international patent filing under the PCT, applicants can simultaneously seek protection for an invention in a very large number of countries.

⁵ WIPS (<u>http://global.wipscorp.com/main.do</u>) is the first online worldwide patent information service provider in South Korea.

Townst		Analysis category				
product	Module type	Targeted components	Processing method	Recovered materials		
		Frame		Aluminum (Al)		
		EVA		Glass		
		(encapsulant)		Cell		
	c-Si PV module			Silicon (Si)		
		Solar cell		Silver (Ag)		
		Copper ribbon	Maghaniaal	Copper (Cu)		
DV/ Modulo	Compound DV	EVA (encapsulant)	Chemical Thermal	Glass		
PV Module	module	Semiconductor material	Optical Electrochemical Combination	Semiconductor material (metal elements)		
	Others (organic solar cell, dye- sensitized solar cell, thin-film silicon solar cell)	EVA (encapsulant)		Glass		
		Semiconductor material		Semiconductor material (metal elements)		

Table 2-1 Classification of PV recycling technologies

Middle classification	Search formula	Number of patents	
c-Si PV modules	(((solar*) adj2 (cell* module*)) photocell* (photo* near2 cell*) photovoltaic*) and ((recycl* recover* disassemb* deassemb* dismantl* dissolu* decompos* disposal* remov* eliminat* reproduct*) near2 (glass insulat* EVA (ethylene adj vinyl adj acetate) metal copp* alumin* silv* lead silicon* cell module frame backsheet (back adj sheet) plastic rubber component) salvage)	EP : 76 DE : 121 FR : 53 GB : 92 US : 657 CN : 1022 JP : 1007 KR : 621 PCT : 103	
Compound PV modules	(module* ((solar*) adj2 (cell* module*)) photocell* (photo* near2 cell*) photovoltaic*) and ((recycl* recover* disassemb* deassemb* dismantl* dissolu* decompos* disposal* remov* eliminat* reproduct*) near2 (cadmium copper gallium tellurium ((compound) adj (solar)) CIS CIGS CZTS GaAs InP CdTe CdS* CuIn* CGSCIGSe Cu-In* CuGaS* CuZn* Cu-Zn* Cd-Te glass insulat* EVA (ethylene adj vinyl adj acetate) metal copp* alumin* silv* lead cell* module* thin-film member)) and (cadmium copper gallium tellurium ((compound) adj (solar)) CIS CIGS CZTS GaAs InP CdTe CuIn* CGSCIGSe Cu-In* CuGaS* CuZn* Cu-Zn* Cd-Te thin-film)	EP : 12 DE : 26 FR : 11 GB : 19 US : 431 CN : 218 JP : 381 KR : 311 PCT : 14	
Others (Dye- sensitized solar modules)	(((recycl* recover* disassemb* dismantl* dissolu* decompos* disposal* remov* eliminat*) near3 ((Dye adj2 (solar photovoltaic*)) DSSC DSC)))	EP : 0 DE : 0 FR : 0 GB : 0 US : 2 CN : 3 JP : 1 KR : 25 PCT : 2	
Others (Organic solar modules)	(((organ* polymer* fluorene* fullerene* thiophene* phenylene*) near3 ((solar* adj2 cell*) photocell* (photo* near2 cell*) photovoltaic*)) and (recycl* recover* disassemb* dismantl* dissolu* decompos* disposal* remov* eliminat*))	EP : 23 DE : 15 FR : 6 GB : 4 US : 246 CN : 156 JP : 120 KR : 263 PCT : 32	
Others (Thin-film silicon solar modules)	((solar* adj2 cell*) photocell* (photo* near2 cell*) photovoltaic*) and ((recycl* recover* disassemb* dismantl* dissolu* decompos* disposal* remov* eliminat*) near2 (glass insulat* EVA (ethylene adj vinyl adj acetate) metal copp* alumin* silv* lead silicon*)) and (((silicon*) near2 (amorphous)) (A-Si) (Non- crystal*) (non adj crystal*))	EP : 1 DE : 6 FR : 0 GB : 1 US : 281 CN : 43 JP : 40 KR : 16 PCT : 4	

Table 2-	2 Initial	natent	search	results	hv (search	kew	words
	' milliai	μαισπ	Search	resuits	Uy i	Search	ve a.	worus

The initial search returned many patents that were not actually for PV module recycling technologies. In some cases, the patents were more narrowly focused on recycling of wastes generated during manufacturing of module components, so they were even further off topic. However, the patents for recycling of finished components were included in this analysis. Table 2-3 reports the counts of patents after screening for relevance to PV module recycling – hereafter referred to as "effective patents." The screening process included adding patents missed in the patent search but were known to the authors.

There were only six effective patents for "other PV modules," which is too small a sample from which to draw conclusions based on trends. Thus, the further analysis was limited to "c-Si PV modules" and "compound PV modules." Detailed information such as patent title, filing year, country, filing number/date, patent number/date, assignee, and legal status on all of the effective patents related to PV recycling technology in Table 2-3 is presented in the appendix of this report, which will also be available to find them in database of IRENA-INSPIRE⁶. In order to retain the rights of the patents, payment of an official fee is periodically necessary. Although patents are abandoned by non-payment due to economic circumstances of assignees, the technology in the patents may still be valid. Therefore, all of the published patents were considered for the patent analysis conducted here regardless of the maintenance of rights.

Middle classification	Country	Count	Sum
c-Si PV module	EP	8	
	DE	6	
	FR	2	
	GB	0	
	US	5	128
	CN	62	
	JP	19	
	KR	21	
	PCT	5	
Compound PV module	EP	5	
	DE	2	
	FR	0	
	GB	0	
	US	12	44
	CN	7	
	JP	9	
	KR	1	
	PCT	8	
Others			6
Total			178

Table 2-3 Number of effective PV module recycling patents, after screening, for each module type

⁶ http://inspire.irena.org/Pages/default.aspx

2.2 Patent trends for crystalline silicon PV modules

(1) Overview of general patent trends

Overall, during the period of our patent analysis (1995-2016), 128 patents were identified as pertaining to recycling of c-Si modules. Looking at Fig. 2-1, which analyzes the patents filed in each country (region) by year, it can be seen that there were relatively few filings in all countries until 2010. Considering the fact that the number of filings did not increase after the first patent, *recycling of solar modules and cells of silicon and its alloys* (patent number: 19541074, assignee: Siemens solar GmbH), for a c-Si PV module recycling technology was filed in Germany in 1995, it can be seen that PV recycling technology was not an active field of research in the years following the initial development of the technology. On the other hand, an increase in patent filings in all countries can be seen from 2011 onwards, to different extents among countries. The rapid increase is most prominent in China. This increase may have been due to countries directly and indirectly experiencing a rise in PV waste at the same time, considering the time period during which the first PV installations were made. However, even with the increase in patent filings after 2010, the gradient is not very steep for most countries, with the exception of China. However, even in China, with the exception of a spike in 2011, the rate of increase appears to be similar to that in other countries.



Fig. 2-1 Patents for recycling of c-Si PV module filed by year

Looking at country/region specific shares in the total effective patent analyzed here, China accounts for nearly half of patent filings (see Fig. 2-2) most likely due to expected waste from significant installations. China is followed in PV module recycling technology patent filings by Korea, Japan, Europe, Germany, and the U.S. In other words, research and development with regard to PV recycling technology has been more active in Asian countries in recent years. Although China appears to have been a latecomer to patent filings for recycling technology, the sharp increase in the number of filings in China means that now it is responsible for around half of all filings. On the other hand, Germany, Europe and the U.S., which developed the technologies for PV recycling in the early years, appear to hold fewer patents at present.

Dividing the assignces by organizational type - corporations, research institutes (universities included), and individuals - the majority of patent filings in Europe, France, the U. S., China, and Japan were filed by corporations, while the majority in Korea were filed by research institutes. A larger number of corporate patent filings reflects greater commercial interest in the technology and suggests that the technologies are



closer to being commercialized.

Fig. 2-2 Cumulative number of patent filings on c-Si PV module recycling by country/region (1995-2016)



Fig. 2-3 Patent assignee organizational type for c-Si PV module recycling by country/region

(2) Patent trends according to targeted components

In order to recycle PV modules, the modules must undergo the processes of dismantling, separation, and recovery. The components resulting from such dismantling/separation/recovery processes can largely be classified into the categories of frames, encapsulants (mostly EVA), solar cells, and copper (Cu) ribbons. These components, including glass and backsheets, are essential parts in the module manufacturing process. Therefore, it is desirable to consider PV recycling in terms of the degree of interest in certain components, as an ideal recycling process is the reversal of manufacturing. Glass and backsheets were not considered in this analysis because there were no patents focused on the recycling of these components due to the presence of numerous patents in areas similar to module glass such as LCD and also the limited reusability of the backsheets.

Looking at the module components that become targets for recycling, most patents were filed for ethylene-vinyl acetate (EVA)-related processing, which involves the removal of the encapsulant (see Fig. 2-4). This is followed by technologies to recycle frames and solar cells. Far fewer patents were filed in relation to the recovery of Cu ribbons compared to those of other components.



Fig. 2-4 Patent filings on c-Si PV module recycling according to targeted components

With regard to the breakdown by country (see Fig. 2-5), EVA processing technology accounts for the majority of patents filed in many countries, with the exception of Germany and China. Thus, module separation through EVA removal is shown to be the approach of greatest interest in c-Si recycling.







Fig. 2-6 Targeted components on c-Si PV module recycling by time period

In order to understand how the target components changed over time in recycling technologies for PV modules, three time periods - up to 2005, 2006–2010, and 2011 onwards - were defined and the proportions of each component during the respective time periods were analyzed. As shown in Fig. 2-6, the majority of technologies for which patents were filed up to 2005 were for EVA processing, with a smaller portion targeting solar cells. There were no patents filed for technologies pertaining to frames or Cu ribbons. From 2006 to 2010, the market scarcity of Si became emphasized, leading to similar numbers of EVA and solar cell processing patents being filed. Additionally, a small number of frame processing technologies began to be filed. From 2011 onwards, there was a rapid rise in the number of patents being filed for frame processing technologies, alongside large increases in EVA and solar cell processing technologies. Patents for Cu ribbon processing technologies also began to be filed. The rapid rise in patents for frame processing

technologies since 2011 can be attributed to the sharp growth in related patents being filed in China. It can be seen that Chinese inventors have had more interest in frame dismantling compared to other countries, possibly because this technology is relatively less complex but has the highest profitability among module recycling steps. The profitability depends on the market demand of secondary materials. To maintain the same level of profitability, the recycler would need to recover a relatively larger amount of material when the price of recovered materials is low than when the price of recovered material is high. In this regard, the frame material (typically aluminum) is at an optimal level of price/quantity ratio amongst PV module materials.

(3) Patent trends according to the processing method used

This section looks at the processing methods used in the recycling of PV modules. Mechanical processing accounts for 40% of the total number of patents in 1995-2016 (see Fig. 2-7), and represent a significantly higher proportion in China than for other countries examined, whereas the allocations of patents across methods were more even in other countries (Fig. 2-8).

With regard to the other processing methods, chemical processing constitutes 19% of patents examined and thermal processing 15%. Even though thermal method was not a large amount, the method can be found in patent filings of most countries/regions in this study (see Fig. 2-8). The majority of thermal methods were for the thermal decomposition of EVAs. Although the first patent for PV recycling was for thermal processing, the further development of this method was limited, given no patenting from 2006 to 2011 and only 14 patents since 2011 (Fig. 2-9). A patent for an optical processing method (laser cutting) was recently filed in China, in 2016, forming 1% of patents identified in our search.



Fig. 2-7 Proportion of patent filings for c-Si PV module recycling according to the processing method used









In order to understand how processing methods for the recycling of PV modules have changed over time, three time periods - up to 2005, 2006-2010, and 2011 onwards - were defined and the proportions of each processing method during the respective time periods were analyzed, as shown in Fig. 2-9. Until 2005, processing methods filed were thermal, chemical, or a combination of different methods, while no patents were filed for mechanical processing methods. However, from 2006 to 2010, mechanical processing methods began to be filed, while chemical and combined methods also continued to be filed. However, there were no thermal processing technologies filed during this middle period. Patent filings from 2011 onwards cover all mechanical, thermal, chemical, and combined methods as well as an optical method. This reflects growing interest in PV recycling in recent years as well as the diversification of approaches with active research and development.

(4) Patent trends according to recovered materials

The aim of PV module recycling is to recover specific target materials from PV modules. These materials include Al (in the frames and back contact electrodes of solar cells), solar cells, glass, Si, Ag, and Cu. With regard to patent filing trends, according to the target materials recovered, the majority of patents were for technologies to recover Al, solar cells, and glass (see Fig. 2-10). It is important to remind that patents can be listed twice if more than one material was targeted for recovery. Fig. 2-10 reveals there are some overlapping categories for solar cells, since the solar cells include each material such as Si, Ag, etc. Some patents just claim the recovery of a "solar cell" form and don't present the recovery of each material in detail, thus limiting further detailed analysis. There were also relatively few patents for technologies to recover Si, Ag, and Cu. Moreover, we found that the recovery of components such as Al frames, glass, and solar cells attracts more interest by firms than does the recovery of individual materials such as Si, Ag, and Cu.



Fig. 2-10 Proportion of patent filings for c-SI PV module recycling by recovered materials

Fig. 2-11 displays the recovered materials in the patents by the respective countries/regions where the patent was filed. In Europe, Japan, Korea, and the PCT, the majority of patents were for technologies to recover cells and glass. This reflects that most of the patents were filed for the recovery as components forms by means of module separation and not for the recovery of each of the materials in PV modules. Given that Al alloy frames make up the majority of the targeted components in China, Al accounted for the majority of the recovered materials.

In order to understand how target materials being recovered from PV module recycling technologies have changed over time, the same three time periods - up to 2005, 2006-2010, and 2011 onwards - were defined and the proportions of each recovered material during the respective time periods were analyzed, as indicated in Fig. 2-12. Until 2005, the majority of patents were for technologies to recover solar cells and glass, with a small number of patents for Si recovery. There were no patents filed for technologies to recover Al, Ag, and Cu in this early period. From 2006 to 2010, technologies to recover Si, solar cells, glass, and Al (all for Al in frame) made up the majority of filed patents, while no patents were filed for Ag and Cu recovery. This middle period was marked by a temporary Si shortage, which led to Si recovery technologies making up the majority of patent filings. From 2011 onwards, there was a substantial increase in patent filings for Ag and Cu recovery technologies together with technologies to recover Al (six patents for Al used in back contact electrodes), solar cells, glass, and Si. This is due to the change of technological trend from the recovery of specific materials or components in the past to that of higher fractions of as many materials as possible in the present.







Fig. 2-12 Recovered materials for c-SI PV module recycling by time period

(5) Patent trends by considering merging two analysis categories

Reviewing by merging two analysis categories - the target component and processing method, or the recovered materials and processing method - can be useful for analyzing technological trend in a big picture. In Fig. 2-13, a large number of mechanical methods involved apparatuses or processes for dismantling the frames from the modules among all patents for c-Si PV module recycling technologies. Frames are usually made of Al alloys and make up a significant mass fraction of c-Si PV modules, making them difficult to treat thermally or chemically. There were also considerable numbers of patents for the removal of encapsulants (mainly EVA), most of which involved apparatus to separate PV modules and for EVA-processing based on the crushing of the PV modules. Among chemical methods, the majority of patents involved the processing of solar cells recovered from modules. There were also patents of methods that chemically swell or dissolve EVAs in PV modules for the separation of the modules. The majority of thermal methods mostly involved the thermal decomposition of EVAs, while there were also some patents for solar cells (recovering in a ferrosilicon form by melting the component together with Fe) and Cu-ribbon (Cu core recovery through reduction) processing. Only one patent was based on an optical method, which involved irradiation with a cutting laser on a vertically positioned module to separate the glass from the mounted module. Regarding combination methods, the majority of patents were for EVA treatment technology, as the removal of EVAs can be done using thermal, mechanical, and chemical methods, or various combinations of the three. There were also patents for combined methods to treat solar cells, the majority of which were for Si recovery.



Fig. 2-13 Targeted components for c-Si PV module recycling by processing method

Approximately a quarter of patents involved a combination of two or more processing methods (Fig. 2-7). Fig. 2-14 reveals more information about those patents classified as using a combination of methods: which pairs of methods have been combined and to what module components are these patents targeted. Each method in the combination patent was counted multiple times in this analysis. For instance, if a technology combining mechanical and chemical methods was applied to three targeted components, it was counted as contributing to each of these three categories. The most frequently used combination involved chemical and thermal techniques, followed by mechanical and chemical, and then mechanical and thermal approaches. Looking at general trends with these combined methods, it was observed that the inclusion of a chemical method indicated that the targeted components included both EVA and solar cells, while the inclusion of thermal or mechanical processes was mostly for EVA decomposition or EVA separation by crushing modules, respectively. The processing for dismantling of frames always involved a mechanical method in the combination. There was one patent for a combination of chemical and electrochemical processing methods filed in Germany. Moreover, there were two patents filed in Japan that involved a combination that included optical methods: one method uses optical and mechanical techniques (using a lamp and a blade); and the other utilizes optical, mechanical, and thermal techniques (using a lamp and hot air).



Fig. 2-14 Targeted components for c-Si PV module recycling patents classified as using combination of methods (based on Fig. 2-7)

With regard to Fig. 2-15, although various materials can be mechanically regained from c-Si PV modules, Al is the material most commonly recovered using relatively simple mechanical methods. There were also many patents for the recovery of glass and solar cells by mechanically crushing the modules. Moreover, many materials can be recovered using chemical methods, and the largest number of patents was for the recovery of Ag, followed by patents for Si. Several patents were filed for recovering the Ag and Al used as electrodes in the front and back contacts of solar cells, respectively. The majority of patents involving thermal methods were for solar cell recovery because solar cells can be recovered simply through the thermal processing of EVAs. Of course, dismantling of the Al frame from the module should be done before thermal treatment. There were also patents that included the additional recovery of glass. Only one patent involved an optical method with laser cutting that was initially filed very recently for a method that mainly recovered glass, especially from glass-to-glass modules. Combinations of two or more methods resulted in the widest variety of recovered materials. The materials ranked in the order of patent counts are glass, solar cells, Si, Al, Cu, and Ag.


Fig. 2-15 Recovered material targets for c-Si PV module recycling by processing method

Fig. 2-16 shows how the targeted materials to be recovered differ when different combinations of processing methods are used. The most frequently used combination was chemical/ thermal techniques, followed by mechanical/chemical and mechanical/thermal approaches. There was a strong tendency towards glass and solar cell recovery when a mechanical method was involved. When chemical methods were involved, the recovered materials included glass and solar cells, as well as raw materials such as metals. Many patents involving thermal methods are for the treatment of EVAs; thus, the recovered materials are often glass and solar cells.



Fig. 2-16 Recovered materials for c-Si PV module recycling by process combinations

2.3 Patent trends for thin-film compound PV modules

(1) Overview of general patent trends

Overall, during the period of our patent analysis (1995-2016), 44 patents were identified as pertaining to recycling of compound PV modules, which includes cadmium telluride (CdTe) and copper indium (gallium) selenide (CI(G)S) module types. Fig. 2-17, based on patent filings by country and year, shows that the first two patents for a compound-based PV module recycling technology were filed in the United States in 1997: *recycling of CdTe photovoltaic waste* (patent number: 5897685, assignee: Drinkard Metalox Inc.); *recycling of CIS photovoltaic waste* (patent number: 5779877, assignee: Drinkard Metalox Inc.). No significant increase in the number of patents filed for the recycling of compound PV modules has occurred since that time.



Fig. 2-17 Patents for recycling of compound PV module filed by year

With regard to the country/regional distribution of patent filings, the largest number was filed in the United States, accounting for about 27% of the total (see Fig. 2-18). The U.S. was followed by Japan, PCT, China, and Europe in descending order for the number of patents filed for recycling technologies of only compound PV modules. If the applicants are categorized as corporations, research institutes (including universities), and individuals (see Fig. 2-19), it is found that corporations were assignees in most countries (95% of the total), which proposes that the technologies are closely linked to commercialization. There was one patent in the United States filed by a research institute and one in Germany filed by an individual.







Fig. 2-19 Patent assignee organizational type for compound PV module recycling by country/region

(2) Patent trends according to targeted components

The recycling of PV modules involves the processes of dismantling, separation, and recovery; these processes target specific components within the module. Targeted components in compound PV module recycling can be categorized into frames, EVAs (which enables the separation of the module), and semiconductor materials. Among compound PV patents, the component targeted the most related to the processing of EVAs to separate modules. This was followed by technologies for processing semiconductor materials to recover semiconductor elements. There were no major differences in the numbers of patents for each targeted component, with 53% for EVAs and 47% for semiconductor materials, which was also true for each country/region (Fig. 2-20). (Frames were not targeted in any of the patents for compound PV modules, and thus frames were eliminated from further analysis.) This equal emphasis between EVA and semiconductor materials suggests a trend toward high-value recycling for compound PV modules, rather than just bulk separation. Furthermore, the dual focus means that patents in most countries claim a total-recycling process that covers all recycling steps of from module separation to material recovery.

In order to understand how the target components changed over time in recycling technologies for compound PV modules, three time periods - up to 2005, 2006-2010, and 2011 onwards - were defined and the proportions of each component during the respective time periods were analyzed. As shown in Fig. 2-21, patents were nearly evenly distributed between EVA processing and semiconductor material processing over all time periods. Although the total number of patents filed dropped from 2006 to 2010 compared to the period before 2005, the number increased once more from 2011 onwards. This can be seen as a reflection of growing interest following the increased visibility of PV waste generation in recent years. However, it is difficult to identify technological trends given the small number of patents overall for each time period.







Fig. 2-21 Targeted components on c-Si PV module recycling by time period

(3) Patent trends according to processing methods

This study also analyzed patent trends by examining the processing methods used in the recycling of compound PV modules, as shown in Fig. 2-22. In general, technologies that combined two or more methods made up 64% of the total. This is in contrast to c-Si recycling technologies, of which only 25% involved a combination of methods. Many patents related to c-Si were filed separately by the process focusing on specific target components, whereas most patents for compound PV recycling address the total process without concentrating on any specific components or materials. A c-Si module is manufactured through the assembly of components such as glass, solar cell, and Cu ribbon produced by other manufacturers, but a compound PV module is not based on the assembly process. A single method focused on disassembly can be effectively used for at least bulk material separation for c-Si modules, but the method does not work well for recycling compound PV modules. For example, glass, which is the most valuable material considering available mass per module, cannot be recovered from a compound PV module separation, thus contaminating the glass unless a further processing step is used to remove the semiconductor materials. This is why the combination method is preferred for recycling compound PV modules.

With regard to the fraction of patents that were focused on a single processing method, a wide range of single methods was used, including optical, electrochemical methods as well as mechanical, thermal, and chemical methods. It can be seen that new methods were attempted more frequently despite the relatively small number of patents filed compared to the number filed for c-Si PV modules.



Fig. 2-22 Proportion of patent filings for compound PV module recycling according to the processing method used

Fig. 2-23 shows the breakdown of processing methods filed by country. Due to the small number of effective patents for compound module recycling, the graph should be used to confirm the prevalence of combination methods in most countries, rather than specific tendencies by country.

In order to understand how the processing methods changed over time with regard to recycling technologies for compound PV modules, three time periods - up to 2005, 2006-2010, and 2011 onwards - were defined and the proportions of each method during the respective time periods were analyzed, as shown in Fig. 2-24. Combined methods made up the majority in all time periods, with some thermal methods being filed up to 2005. From 2006 to 2010, there was a relative drop in the number of patents filed, but a patent for a new technology using an optical method was filed. From 2011 onwards, the total number of patents filed increased, together with the diversity of methods used.









(4) Patent trends according to recovered materials

Seventy-eight percent of compound PV recycling patents target semiconductor materials and those for glass constituted the remainder. In the analysis of the materials targeted for recovery in patent filings according to country/region, the recovery of semiconductor materials formed the majority in most countries (see Fig. 2-25). This can be attributed to the scarcity of semiconductor materials, making their recovery a more urgent matter. Although it is problematic to assign statistical meaning to this analysis due to the small number of effective patents, it can be seen that the recovery of semiconductor materials is the clear focus of compound PV module recycling technologies.







Fig. 2-26 Recovered materials for compound PV module recycling by time period

In order to understand how the target materials being recovered from compound PV modules changed over time, three time periods - up to 2005, 2006-2010, and 2011 onwards - were defined and the proportions of each material during the respective time periods were analyzed, as shown in Fig. 2-26. It was observed that more patents were filed in the early years when compound PV modules began to be installed and in recent years when waste modules began to be generated. It can be deduced that while technologies for both semiconductor recovery and glass recovery have been researched for the recycling of compound PV modules, more active research is being conducted on semiconductor material recovery at present.

(5) Patent trends by considering merging two analysis categories

With regard to Fig. 2-27, most of the processing methods evenly target the recycling of the both components except for electrochemical and optical methods, which results in aiming at high-value technology with multi-stage recycling. This could be confirmed by the fact that combination methods involving two or more methods made up about 64% of all patents (Fig. 2-22).



Fig. 2-27 Targeted components for compound PV module recycling by processing method

Fig. 2-28 explores whether different combinations of processing methods relate to different targeted components. The mechanical and chemical combination accounted for 36% of combination methods filed for the recycling of compound PV modules. It can also be seen that mechanical methods are included in the majority of patented combined methods, as the recycling of compound PV modules often begins with the crushing of the modules. For semiconductor materials, the majority of combination methods used involved chemical methods, and the electrochemical method was also included in some of combination methods.



Fig. 2-28 Targeted components for compound PV module recycling patents classified as using combination of methods

Looking at the recovered material breakdown by processing method (Fig. 2-29), semiconductor materials were the materials targeted for recovery in 78% of the compound PV recycling patent filings. Patents for recovering semiconductor materials were found for all processing methods, while the number

of patents for glass recovery was relatively small for all processing methods. There were no patent filings for technologies to recover glass using chemical or electrochemical methods. Based on examining the filings from the first patent to those in the present, the focus of compound PV recycling technology development has been on the recovery of semiconductor materials.



Fig. 2-29 Recovered material targets for compound PV module recycling by processing method

Patents for combinations of methods for the recovery of component materials from compound PV modules, as shown in Fig. 2-30, indicate that the combination of mechanical and chemical methods makes up the majority, followed by mechanical and thermal and then chemical and thermal approaches. The figure also shows that combinations of three methods or more are mainly for the recovery of semiconductor materials.



Fig. 2-30 Recovered materials for compound PV module recycling by process combinations

3. Overview of Technology R&D for PV Module Recycling

Technology R&D for PV module recycling processes has been implemented since 1990s [23-27]. Although, a recycling of c-Si PV modules and compound PV modules is currently commercialised, new technologies to improve process efficiency, recovery and recycling rates, cost effectiveness, and environmental performance have been continuously developed by several R&D projects. Most of such R&D projects have been publicly-funded, while it seems there are some non-subsidized projects.

In this chapter, trends in technology R&D for PV module recycling are overviewed. First, current treatment of end-of-life PV modules, and historical changes in objectives and motivations for PV module recycling are briefly summarized (chapters 3.1 & 3.2). Next, recycling technologies for both c-Si module and compound module under development are overviewed. Information on recycling technologies were surveyed by using literatures and papers, which are published by firms implementing R&D projects (including working papers from publicly-funded R&D projects).

A recycling process is roughly divided into pre-disassembly, such as the removal of the metal frames, eliminating encapsulant from laminated structure and recovering metals (and substrate, in case of compound PV modules). In the patent analysis in Chapter 2, the divide is not used because it was difficult to clearly divide contents of patents. However, in this chapter, we mainly focused on eliminating the encapsulant from the laminated structure as it is one of the most difficult and important targets of recycling technology R&D.

3.1 Current treatment of end-of-life PV modules

(1) Overview: general flow

At present, most countries around the world classify PV modules as general or industrial waste, while the EU has adopted PV-specific waste regulations. Although only moderate PV waste quantities exist on the global waste market currently, dedicated PV module recycling plants already are in operation, and the combination of low end-of-life volumes with warranty return and production scrap recycling justifies their operation.

A general flow of the end-of-life treatment process of waste PV modules can be drawn as shown in Fig. 3-1. Waste PV modules used at sites and manufacturing facilities, for example, are transported to plants operated by recyclers or intermediate processors. At the plants, intermediate processes for separating valuable materials contained in PV modules, such as glass, metals, and their compounds, are used. The valuable materials recovered are used as secondary materials for products after purification and refining by material manufacturers such as metal refinery companies. There may be a path toward implementing additional intermediate processes before treatment by materials manufacturers if necessary depending upon level of separation at the first intermediate process. On the other hand, non-valuable materials or those with little value, including dust, which recyclers, intermediate processors, and materials manufacturers generate can be disposed of in landfills. It should be noted that during the treatment flow, some materials such as polymers may be treated thermally, with the heat then recovered as fuel during advanced processes.



Fig. 3-1 General flow of the end-of-life treatment of waste PV modules

(2) Example of the treatment of c-Si modules

For the recovery and recycling of materials used in PV modules, separation of the major components such as laminated structures, metal frames, and terminal boxes (cable and polymers) is the first step. Aluminium or steel from frames, and copper from cables can become part of the already well established metal recycling loops and therefore have potential for easy recycling. After the process, the most important and technically difficult process involves the separation of laminated structures consisting of glass, Si-based PV cells and polymer layers.

In Europe, more than 15 000 tons of waste PV modules were collected by the end of 2016 by PV CYCLE, and most of them were Si-based PV modules [28]. Most such modules are treated by glass recyclers, as recycling the laminated glass component of c-Si modules is a relatively low-cost process that flat glass recycling companies can implement with little additional investment. After the glass recovery process, other materials, such as metals and other compounds, are treated by other processors. The glass recovery process, as shown in Fig. 3-2, is frequently run in batches to enable adjustments of parameters and to account for the modest quantities available for processing today. Typical equipment for removing impurities such as polymer (glue) residues or screws from the glass cullet includes magnets, crushers, sieves, eddy-current devices, optical sorters, inductive sorters, and exhaust systems. The resulting crushed-glass fraction, which may still be heavily contaminated with silicon, polymers, and metals, can be blended with other recycled glass as a thermal insulating material in the glass-foam or glass-fibre industries. However, with an increase in waste PV streams, this market may become saturated, and investments in new recycling technologies will be required.

In other countries, certain valuable metals such as silver are recovered by intermediate processors, in addition to glass, for technical and/or economic reasons.



Fig. 3-2 Example of the process of laminated glass recycling [7]

Currently, the mechanical approach is the major process used for separating the laminated structures of c-Si PV modules. This achieves a high material recovery rate according to the module mass, although some high-value materials (that are small in mass) may not fully be recovered. This current strategy offers legal compliance without the need for new PV-specific recycling investments. However, in future the treatment operators will be required to remove lead and lead-compounds from the output glass fraction. This will most likely entail additional processing going beyond mechanical treatment as required by, for example, the WEEE Directive and the implementation of the minimum treatment requirements of the standard and related technical specification for depollution. Constructing dedicated PV module recycling plants will increase treatment capacities and maximise revenue owing to better output quality. In addition, doing so will contribute to increasing the recovery rates of valuable constituents.

(3) Example of the treatment of compound modules

Thin-film modules are currently processed and recycled using a combination of mechanical and chemical treatments. The process for a CdTe module operated by First Solar, shown in Fig. 3-3, can achieve a recovery rate of nearly 90% for glass and approximately 95% for semiconductor materials by mass. The process includes the following steps [7]: 1) shredding and crushing in a hammer mill into particles of about 5 mm in size to break the lamination bonds, collecting dust in an aspiration system equipped with a high-efficiency particulate air filter; 2) etching a semiconductor layer with a mixture of sulphuric acid and hydrogen peroxide, separating the glass and larger pieces of EVA in a classifier and on a vibrating screen, and then rinsing the glass with water and drying it on a belt filter unit; and 3) extracting filtration liquids with metals via ion exchangers or precipitation, further purifying cadmium and tellurium by third parties, if desired, for reuse in the solar industry.



Fig. 3-3 Example of the process of compound (CdTe) module recycling [7]

Other than CdTe, the recycling of thin-film PV modules is still in its early stages. However, as waste volumes and the corresponding amount of waste treatment knowledge increase, the process will be improved.

3.2 Trends in technology R&D for PV module recycling

As long as the numbers of waste PV modules are not excessive, the current technological situation will be able to cover the needs for proper end-of-life management. However, recycling technologies for PV modules should be prepared for the mass-treatment of waste PV modules.

Technology R&D for PV modules recycling has been implemented in some countries and companies for twenty or more years. Past objectives or motivations for such R&D are changing along with changes in PV technology and the market situations. Table 3-1 summarizes such changes comprehensively.

Initially, the recycling of c-Si focused on recovering Si cells/wafers to reduce production costs. Subsequently, the recovery of high-value and hazardous materials came to the fore. In the case of compound, the major focus has been to mitigate environmental impacts by recovering hazardous and valuable materials with consistency and high yield.

Over the past decade, growing concerns over the efficient use of resources and increases in recovery and recycling rates for glass were recognized as economic enablers, as was the recovery of valuable and hazardous materials. The WEEE Directive in Europe accelerated this trend. Recently, recovery of high-weight components at lower costs has been the main focus of technical innovations. Recovery of low-weight valuable materials for increasing recovery and recycling rates is likely to be an additional focus moving forward. Also, improving the quality of recovered materials to improve their secondary use is an issue to be addressed.

		c-Si	Compound (CdTe and CIGS)
1990s		Recovery of Si wafers without breakage, as	Recovering hazardous materials such as
		the module cost was very high and was	Cd and Se due to environmental issues,
		dominated by the cost of the Si cell	and recovering rare metals such as Te and
			In owing to the potential resource constraint
	1		issue
2000s	First	In addition to Si wafers, recovering Ag due	Recovering semiconductor metals/layers is
	half	to high value, and recovering Pb owing to	a major objective, with the issue of resource
		environmental issues	constraint being less of a concern
	Second	Recovery of glass is also a major concern to i	increase the efficiency of resource utilization,
	half	and for increasing the recovery/recycling rate	(weight %)
2010s		Recovery of high-weight components, such	Recovery of both high-weight components
		as glass, at a lower cost is a major aim. On	such as glass and low-weight
		the other hand, low-weight valuable	semiconductor metals/layers at a lower cost
		components can be recovered if	is an innovation driver. In addition to
		economically justified. Recovering metals at	increasing the recovery/recycling rates, the
		a lower cost is likely to be a major concern.	quality of the materials recovered is also an
			issue.

Table 3-1 Changes in objectives and	motivations for PV module recycling
-------------------------------------	-------------------------------------

The treatment process of PV module recycling can be roughly drawn as shown in Fig. 3-4.

Among the processes, the most important and most difficult process is eliminating the encapsulant from the laminated structures. During this particular process the structures are decomposed and the components are separated, with metals recovered during the next steps. Due to differences in the structures and components of PV modules, separate processes for c-Si modules and thin-film modules are often distinguished.



Fig. 3-4 Separation process for PV module recycling

3.3 Technology R&D on crystalline Si PV module recycling

In this section, a brief overview of early approaches to c-Si PV module recycling is provided, followed by a more detailed overview of recent approaches.

(1) Early stages

Technology R&D on c-Si PV module recycling started in the 1990s [23-27]. At the early stage, the most important factor in this line of R&D was to recover Si cells without breakage to use as cells or wafers after a treatment.

The most difficult process was to eliminate the encapsulant from the laminated structures, e.g., separating glass, polymers, Si cells and other metals, and to recover PV cells without breakage. Approaches for eliminating the encapsulant from the laminated structures were characterised as both thermal and chemical approaches, as shown in Fig. 3-5.



Fig. 3-5 Approaches for eliminating encapsulant from laminated structures of c-Si PV modules in the early stage

a) Thermal approaches

The thermal approach typically represents combustion/burning or a cracking process. PV modules are heated in a furnace at 500-600°C, with heating in two stages. Such an approach was attempted by Solarworld [29], Solar Cells [23], Sharp [24], and AGC [24], among others. In the furnace, polymer components are burned/cracked and remaining materials such as Si cells, glass, and metals are separated manually. For a higher recovery rate of Si cells, Soltech used a fluidized bed in the furnace and attempted various layouts, such as different ways to place the modules in the bed [25]. Glass and metals removed from modules are sent for recycling. Carbonization caused by burned polymers can be prevented by controlling the furnace condition. However, it was noted that fluoride gas may cause damage to the furnace when the polymers burned included fluorinated compounds. The separated Si cells are recycled into Si wafers by etching. The recycled Si wafers can be re-produced to create new wafers after undergoing a PV cell process, being processed again in a standard cell production line and integrated into PV modules.

These R&D activities have not been commercialized for economic reasons and the limited need for actual module recycling at that time. However, such experiences have been lessons learned for recent R&D using thermal approaches.

b) Chemical approaches

A chemical approach refers to one in which PV modules are immersed in a solvents and the components are separated by chemical reactions. In general, the chemical approach requires more time than the thermal approach; however, the yield of the recovered Si cells without damage is higher in the chemical approach than in the thermal approach.

One approach by BP Solar in the 1990s involved the use of nitric acid [26]. PV modules were immersed in the nitric acid and, after a day, encapsulation (EVA) was dissolved and the glass, Si cells, and metals were separated and recovered. The recovered Si cells can then be etched by sodium hydroxide and reprocessed from wafers into cells again. Counter-measures for nitric oxide caused by chemical reactions and the disposal of waste acid after the process were found to be significant issues.

As another approach, AIST and TUAT assessed the availability of organic solvents for separating laminated structure [27]. It was observed that many organic solvents can dissolve EVA before a thermal treatment (e.g., for lamination), though most of them are not effective for EVA after a thermal treatment. Although it was observed that the trichloroethylene can swell the head parts of laminated EVA, it was concluded that an alternative solvent should be utilized given certain economic and environmental factors.

(2) Recent approaches

Corresponding to the requirements at present and expected in the future, such as regulations for higher recovering/recycling rates, and mitigating the environmental impact caused by waste PV modules and their treatment methods, various types of technology R&D activities for c-Si PV module recycling have been proposed and implemented.

Fig. 3-6 shows a diagram of recent technological R&D pertaining to c-Si PV module recycling.



Fig. 3-6 Recent R&D for c-Si PV module recycling

Technological R&D currently underway attempts to eliminate the encapsulant from the laminated structures for separating glass and other materials and recover metals from Si cells and electrodes. In some

of the R&D activities, an effective means of removing the frame and the terminal box is included in the process before eliminating the encapsulant from the laminated structure.

Eliminating the encapsulant from the laminated structures remains the most difficult process in the recycling of waste PV modules. In addition to improved thermal approaches, mechanical processes have recently been developed. Going forward, most likely the chemical approach will be combined with feasible thermal processing technologies.

Here, outlines of recent technological R&D for the recycling of c-Si PV modules are described and grouped into thermal, mechanical, and chemical approaches for eliminating the encapsulant from the laminated structures.

a) Thermal approach

The technical potential of the thermal approach was confirmed by R&D at the early stage. One of the expected advantages is that the thermal approach will be able to recover glass and Si cells without damage. After separating PV module components, such as glass, Si cells and other metals, processes are applied for recovering metals from separated materials.

FAIS (Kitakyushu Foundation for the Advancement of Industry, Science and Technology, Japan) and others developed a PV module recycling technology consisting of processes of aluminium-frame removal, back-sheet removal, and EVA resin burning for thermal recycling [30]. The processing machines used loader-unloaders devices synchronized by the system controller to treat PV modules consistently and automatically from the module loading stage to the recovery of valuable materials. As the first step, the aluminium frame is removed by an air cylinder actuator from the module. Next, the backsheet is removed by a milling machine to prevent the module glass from developing thermal cracks in the post-processing step. The aluminium frame is recycled, while the removed backsheet is disposed of as industrial waste. Modules without aluminium frame and backsheet are heated; EVA resin is thermally decomposed in a muffle furnace, and the decomposition gas is sucked and burned out. The furnace condition is pre-heated at 350°C, heated to 500°C (for c-Si), and then cooled down to 250°C. The heat generated from the combustion of the EVA resin is thermally recycled to the furnace. All components, including the glass plates, silicon cells, and electrodes, are recovered after the first three main processes for c-Si modules. The technology can separate PV module structures of c-Si, thin-film Si, and CIS; for CIS modules, the scraping of the CIS device layer is added after these processes. The technology is available for the processing of commercial modules on the market, and the processing throughput of the recycling system is approximately 12 MW/year for c-Si modules depending on the type and size. The recycling rate is nearly 95% including the thermal recycling of the EVA, which can reduce the required fuel gas by approximately 90% for the heating of the furnace. The recovered glass can be recycled into float glass without being over-crushed. Although metal recovery processes from Si cells and electrodes are not included in this type of technology, efficient Ag recovery from Si cells is possible because of the perfect separation between the glass and the Si cells. On the other hand, it is expected that Si cells will be recovered as Si materials. This technology has been relegated to the Shinryo corporation since 2015, and Shinryo is implementing a R&D project to improve the technology and commercialize it [31].

Korea Institute of Energy Research (KIER) has been studying low-cost recovery processes for unbroken solar cells from PV modules [32]. Their project focuses on recovering Si cells/wafers and metals rather than glass, with the process consisting of eliminating the encapsulant from the laminated structures to recover Si cells without damage, recycling Si cells into Si wafers, and recovering pure metals such as Ag and Cu from Si cells. Currently, PV modules are combusted at 500°-550°C under an air atmosphere to separate the glass, Si cells, and electrode metals. It has been found that conducting the EVA patterning and glass cracking steps before the combustion process is an effective pre-treatment leading to the recovery of unbroken Si cell. Additionally, it has been confirmed that Si cells thus recovered can be re-fabricated as new high-efficiency Si cells with current commercialized technology. Not only can Si cells be recovered after the combustion process, but also electrode metals and cracked glass. Although these experiments use single-cell modules, the technology will be scaling up to a pilot plant in 2017.

Korea Electronics Technology Institute (KETI) implemented R&D pertaining to the recycling of c-Si PV modules [34]. This technology includes a thermal process for separating laminated structures and a chemical etching and mechanical process. When a PV module containing one cell is heated to 480°C with a ramp-up rate of 15°C per minute, a Si cell is recovered without any damage. The Si cell thus recovered is etched by nitric acid, and Ag is separated out. The anti-reflective-coating, emitter and p-n junction of the recovered cell are removed by mechanical grinding. Subsequently, Al electrode on the rear side is removed by using potassium hydroxide. The recovered Si wafers are recycled into Si cells. The efficiency of these cells as measured in an experiment was nearly identical to that of the initial Si cell. It was confirmed that this technology would be feasible for 0,2 mm thick Si cells, as the thickness of the recovered wafer was 0,18 mm.

Chonnam National University developed a technology consisting of a thermal process for separating laminated structure and chemical etching for recovering metals [35]. With chemical etching, nitric acid and sodium hydroxide are in an ultrasonic treatment. After etching, the Si recovered is purified to >99,998% at 1 520°C with CaO-CaF-SiO₂.

The Chinese Research Academy of Environmental Sciences (CRAES) and the Electrical Engineering Institute, Chinese Academy of Sciences (IEE CAS) implemented an approach using a tube furnace [36]. The combustion temperature relies on a two-step heating process in which the initial temperature was at 250°-300°C and the final temperature was at 500°-550°C. The thermal process was repeated with oxygen and nitrogen in the tube. After the combustion process, glass and Si cells were recovered. The Si cells were chemically treated by using sodium hydroxide, nitric acid and hydrofluoric acid, and Si, Ag, and Al were recovered. Although details are not available, it was found that the energy consumption level was high and countermeasures for gas and liquid emissions, which cause certain environmental issues, are necessary. Based on the tube furnace experiment, CRAES developed an incinerator for the high temperature thermal method. The incinerator can dispose of the commercial size PV modules and is also designed to recycle the tail gas in the thermal process. The incinerator is currently in trial operation, and the gas collection and recycling process has been found to need improvement. Moreover, the high purity Si recycling technology by chemical treatment is under development as well. The Si is expected to be reused for the PV cell.

Industrial Technology Research Institute, Taiwan (ITRI) and others researched a heating method that uses single-cell (six inches in size) modules with poly-vinyl-fluoride (PVF) as a backsheet [37]. The module is heated to 330°C for 30 minutes during the first step, and the PVF is then separated from its back surface. A second heating step is carried out for the thermal burning out of the EVA and PVF at 400°C for two hours. After this two-step heating process, glass, broken Si cell chips, and copper ribbons are recovered. The Si chips are etched with hydrochloric acid and hydrogen peroxide to remove the Al electrode, by hydrofluoric acid to remove the SiNx layer (anti-reflecting coating [ARC]) and Ag, and by sodium hydroxide to remove the p-n junction and back-surface-field (BSF) layer. It was noted that the flue gases caused by burning the PVF and EVA would be a problem.

Table 3-2 summarises the recycling technologies involving a thermal approach as described above.

In addition to these processes, Padua University in Italy reported a dielectric heating process to replace direct heating and combustion [38]. They used a single-cell module, with the module delaminated by a radio-frequency heating process. In addition, Accurec Recycling in Germany implemented a novel vacuum-distillation pyrolysis technology [39].

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		FAIS and others (Japan)	KIER (Korea)	KETI (Korea)	Chonnam Nation. Univ. and others (Korea)	CRAES and IEE-CAS (China)	ITRI (Taiwan)
Eliminating encapsulant	Process and conditions	Combustion at 350° and 500°C	Combustion at 500°- 550°C	Combustion at 480°C.	n.a.	Combustion at 250°- 300° and 500°-550°C	Combustion at 330° and 400°C
structures			Pre-treatment of glass and EVA surfaces				
	Recovered	Glass(unbroken), Si	Glass, Si cells	Glass, Si cells	n.a.	Glass, Si cells,	Si chip, electrode metal
	material	cells, electrode metals	(unbroken), electrode	(unbroken), electrode		electrode metals	
			metals	metals			
	Remarks	Automated control	Single-cell module	Single-cell module		Using a tube furnace	Single-cell module
		Heat recovery from EVA combustion	Pilot plant is planned				
		Available for					
		commercial modules of c-Si. thin-film Si and					
		CIS					
		Demonstration stage at a pilot plant					
Recovering	Process and	-	Chemical etching	Chemical etching	Chemical etching	Chemical etching (nitric	Chemical etching
metals from Si	conditions			(nitric acid, potassium	(nitric acid, sodium	acid, sodium hydroxide,	(hydrochloric acid,
cells				hydroxide)	hydroxide) under	hydrofluoric acid)	sodium hydroxide,
				Mechanical grinding	ultrasonic treatment		hydrofluoric acid)
					Thermal process		
	Recovered material	1	Si wafers, Ag, Al	Si wafers, Ag, Al	Si, Ag, Al	Si, Ag, Al	Si, Ag, Al
	Remarks	Process for recovering	Si wafer can be	Non-HF process		1	1
		metals is out of the	recycled into a new Si	Si wafers can be			
		scope	cell	recycled into a new Si			
				cell			

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b) Mechanical approaches

Currently, a mechanical method for recovering glass from waste PV modules is used by glass recyclers in Europe. Although the method is not specific for PV modules, some technological R&D activities for PV module recycling via a mechanical approach have recently occurred.

The mechanical approach for the processing of PV modules includes crushing, scraping glass or layers, and cutting the encapsulation layer. These methods break-up the laminated structures, with subsequent additional step(s) for separating glass, metals including Si cells, and polymers combined.

Mitsubishi Materials Corportion is developing a scraping method for recovering glass [40] that involves mechanically scraping the cover-glass so as not to contaminate the glass with the encapsulation (EVA) layer. The equipment can process one module per minute. The recovered glass is filtered, and it is assumed that transparent glass grains are provided for secondary usage. The remaining layer with a small amount of glass can be treated by metal refinery technology. At present, the main target of the metal refining process is Ag because of its high value.

The approach of Toho Kasei is to scrape non-glass layers mechanically [41]. The first two steps are to scrape the backsheet and then encapsulation layer, including the Si cells and electrodes. Next, the scraped encapsulation layer is treated by a solvent developed by their group, and the Si, other metals and polymers are then recovered. To recover high-purity Si is one of the goals of project, and the encapsulation polymer recovered is recycled as fuel or material. On the other hand, the scraped backsheet is disposed of as industrial waste. The cover-glass remaining after the scraping processes does not have any damage, although a small amount of the encapsulation layer is attached. The attached encapsulation layer can be removed by another solvent, also developed by the group. In addition, the solvents can be used for modules before scraping and the structures can be resolved. However, the process consumes considerable time as compared to those without scraping steps.

Hamada Corporation and NPC Inc. are jointly developing a means of cutting the encapsulation layer alongside the cover-glass using a heated cutter [42]. After removing the Al frame with a machine and scraping the backsheet, the laminated structure is incised by heated cutter. The cutter is inserted into the bonding plane between the glass and the encapsulation layer while avoiding damage to the glass surface. After removing the encapsulation materials attached to the glass surface, the glass is recycled as a cullet. Any remaining layer can be treated by a chemical process or a metal refinery process to recover any metals they may contain.

Sasil, S.p.A. and other organizations developed PV module recycling technology under the Full Recovery End of Life Photovoltaic (FRELP) project in Europe, consisting of processes for the removal of Al frames and terminal boxes and for recovering glass, combusting polymers, and recovering metals from Si cells and electrodes [43]. First, the Al frame and terminal box are removed from the PV module by a machine. Subsequently, the laminated structure is heated to 90°-120°C by an IR heater and the structure is inserted into a roller mill and vibrating knife equipment. With this equipment, the glass is separated and recovered. During the next step, the remaining structure containing the encapsulation, the Si cells, the electrodes are separated. Waste gas from burning polymers is then recovered for combustion. The separated metals are treated by chemical methods. Si cells are etched by nitric acid, and the Si is recovered. After etching, electrolysis and a calcium hydroxide treatment recovers other metals (Ag and Cu) as a hydroxide form of the metals.

Sapienza University of Rome and other organizations are utilizing an automatic shredding process under the Photolife project in Europe [44]. This process consists of the manual dismantling of Al frames, the automatic shredding of laminated structures and separating glass, and the recovery of metals. The project covers crystalline Si, amorphous Si, and CdTe PV modules. Two approaches were tested as a shredding process. The first is a simple crushing method using a two-bladed rotor; the second involves crushing by a two-bladed rotor followed by hammer milling. From an analysis of the distribution of sizes of the crushed module pieces, it is tentatively concluded that the latter is better. The crushed pieces are treated in three ways; those with d (diameter)>1mm are combusted at 650°C to separate the polymers, those with 1mm>d>0,08mm are directly recovered as glass, and those with d<0,08mm are treated by a hydrometallurgical process to recover metals.

La Mia Energis S.c.a.r.l. is among the consortium that are developing a mobile system for PV modules under the PhotoVoltaic panels Mobile Recycling Device (PV-MOREDE) project in Europe [45]. The objective is to develop an on-site recycling system that undertakes volume reduction, the detachment of scrap glass, the detachment of silicon (cells), and the separation of polymers from copper. All equipment can be stored in a container for transportation. During the pre-treatment step, the Al frame and terminal box are removed from the PV module. The pre-treated module is cut into 100x100 mm pieces by machine. The module pieces are sent to the first hammer mill, ground into grains with diameters of less than 6 mm, and sieved by a mesh network with holes 6mm in size. The grains are then sent to a second hammer mill and ground to particles with diameters of less than 2 mm. The particles are sieved into three sizes: 0,5-2 mm, 0,315-0,5 mm, and <0,315 mm, with respective net vibrating plates. As the first coarse fraction is mainly composed of polymer and copper, this fraction has the copper removed; other metals and polymers are then removed by using a rotating magnetic field. The second and third fractions are separated as glass containing low silicon levels and glass containing a high content of silicon, respectively.

Yingli Solar and the Electrical Engineering Institute, Chinese Academy of Sciences, implemented a grinding technology under refrigerated conditions [46]. PV modules have their Al frame and terminal box removed and crushed, and the modules are then refrigerated at -197°C by using liquid nitrogen. The refrigerated module is ground, and particles of the encapsulation layer (EVA), glass, and mixed powder containing Si, Ag, Cu, and other materials undergo a physical separation. The predicted recycling rate is approximately 90%, but the Si cannot be recycled for the PV industry due to its low purity.

Table 3-3 summarises the recycling technology involving mechanical approaches, as described above.

		Mitsubishi Materials (Japan)	Toho Kasei (Japan)	Hamada and NPC (Japan)	Sasil and others (Italy)	Sapienza Univ. and others (Italy)	La Mia Energy Scarl and others (Italy)	Yingli Solar (China)
Process for glass recovery	Process and conditions	Scraping the cover- glass	Scraping the backsheet	Scraping the backsheet	Heated to 90°- 120°C	Crushing by a two- bladed rotor	Cutting as 100x100mm	Crushing Ground in
and separation			Scraping the	Cutting the	Breaking by a roller	Crushing by a	Two -stage grinding	refrigerated
			encapsulation	encapsulation layer	mill and a vibrating	hammer mill as a	by two hammer	conditions (-197°C)
-			materials and the Si	using heated cutter	knife	subsequent option	mills until the	
			cells layer				particles have	
_			Glass treatment				diameter of less	
_			using solvent				than 2 mm	
-	Recovered	Glass grains,	Glass (unbroken),	Glass (unbroken),	Glass grains,	Classified particles	Classified particles	Mixed particles and
_	material	remainig layer	mixture of	remaining layer of	mixture of	by size; d>1mm,	by size;	powder containing
_		(EVA/Si cells/	encapsulation and	encapsulation	encapsulation and	1mm>d>0,08mm,	2mm>d>0,5mm,	metals and
_		EVA/backsheet)	Si cells layer	materials and Si	Si cells layer	0,08mm>d	0,5mm>d>0,315mm	polymers
_				cells			, 0,315mm>d	
	Remarks	Transparent glass	Glass can be	Glass can be	Glass can be	Particles for which	Particles for which	1
_		grains can be	recovered without	recovered without	recycled	1mm>d>0,08mm	0,5mm>d>0,315mm	
_		recycled.	damage and then	damage and then	The backsheet is	can be recovered	are separated as	
_			recycled	recycled	disposed of	and recycled as	glass with a low	
			The backsheet is	The backsheet is		glass	content Si	
			disposed of	disposed of		Available for c-Si,	Particles for which	
			-	-		thin-film Si and	0.315mm>d are	
_			Technologically			CdTe modules	eenarated as diase	
-			available for non-				sepai aleu as glass	
_			crushed modules				with a high content Si	
Combined	Process and	Metal refinery	Chemical treatment	A chemical process	Combusted at	Combustion at	Rotating particles	Physical separation
process after	conditions	process for the	of the remaining	or a metal refinery	850°C, and	650°C for particles	for which	
glass		remaining layer	mixture	process for	chemical etching	of d>1mm	2mm>d>0,5mm	
separation				remaining layer	(nitric acid),	Hydrometallurgical	under a magnetic	
_					electrolysis, tor the	process for particles	Tield	
_						for which 0 08mm>d		
_	Recovered	Ag	Si, metals, polymers	n.a.	Si, Ag, Cu	n.a.	Cu and other	Si, metals, polymers
-	material		(EVA)				metals, polymers	
_	Remarks	The project is	Polymers may be	1	Burning gas at	Polymers are	All processes can	Si is not available
_		implemented by a	recycled as fuel or		combustion can be	burned out	be operated on site,	for the PV industry
		metal refinery	materials		recovered as heat		as mobile	due to its low purity
		company					technology	

Table 3-3 Examples of technology R&D for c-Si PV module recycling by mechanical approach

c) Chemical approaches

Chemical approaches were used in the early stages. Although the technical feasibility of eliminating the encapsulant from the laminated structure was confirmed, it was found that countermeasures for environmental burdens related to potential gaseous and liquid emissions are necessary, and the time required for the reaction is too long. To improve on such issues, several technologies have been developed.

Yokohama Oils & Fats Industry developed solvents and processes for eliminating the encapsulant from the laminated structures [47]. First, Al frames and terminal boxes were removed from PV modules manually and the backsheet is removed mechanically. Next, the remaining laminated structure was immersed in a neutral solvent, and glass and other layers for encapsulation (EVA), the Si cells, and the electrodes are separated. The separated glass typically experienced no damage and was easily recycled or reused. Next, the remaining layer was crushed and immersed in an alkali solvent. After the immersion step, EVA, silicon and the electrode ribbon were recovered. To recover Ag attached to the silicon, an additional process was required. The expected processing time was almost one day for commercial modules. Although the process requires much treatment time, the developed solvents were environmentally friendly compared to acids and organics. Therefore, the solvents may be effective if used with the glass separation and metal separation mechanical approaches (i.e., after crushing, grinding, and cutting).

Korea Research Institute of Chemical Technology (KRICT) with Kangwon National University developed a technology for dissolving EVA by submerging modules in an organic solvent and using additional ultrasound irradiation [48]. The objective of using ultrasound irradiation was to overcome the shortcomings of chemical separation, which typically requires a long treatment time. EVA was dissolved at 70°C and at an irradiation power of 900W, and Si cells were recovered without damage.

In both technologies, an additional process for recovering metals from Si cells will be required after eliminating the encapsulant from the laminated structure. However, some technologies rely on thermal and mechanical approaches; for example, using an acid and alkali hydroxide for chemical etching may be possible. In addition, Loser Chemie has developed a technology which uses aluminium chloride and water [49]. Aluminium electrodes on the backsides of Si cells can be recovered with poly-aluminium-chloride, which is a valuable product for the treatment of wastewater. The remaining silver on the front contact can be dissolved with nitric acid.

While R&D activities for mechanical approaches are increasing, it appears that chemical approaches for eliminating the encapsulant from the laminated structures are waning, as chemical approaches require long treatment times in general and may not suitable as a mass-treatment method, even if environmental concerns are addressed. However, these approaches may be suitable for small-scale on-site treatment, such as those that can operate at c-Si module manufacturing facilities.

As mentioned in the previous sections, each R&D project for PV module recycling has been testing different processes based on their objectives and experiences. These processes are comprehensively synthesized as shown in Fig. 3-7.



3.4 Technology R&D on compound PV module recycling

The compound include CdTe and CIGS layers. The compound layer is deposited on a substrate such as glass. Therefore, a technology for PV module recycling requires the eliminating the encapsulant from the laminated structures, e.g., the separation of substrates containing compounds and encapsulation materials, and the recovery of metals from the substrates.

In the early stages, chemical processes were mainly examined. Solar Cells [50] developed an etching method for the recycling of CdTe modules. After crushing the PV modules by a hammer mill, the crushed modules were exposed to sulphuric acid and hydrogen peroxide. EVA was separated from the glass, and Cd and Te were solved as compounds. The Cd and Te compounds were treated with sodium carbonate, and cadmium carbonate and tellurium oxide were recovered. Cd and Te can be recovered by a thermal or chemical process and purified by a metal refinery process. First Solar's current technology as mentioned above was based on such a method. As another approach for recovering metals from separated substrates, Drinkard Metalox [51] and Inter Phase Research [52] attempted to develop an electrochemical method for CdTe and CIS modules.

Currently, the most common method is a combination of mechanical and chemical processes. It has been developed and commercialized by First Solar and involves eliminating the encapsulant from the laminated structures and recovering metals. In addition, several technologies are under development by a number of organizations. For eliminating the encapsulant from the laminated structures, thermal, mechanical, and optical approaches have been studied.

Fig. 3-8 depicts recent R&D focus in compound PV module recycling.



Fig. 3-8 Recent R&D for compound PV module recycling

a) Thermal approaches

As described in the discussion of technology for c-Si PV module, FAIS and others developed a technology that will be available for c-Si, thin-film Si and CIGS [30]. The recycling technology consists of the four main processes of aluminium frame removal, backsheet removal, EVA resin burning for thermal

recycling, and layer scraping of CIS device. During the first step, the aluminium frame is removed by an air cylinder actuator from the modules. In the next step, the backsheet is removed by a milling machine to prevent module glass from thermally cracking in the post-processing step. The modules without aluminium frame and backsheet are then heated and the EVA resin is thermally decomposed in a muffle furnace, after which the decomposition gas is sucked out and burned. The heat generated from the EVA resin combustion process is thermally recycled to the furnace. After the three processes, glass substrates having CIGS layers and a cover-glass are recovered from the CIGS module. As a member of the project, Solar Frontier developed a technology for scraping the CIGS layer on the substrate glass with wire brushes. The CIGS metals are recovered through a cyclone collector and can then be recycled by metal refinery companies. For the CIGS modules, the expected processing throughput of the system is around 8MW per year.

Accurec Recycling implemented a method developed using their Vacuum-Distillation pyrolysis technology under the Photorec project [39]. Although the details are not clear, after removal of the frame and the terminal box, PV module flakes were prepared by a pre-treatment. Through microwave vacuum-distillation and mechanical separation processes, metals such as In, Ga, and Te, as well as glass, could be recovered from the flakes.

The expected advantage of the thermal approach was the recovery of glass without damage or contamination because mechanical pre-treatment was not used. On the other hand, if additional processes for recovering metal from glass are necessary and chemical processes will be used, the use of crushed glass will be better to enhance the performance and speed of the chemical reactions.

b) Mechanical approaches

As mechanical approaches for compound PV modules, crushing and the cutting of the encapsulation layer can be performed. As with c-Si modules, such an approach is a process of decomposing laminated structures, with an additional process for recovering metals from substrate glass combined. A significant difference between c-Si and compound is that a compound semiconductor layer is deposited on the substrate glass, while c-Si cells are separate from cover glass and backsheet/back glass.

First Solar has already commercialized a CdTe PV module recycling technology, which is a combination of a mechanical and a chemical treatment. The technology involves shredding and crushing in a hammer mill to particles of approximately 5 mm to break the lamination bond. The dust is then collected in an aspiration system equipped with a high-efficiency particulate air filter. Next is the etching of a semiconductor layer with a mixture of sulphuric acid and hydrogen peroxide. Glass and larger pieces of EVA (ethylene-vinyl acetate) are separated in a classifier and on a vibrating screeen, and the glass is rinsed with water and dried on a belt filter unit. Finally, filtration liquids with the metals are extracted via ion exchangers or precipitated. Cadmium and tellurium can be further purified by third parties for reuse in the solar industry. First Solar started operating their first version of this technology in 2006 in Germany (10 tons/day), with an updated second version of the technology operated in the United States in 2015 (50 tons/day) [53]. The third version of the technology is a continuous process, whereas the earlier versions are batch processes. The fourth version is expected to have a treatment capacity of 350 tons/day. In addition, mobile technology on a smaller scale to reduce the transportation cost is to be developed.

Sapienza University of Rome, among others, are using automatic shredding under the Photolife project in Europe [44], which is described as a type of technology for c-Si PV modules. The processes of this project are the manual dismantling of Al frames, the automatic shredding of laminated structure and separating glass, and the 'recovery of metals'. The project covers CdTe PV modules in addition to crystalline Si and amorphous Si. Two approaches have been tested with regard to the shredding process. One involves simple crushing by a two-bladed rotor; the other involves crushing by a two-bladed rotor followed by crushing with a hammer. The crushed pieces are treated in three ways: Those with d>1mm are combusted at 650°C to separate polymers, those with 1mm>d>0,08mm are directly recovered as glass and those with d<0,08mm are treated by a hydrometallurgical process for the recovery of metals.

The Reclaim (Reclamation of Gallium, Indium, and Rare-earth Elements from Photovoltaics, Solid-State Lighting, and Electronics Waste) project led by Nederlandse Organisatie voor Toegepast Natuurwetenschappelijk Onderzoek (the Netherlands) aims to develop technological solutions for recycling gallium, indium and rare earth elements from photovoltaics (CIGS), solid-state lighting, and other electronic waste such as flat panel displays and printed circuit boards [54]. CIGS modules are crushed and sorted, and cover glass and substrate glass containing CIGS layer are separated and recovered [55]. Substrate glass recovered is chemically treated with sulphuric acid and hydrogen peroxide, and rare metal such as In and Ga are recovered. Recovered metals are purified by further chemical processes.

As another mechanical approach, Solar Frontier is developing a cutting encapsulation method using a heated cutter [56]. After the removal of the Al frame and the terminal box, the cutter is inserted between the cover glass and the substrate glass. The treatment speed is currently 400 seconds per module (commercial size). The cover glass with some EVA still attached is recovered. The substrate glass, having CIGS and Mo layers and some polymers, is also recovered, although the substrate is typically broken. Both types of glass are treated chemically, and glass and metals are recovered. At this time, an organic solvent is used to separate the EVA. Although the solvent for metal separation is under testing, a solvent based on hydrogen peroxide is one of the candidates.

It appears that the combination of mechanical and chemical processes is a promising approach. In addition to improving the process efficiency, the use of environmentally friendly solvent(s) and the reduction of amounts used are required, as it has been found that waste liquid disposal after chemical processes is critical.

c) Optical approaches

Optical approaches represent a unique alternative to existing methods.

Loser Chemie is developing a technology involving an optical approach for the separation of glass-glass structures [57]. After the removal of the frame and terminal box, the PV module is automatically loaded into the optical treatment equipment. There are two options for an optical treatment: the first involves the use of laser, the second involves flash lamp annealing. The expected treatment time will be one minute per commercial module. After the optical treatment, the cover glass and substrate glass having compound layers are separated. Compound layers such as CdTe and CIGS are treated by a chemical approach using methanesulfonic acid. Metals in the layers can be separated and recovered as individual metal compounds and then recycled and purified by a metal refinery company.

This technology can recover glass without damage or contamination, and the glass can be used for float glass production.

Table 3-4 summarises the recycling technology for compound PV modules, as described above. Also, Fig. 3-9 shows a synthesized diagram of the process flow for compound PV module recycling.

		Thermal approaches			Mechanical approaches			Optical approaches
		FAIS and others	Accurec recycling	First Solar (USA)	Sapienza Univ. and	TNO (Netherlands)	Solar Frontier	Loser Chemie
		(Japan)	(Germany)		others (Italy)	and others	(Japan)	(Germany)
Process for	Process	Combustion at 350°	Vacuum-distillation	Shredding and	Crushing by a two-	Shredding, sieving,	Cutting the	Optical treatment
eliminating	and	and 500°C	pyrolysis, after a	crushing in a	bladed rotor, and by	and separation with	encapsulation layer	using a laser or a
encapsulant	conditions		pre-treatment step	hammer mill	a hammer mill as an	an air table	with a heated cutter	lamp
from					additional option			
laminated	Recovered	Substrate glass,	Metals such as In,	Broken modules	Classified particles	Cover-glass cullet,	Cover-glass with	Cover glass with
structures	material	cover-glass,	Ga, and Te, and	(mixture of glass,	by size: d>1mm,	flakes of EVA, and	EVA attached,	EVA attached,
_		electrode metals	mixtures of glass	polymers, and	1mm>d>0,08mm,	substrate glass with	substrate glass	substrate glass
_			and polymers	others) with	and 0,08mm>d	CIGS layer	having a CIGS layer	having a
_				diameters of about				semiconductor layer
_				5mm				
_	Remarks	Automated control	PV flakes are	Commercialized	Particles for which			The laser will be
		Heat recoverv from	prepared by pre-	technology,	1mm>d>0,08mm			feasible for only non-
_		EVA combustion	treatment step	including a	can be recovered			cracked modules.
_			Metals are	combined chemical	and recycled as			The lamn will he
_		commorcial modulos	condensed from	process: -50tons/day	glass			suitable for both
				Eurther scaling up	Easeible for c-Ci			
_		of c-Si, thin-film Si,	Vapour					
_		and CIS		and development of	thin-tilm Si, and			cracked modules
_		Demonstration stade		smaller-scale and	CdTe modules			
_				mobile technologies				
		מו מ אווטו אומו וו		are planned				
Combined	Process	Mechanical scraping	Mechanical	Etching	Combustion at	Leaching by	Chemical treatment	Chemical treatment
process for	and	of the substrate	separation of the	semiconductor layer	650°C for particles	sulphuric acid and		using
recovering	conditions	glass	remaining mixture	of substrate glass	for which d>1mm	hydrogen peroxide		methanesulfonic
glass and				with sulphuric acid	Hydrometallurgical	at 80°C		acid
metals from				and hydrogen	process for particles	Extraction and		
substrates				peroxide	for which 0,08mm>d	purification by acid		
_				Separating liquids				
				and metal				
_				compounds				
	Recovered material	CIGS metals, glass cullet	Glass cullet	Glass cullet, metal compounds	n.a.	Indium, Gallium, and dlass cullet	Glass, metal compounds	Glass, metal compounds
_	Remarks	CIGS metals are	Polymer is used as a	Metal compounds	Polymers are burned) ,	At present, the use	Metal compounds
_		recycled by a metal	fuel	are refined by a	out		of solvent and a	are refined by a
_		refinery company		metal refinery			solvent based on	metal refinery
_				company and metals			hydrogen peroxide	company
_				are recycled as PV			are being discussed	
_				modules)	

Table 3-4 Examples of technology R&D for compound PV module recycling



4. Summary

All technologies eventually degrade to the point where they enter their end-of-life stage and eventually must be replaced. This is also true for PV modules, though PV modules in particular have relatively long lifetimes of approximately 30 years or more.

In anticipation of the large volume of waste PV modules and to continue to be considered a clean energy technology, various activities related to the proper management of waste PV modules have been developed. Generally, sustainable waste management will offer opportunities known as the three Rs (3Rs): reduce, reuse, and recycle. Among the 3Rs, recycling systems and their concomitant regulatory schemes to deal with PV end-of-life management issues have only recently emerged, yet PV module recycling technologies have been studied and developed to a considerable extent over the past decade.

Currently, the recycling of both c-Si PV modules and compound modules is commercialised. However, to improve the process efficiency, recovery and recycling rates, cost effectiveness, and environmental performance capabilities of these methods, several approaches have been developed.

Recycling technologies for crystalline Si PV modules and compound PV modules have different characteristics owing to the differences in the module structures and the metals contained in them. One important difference is that the objective of eliminating the encapsulant from the laminated structure of compound PV modules is to recover both the cover glass and the substrate glass with the semiconductor layer, whereas the objectives for c-Si modules are separating and recovering glass, Si cells, and other metals.

Processes for c-Si PV module recycling can be roughly divided into those that eliminate the encapsulant from the laminated structure (i.e., delaminating) and those that recover the metals from the Si cells, after pre-disassembly, such as the removal of the metal frames and terminal boxes from the modules. Eliminating the encapsulant from the laminated structure is one of the most difficult and important targets of recycling technology R&D. Patents dealing with glass and encapsulants utilize this process. For examples, thermal, mechanical, and chemical approaches can also be used for delaminating. Recovering metals from Si cells can be achieved by chemical approaches such as etching, and another method is a direct treatment by a metal refinery company.

With regard to the recycling of compound PV modules, processes are roughly divided into those that eliminate the encapsulant from the laminated structures and those that recover metals and substrate glass, after pre-disassembly. To eliminate the encapsulant from laminated structures, a mechanical crushing has been already proven, and thermal, mechanical and optical approaches have been developed. Chemical approaches such as etching are effective to recover semiconductor metals from substrates, and the substrate glass can be recovered and recycled, as well. If a substrate is recovered without breakage, mechanical scraping may be an alternative process.

In this report, trends related to the development of PV module recycling technology were surveyed. In the patent analysis, patents mainly filed by private sector were analysed. In addition, by surveying technical papers, technology R&D projects for PV module recycling, which are mainly publicly-funded, were overviewed. The overview of R&D projects mainly focused on eliminating the encapsulant from the laminated structure as it is one of the most difficult and important targets of recycling technology R&D.

4.1 Patent analysis of PV module recycling technology trend

In order to understand the technological trends related to PV module recycling, a global patent database (worldwide intellectual property service (WIPS)) was queried to identify patents for recycling of c-Si and compound PV modules from January 6, 1976 through December 9, 2016. Initial search results were then screened to ensure relevance and supplemented with additional patents known to the authors. The numbers of effective patents directly related to PV recycling technology are 128 for c-Si and 44 for compound modules. More significant numbers of patents in c-Si might be related to installation market trends, which reflect needs for recycling technologies. Currently, c-Si PV modules take up most of the installation market. (The total number of effective patents related to other module types is only six, a number too low for an analysis.) Detailed information such as patent title, filing year, country, filing number/date, patent number/date, assignee, and legal status on the 178 effective patents is provided in the appendix of this report and the database of IRENA-INSPIRE⁷. In the patent analysis, recycling technologies were classified based on the mainstream classification of PV module type were then analysed in depth in terms of the independent analysis categories of the targeted component, the processing method, and the recovered material.

In trends associated with c-Si PV module recycling patents, after the first patent for c-Si PV module recycling technology was filed in Germany in 1995, and in all countries up to 2010, there were relatively few filings. However, the number increased after 2011. The rapid increase is most prominent in China, where nearly a half of all c-Si patent filings were filed, followed by Korea and then Japan. This indicates that R&D with regard to c-Si PV recycling technology has become more active in Asia than in Europe and the United States. According to an analysis of the targeted components, technologies targeting encapsulants (mostly EVA) account for 45% of patents, indicating that many patents focus on removing encapsulants from module components for module separation. The percentage of these patents is followed by those for frames (30%), solar cells (24%), and Cu ribbons (1%). An analysis based on the processing method used shows that mechanical methods, used mainly in China, constitute 40% of the total, followed by combination methods at 25%. Chemical and thermal methods comprise 19% and 15%, respectively. Although not a large amount, thermal methods are used in most countries/regions in this field. Optical methods with laser cutting, for which patents were very recently filed in China, account for only 1%. With regard to patent trends related to recovered materials, most patents are for technologies to recover Al frame (25%), solar cells (24%), and glass (23%). This reflects that most of the patents were filed to recover components by means of module separation but not to recover each material such as Si, Ag and Cu from the PV modules. There were only a few patents for technologies to recover Si (12%), Ag (10%), and Cu (6%).

With regard to trends in patents related to compound PV module recycling technologies, the first patent for a compound-based PV module recycling technology was filed in the United States in 1997, with no substantial increase since then. The largest number have been filed in the United States, accounting for 27% of the total. The United States is followed by Japan (21%), China (16%), and several European

⁷ http://inspire.irena.org/Pages/default.aspx

countries (11%). Unlike c-Si, corporations are all assignees in many countries, except for one in each of Germany and the United States, implying greater levels of commercial interest in the technology and suggesting that these technologies are apt to be commercialized. In terms of targeted components, both EVA (component enables to separate the module) and semiconductor materials (substances are scarce or toxic) were targeted quite equally. The similar interest between EVA and semiconductor materials suggests a trend toward high-value recycling for compound PV modules, rather than just bulk separation. Moreover, the double focus reflects that patents claim a total-recycling process with all recycling steps from separation to recovery, which is in contrast to the patents for c-Si modules with a focus on a specific recycling step. Patents for other components were not filed in relation to compound PV modules. In a trend analysis of the processing method used, technologies that combined two or more methods made up 64% of the total, in contrast to c-Si recycling technologies, in which only 25% involves a combination of methods due to the different module structure. A single method focusing on disassembly can be effectively used for at least bulk material separation for c-Si modules which is manufactured through the assembly of components produced by other manufacturers, but the method is not useful for recycling compound PV modules which is manufactured through the deposition of functional layers. For example, glass cannot be recovered from a compound PV module by the single method because semiconductor materials remain on the surface of glass after module separation, thus an additional step for detaching the semiconductor materials from the glass is necessary. This is a reason that the combination method is preferentially considered for recycling compound PV modules. The majority of combination methods include mechanical methods for the crushing of the modules and chemical methods for the recovery of metallic elements. A trend analysis of the recovered materials shows that patents to recover semiconductor materials amounted to as much as 78% of the total, while those for glass made up the rest. In general, based on the patents analysed, the recovery of semiconductor materials is the key objective of compound PV module recycling technologies.

This patent analysis will provide beneficial information to readers with an interest in PV recycling, as they can learn how to approach the development of PV recycling technology by understanding past and current patent trends. For anyone interested in the recovery of frame and electrode materials, this analysis will help them choose combination methods consisting of mechanical and chemical methods and easily to find relevant patents on the list of effective patents in the appendix. Technologies from multiple processing methods will likely be needed to satisfy high-value PV module recycling treatment requirements such as those documented in Box 1-1.

4.2 Technology R&D for PV module recycling

To improve process efficiency, recovery and recycling rates, cost effectiveness, and environmental performance, several technology R&D projects have been implemented. Recycling technologies for both types of modules have different aspects owing to the differences in module structures and the metals contained in them.

As for c-Si PV modules, a mechanical approach, e.g. crushing and sorting, is currently implemented in Europe by glass recyclers as a part of their business. This represents a promising technology for separating and recovering glass from c-Si PV modules. Metals will be recovered from remaining and separated materials by additional processes. Under the current technology, glass and valuable metals such as Ag will

be recycled. However, Si cells cannot be recycled as Si wafers. The capacity of the treatment of waste PV modules is not very large, and the glass recovered is recycled as a low-grade product. Preparing for future mass treatments, several technologies are under development to realize economical processes, achieve higher recovery/recycling rate, and improve the quality of recovered materials.

After pre-disassembly, such as the removal of the metal frames and terminal boxes from the modules, processes for PV module recycling can be roughly divided into eliminating encapsulant from laminated structure and recovering metals from the Si cell. Eliminating the encapsulant from the laminated structure (i.e., delaminating) is the most difficult process and the most important target of recycling technology R&D. As a process for eliminating the encapsulant from the laminated structures, thermal approaches, mechanical approaches and chemical approaches can be used. The thermal approach is a combustion process; the expected materials recovered are glass, Si cells, and electrode ribbons. Under certain conditions, glass and Si cells can be recovered without breakage, which is the benefits of this approach, as is the expected higher value of the recovered materials for recycling. The recovery rates of Si cells without breakage depend upon the thicknesses of cells/wafers and the burning conditions. In general, the thinner the cells are, the lower the recovery yield achieved. Moreover, if the cells have flaws such as edge chipping and/or micro-cracks they typically cannot be recycled into an intact wafer and would be allocated as Si raw materials. On the other hand, the thermal approach will require a mass treatment to increase its economy and efficiency. It was also found that higher energy consumption will be a critical issue; thus, processes that consume low energy, for instance, during the heat recovery step are required. When burning a fluoridebased backsheet with other structures, it becomes necessary to plan countermeasures for the generation of fluorine gas. Cutting the encapsulation layer, scribing non-glass layers, scribing glass, and crushing/grinding technologies are examined as a mechanical process. The first two technologies can recover glass without breakage and other technologies can recover broken glass, though Si cells cannot be recycled as Si wafers. For glass of a higher quality and recovery rate, processes that are without breakage are superior, and may extend to material other than glass. These mechanical technologies are basically combined with a post-treatment step, typically a chemical treatment, to separate Si chips and other metals from the remaining mixture. A mechanical process will consume less energy compared to a thermal process; but the treatment of PV modules can only be done in sequence. Combinations that involve thermal processing consume more energy, and combinations with chemical processes may require improving the processing speed and treatment of waste chemicals. The chemical processes, such as the use of solvent treatments to eliminate the encapsulant from the laminated structures, will be technologically feasible and will enable the recovery of Si cells. However, such processes require long treatment times and require liquid waste treatment steps as well. Although they may not be suitable for mass treatment even if environmental issues are resolved, they may be suitable as on-site, small-scale treatment, akin to combinations of thermal and mechanical processes for the recovery of Si cells and metals.

Recovering metals from Si cells can be achieved by chemical approaches such as etching with acid or alkali hydroxide, for example, and a proper treatment for chemical waste (e.g., hydrofluoric acid) is indispensable. Another method is a direct treatment by a metal refinery company.

With regard to the recycling of compound semiconductors PV modules, a combination process involving mechanical (crushing) and chemical etching is in operation on a commercial scale. Glass and

semiconductor metals have been recovered and recycled, with recycling rates as high as 90% for glass and up to 95% for metals [53]. However, preparing for the future with regard to waste PV modules, several additional technologies are under development.

Processes are roughly divided into those that eliminate encapsulant from laminated structures and those that recover metals and substrate glass, after the pre-disassembly process. An important difference with reference to c-Si modules is that the objective of eliminating the encapsulant from the laminated structure is to recover both the cover glass and the substrate glass with the semiconductor layer, while separating and recovering glass, Si cells, and other metals form the objectives for c-Si modules. After eliminating the encapsulant from the laminated structure, the metals and substrate glass can be separated and recovered effectively during the next step of the process.

In addition to the already proven crushing technology, combustion as a thermal approach, cutting the encapsulation layer as a mechanical approach, and a laser treatment as an optical approach have been developed to eliminate the encapsulant from the laminated structures. These processes will enable the separation of double-glass structures and recovery of cover glass components without any damage or contamination. Under certain conditions, substrate glass with the semiconductor layer will be recovered while also maintaining the shape. Considering the treatment speed and yield during the next step for the recovery of metals from substrates, crushing the substrate will also be an effective approach. However, to increase the quality and value of the recovered glass, non-damaged glass and glass cullet components with a larger particle size are attractive, as they offer the potential to improve the recovery/recycling rates. Moreover, these new approaches will have technical aspects similar to the technologies used with c-Si modules, because separating laminated structures as cover glass components, and other layers with them, will enable the recovery of Si cells. Indeed, one combustion technology is feasible for use with c-Si, thin-film Si, and CIGS. On the other hand, crushing/grinding processes are also suitable for c-Si PV module. However, Si cells cannot be recycled as Si wafers, as Si cells are typically crushed to small pieces.

With regard to recovering semiconductor metals from substrates, chemical approaches such as etching are promising, and substrate glass can be recovered and recycled as well. However, treatments that generate exhaust gases and waste liquids are critical issues. If a substrate is recovered without breakage, mechanical scraping may be an alternative process.

Among the R&D projects surveyed in this report, a few projects are nearly at the commercial or demonstration stage, while others are still in the laboratory or pilot stage. In preparation for mass-treatment methods for waste PV modules in the future, it is expected that the pace of R&D projects will accelerate, allowing researchers to resolve remaining issues and contribute to the development of proper schemes for PV module recycling businesses, as well as for the end-of-life management of PV modules.
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Appendix A: List of effective patents

I. Crystalline silicon solar module

Legal status	Expired	Abandoned	Granted	Abandoned	Abandoned	Abandoned	Abandoned	Abandoned	Abandoned	Granted	Abandoned	Abandoned
Assignee	Siemens Solar GmbH	Wambach, Karsten Dr.	First Solar, LLC.	Canon Kabushiki Kaisha	Tokyo Electric Power Co., Inc.	Sharp Corp.	Canon Kabushiki Kaisha	National Institute of Advanced Industrial Science and Technology	Kyowa Hakko Chemical Co., Ltd.	Kyocera Corp.	Mo Menglong	Loser Ulrich ; Palitzsch Wolfram
Title of invention	Recycling of solar modules and cells of silicon and its alloys	Method for separating the components of a laminated glazing	Recycling silicon photovoltaic modules	Semiconductor device, solar cell module and methods for their dismantlement	Method and device for separating element of solar battery module and method for manufacturing solar battery module	Extraction method of solar cell board material, regenerating method of solar cell, and formation method of ingot for solar cell	Semiconductor device, solar cell module, and methods for their dismantlement	Method for separating constituent members of solar cell module	Method for recovering solar battery cell and/or reinforced glass from solar cell module	Disassembling method of solar cell module	Method for reclaiming solar battery thin splinter or ic splinter	Method for removing front and rear side contacts of solar cells, involves processing solar cells with aqueous, sour metallic salt solution, particularly aluminum chloride solution
Date of patent	January 29, 1998	June 4, 2003	May 16, 2000				Septemb er 6, 2005			May 13, 2011	April 22, 2009	
Patent number	19541074 C2	893250 B1	6063995 A				6940008 B2			4738167 B2	100480402	
Filing date	November 3, 1995	July 20, 1998	July 16, 1998	February 5, 1999	November 7, 2001	April 23, 2004	June 28, 2004	December 24, 2004	November 8, 2005	December 26, 2005	October 4, 2006	July 20, 2007
Application number	1995- 10041074	1998- 113527	1998- 116287	1999- 102294	2001- 341407	2004- 128390	2004- 876666	pct- jp2004- 019358	2005- 322972	2005- 373421	2006- 10053795	2007- 10034441
Country	DE	EP	SN	EP	٩	٩	SN	MO	<u>م</u>	٩L	CN	DE
Filing year	1995	1998	1998	1999	2001	2004	2004	2004	2005	2005	2006	2007

Granted	Abandoned	Granted	Abandoned	Granted	Abandoned	Granted	Granted	Abandoned	Granted	Granted	Abandoned	Abandoned	Granted	Granted	Granted
Du Pont Mitsui Polychem Co., Ltd.	Sharp Corp.	Guangdong Golden Glass Technologies Ltd.	Korea Research Institute of Chemical Technology	Korea Research Institute of Chemical Technology	Tianwei New Energy Holdings Co., Ltd.	Showa Shell Sekiyu KK	Lee, Hyun-Joo	Korea Research Institute of Chemical Technology	Korea Research Institute of Chemical Technology	Leye Photovoltaic Co., Ltd.	Ningbo Xinyou Photovoltaics Industry Co., Ltd.	Yingli Group Ltd.	Yingli Group Ltd.	Yingli Group Ltd.	Yingli Group Ltd.
Method for recovering solar cell module member	Disassembling method of solar cell module	Method for recovering crystalline silicon cell plate in double- glass solar cell assembly with pvb interbred	The solar cell recycling method from the waste solar module	Method for recycling silicon from waste solar cell	Tool for dismantling frame of crystalline silicon solar battery component	Method of recycling solar cell module	Recovery method of high-purified poly silicon from a waste solar wafer	Method for recycling silicon from waste solar module	Method for recycling silicon from waste solar module	Solar cell panel frame dismounting machine	Recycling system for waste silicon solar cell	Heating temperature control device and photovoltaic module decomposition and recovery equipment provided with same	Solar module decomposing equipment and rotary clamp thereof	Solar battery recovery decomposition device and its rotation balance disk	Equipment and method for recycling photovoltaic module
2012.10. 05		July 6, 2011		Decemb er 5, 2011	July 6, 2011	July 11, 2014	August 8, 2013		Novemb er 27, 2012	January 4, 2012	July 4, 2012		January 2, 2013	Decemb er 4, 2013	July 16, 2014
5099819 B2		101719529 B		10-1092259 B1	201893366	5574750 B2	10-1296797 B1		10-1207297 B1	202103080 U	202307807 U		102354677 B	102509717 B	102500602 B
June 15, 2007	March 12, 2008	November 17, 2009	September 21, 2009	December 18, 2009	December 1, 2010	February 25, 2010	March 24, 2010	June 25, 2010	August 27, 2010	June 15, 2011	November 1, 2011	November 7, 2011	November 7, 2011	November 7, 2011	November 7, 2011
2007- 159589	2008- 062050	2009- 10194094	2009- 0089039	2009- 0126570	2010- 20636218	2010- 040776	2010- 0026032	2010- 0060328	2010- 0083206	2011- 20200206	2011- 20425006	2011- 10348776	2011- 10348777	2011- 10348806	2011- 10349389
٩Ĺ	٩ſ	CN	КR	KR	CN	٩L	KR	KR	KR	CN	CN	CN	CN	CN	N
2007	2008	2009	2009	2009	2010	2010	2010	2010	2010	2011	2011	2011	2011	2011	2011

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Granted	Abandoned	Abandoned	Granted	Granted	Abandoned	Granted	Abandoned	Abandoned	Granted	Abandoned	Abandoned	Abandoned	Abandoned	Granted
Suzhou Industrial Park Goldway Technologies Co., Ltd.	Suzhou Industrial Park Goldway Technologies Co., Ltd.	Korea Research Institute of Chemical Technology	Korea Research Institute of Chemical Technology	Yingli Group Ltd.	Ceeg Shanghai Solar Science & Technology Co., Ltd.	Changzhou Trina Solar Energy Co., Ltd.	Anyang Phoenix Photovoltaic Technology Co., Ltd.	Anyang Phoenix Photovoltaic Technology Co., Ltd.	Taitong Taizhou Industry Co., Ltd.	Qinhuangdao Xinmeiyuan Controlled Equipment Co., Ltd.	Qinhuangdao Xinmeiyuan Controlled Equipment Co., Ltd.	Junfeng Solar Energy (Jiangsu) Co., Ltd.	Jiangsu Tihein Photovoltaic Technology Co., Ltd.	Technische Universität Bergakademie Freiberg
Solar cell frame dismantling method	Solar cell frame dismantling system	Method for recycling silicon from waste solar module	Method for recycling silicon from waste solar module	Method and device for decomposing and recycling photovoltaic component	Apparatus for disassembling photovoltaic assembly	Photovoltaic assembly-used hidden crack-free automatic de- framing method	Method for carrying out desilvering processing on waste solar cell slice	Method for extracting and recovering silver from waste solar cell	Simple solar photovoltaic module frame dismantling device	Solar cell panel long edge frame dismantler	Solar cell panel short edge frame dismantler	Frame disassembly device for photovoltaic assembly	Workbench used for manual disassembly of photovoltaic module	Recycling disused solar modules and solar cells, comprises separating cell breakage having silicon from starting materials, and treating the breakage with chloromethane/dichloromethane and hydrogen in the presence of catalyst
May 4, 2016			April 15, 2013	March 12, 2014	Decemb er 19, 2012	August 10, 2016			July 3, 2013	Decemb er 13, 2012	Novemb er 13, 2013		2013.04. 10	Septemb er 16, 2016
103165740 B			10-1256574 B1	102544239 B	202616274 U	103515472 B			203031219 U	202977513 U	203288629 U		202862178 U	DE 10201201854 8 B4
December 13, 2011	December 13, 2011	March 15, 2011	November 14, 2011	March 7, 2012	April 9, 2012	June 20, 2012	August 12, 2012	August 12, 2012	December 12, 2012	December 13, 2012	December 14, 2012	May 7, 2012	September 17, 2012	September 20, 2012
2011- 10414870	2011- 10414872	2011- 0023090	2011- 0118397	2012- 10058374	2012- 20146877	2012- 10205461	2012- 10284147	2012- 10284148	2012- 20682154	2012- 20685552	2012- 20691921	2012- 10136667	2012- 20473647	2012- 10018548
ON	CN	КВ	КВ	CN	CN	CN	CN	CN	CN	CN	CN	CN	CN	DE
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Lobbe Industrieservice GmbH & Co. KG	Toray Fine Chemicals Co., Ltd.	Yokohama Yushi Kogyo KK	Shinryo Corp.	Tanabe Sangyo KK	Shinryo Corp.	Symphony Energy Co., Ltd.	Symphony Energy Co., Ltd.	Kangwon National Univ.	Symphony Energy Co., Ltd.	Henan Institute of Science & Technology	Fuyu Energy Science & Technology Kunshan Co., Ltd.	Baoding Tianwei Yingli New Energy Co., Ltd.	Jinko Solar Co., Ltd. Jinko Solar Holding Co., Ltd.	Shanghai Jiao Tong Univ.	Variata Dorit Lang GmbH & Co. KG
Method and assembly for the recovery of metals from composite materials, in particular from silicon solar modules, thin film solar modules, LCD displays or the like	Method of disintegrating solar cell module	Solar cell module recycling method	Solar cell module dismantling apparatus	Glass panel separation method and heat treatment device	Method of recovering constituent material of solar cell element	Method for dismantling eco-friendly waste solar module	Apparatus for disassembling solar module frame	Device for recycling cell from solar module	Apparatus for dismantling waste solar module thermally	Cleaning recovery treatment process of solar cell sheet	Photovoltaic module dismounting device	Device for detaching solar cell assembly side frame	Crystalline silicon battery piece recycling and reusing method	Heating wire cutting device of ethylene vinyl acetate (EVA) layer in solar cell panel recovery processing	Recycling of photovoltaic module and/or solar modules
February 13, 2013			Septemb er 2, 2016	2015.02. 06				June 12, 2014			May 21, 2014	Decemb er 9, 2013		2015.01. 21	
2556893 A3			5996405 B2	5688964 B2				10-1409319 B1			203600179 U	203617327 U		103085116 B	
August 7, 2012	November 7, 2012	November 27, 2012	December 6, 2012	June 18, 2012	November 30, 2012	January 6, 2012	February 21, 2012	August 20, 2012	March 15, 2012	November 13, 2013	November 14, 2013	December 9, 2013	December 17, 2013	January 15, 2013	October 31, 2013
2012- 179513	2012- 245353	2012- 258214	2012- 267467	2012- 136973	2012- 263172	2012- 0001852	2012- 0017317	2012- 0090754	2012- 0026646	2013- 10572107	2013- 20714135	2013- 20802510	2013- 10692569	2013- 10014894	2013- 10112004
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Korea Institute of Energy Research	Korea Institute of Energy Research	Liu Jingyang	Liu Jingyang	Liu Jingyang	Titan PV Co., Ltd.	Titan PV Co., Ltd.	Suzhou Suncome Solar Science & Technology Co., Ltd.	Urumqi Tuohuangzhe Information Technology Co., Ltd.	Yingli Solar China Co., Ltd.	Tongwei Solar Hefei Co., Ltd.	Hainan Yingli New Energy Co.,Ltd.	Hengshui Yingli New Energy Resources Co., Ltd.	Ulrich, Loser, Wolfram, Palitzsch	Ulrich, Loser, Wolfram, Palitzsch	Ulrich, Loser, Wolfram, Palitzsch
Apparatus and method for recovery of metal of photovoltaic module	Method for disassembling solar cell module	Waste crystalline silicon solar cell panel disassembling and recovering method	Method for recycling resources in waste crystal solar silicon cell piece in classified mode	EVA heat treatment method of waste crystalline silicon solar cell module	Auxiliary tool for frame detachment of photovoltaic assembly	Auxiliary tool for dismounting photovoltaic assembly frame	Photovoltaic module dismantling clamp	Photovoltaic module frame disassembly workbench	Solar cell frame detaching tool	Frame disassembly tool for crystalline silicon solar cell modules	Frame dismantling device for photovoltaic module	Photovoltaic component frame disassembly work table	Method for concentration of metals from metal-containing waste	Method for concentration of metals from metal-containing waste	Method for concentrating metals from scrap containing metal
July 27, 2015	January 21, 2015	August 24, 2016	April 6, 2016	August 24, 2016	Decemb er 10, 2014	February 11, 2015		April 1, 2015	February 18, 2015	March 11, 2015	2014.08. 20	2014.09. 24			
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October 1, 2013	October 1, 2013	May 8, 2014	May 8, 2014	May 8, 2014	August 8, 2014	August 8, 2014	September 26, 2014	October 18, 2014	November 11, 2014	November 20, 2014	March 25, 2014	March 26, 2014	April 10, 2014	April 10, 2014	April 10, 2014
2013- 0117478	2013- 0117487	2014- 10192135	2014- 10192149	2014- 10194318	2014- 20448190	2014- 20448218	2014- 10498684	2014- 20606555	2014- 20668779	2014- 20702057	2014- 20137370	2014- 20139803	10-2014- 105143	11-2014- 001923	2014- 723696
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Eco Recycling S.R.L.	Korea Institute of Energy Research	La Mia Energia Scarl	Recyclage Valorisation Photovoltaique R V P	Commissariat Energie Atomique	Mitsubishi Electric Corp.	Nihon Superior Co., Ltd.	Nihon Superior Co., Ltd.	Korea Institute of Energy Research	Ulrich, Loser, Wolfram, Palitzsch	Kumoh National Institute of Technology Industry- Academic Cooperation Foundation	Korea Interfacial Science and Engineering Institute	Korea Institute of Energy Research	Ulrich, Loser, Wolfram, Palitzsch	Korea Electronics Technolc y Institute	l imited Dartnershin luan
Process for treating spent photovoltaic panels	Method for disassembling photovoltaic module	De-assembling system for a photovoltaic panel enabling salvage of original materials	Process and plant for recycling photovoltaic panels	Method for the removal of metals in a silicon substrate	Solar battery module recycling method, solar battery module recycling device, and recycle material whose raw material is glass piece	Regeneration method of solar battery panel	Recycling method of solar battery panel	Method for disassembling photovoltaic module	Method for concentrating metals from scrap containing metal	A method for recovering silver from the waste solar cell	The recycling method of solar battery cell	Apparatus for disassembling solar cell module	Method for concentrating metals from scrap containing metal	A chemical and mechanical etching method for reuse a solar cell	
			2016.03. 11							July 20, 2015		May 12, 2016			
			3017551 B1							10-1539528 B1		10-1622345 B1			
May 9, 2014	September 30, 2014	December 18, 2014	February 20, 2014	November 18, 2014	March 31, 2014	May 20, 2014	June 3, 2014	October 1, 2014	April 10, 2014	February 20, 2014	February 26, 2014	March 27, 2014	April 10, 2014	August 28, 2014	December
2014- 739960	2014- 187023	2014- 833229	2014- 051356	2014- 061112	2014- 071792	2014- 104783	2014- 115203	2014- 203208	2016- 506787	2014- 0019498	2014- 0022750	10-2014- 0036249	10-2015- 7032379	10-2014- 0113270	10-2014-
ЕР	ЕР	EP	FR	FR	Чſ	Чſ	Чſ	Чſ	Ъ	KR	КR	KR	KR	KR	
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Korea Institute of Energy Research	Korea Interfacial Science and Engineering Institute	Ulrich, Loser, Wolfram, Palitzsch	Ulrich, Loser, Wolfram, Palitzsch	La Mia Energia Scarl	Korea Institute of Energy Research	Eco Recycling S.R.L.	La Mia Energia Scarl	Changzhou Trina Solar Energy Co., Ltd.	Juli New Energy Co., Ltd.	Changzhou Trina Solar Energy Co., Ltd.	Leshan Topraycell Co., Ltd.	Tianhe Optical Energy Co., Ltd., Changzhou	Changzhou Trina Solar Energy Co., Ltd.	Dongguan Corehelm Electronic Material Technology Co., Ltd.	Sasil S.P.A.
Method of collecting solar cell	Solar cell recycling jig from waste solar modules and solar cell recycling method from waste solar modules using the same	Method for concentrating metals from scrap containing metal	Method for Concentrating Metals from Scrap Containing Metal	De-assembling system for a photovoltaic panel enabling salvage of original materials	Method for disassembling photovoltaic module	Process for treating spent photovoltaic panels	De-assembling system for a photovoltaic panel enabling salvage of original materials	No-damage recycling method for photovoltaic module	Solar module frame dismounting device	Glass separation method for crystalline silicon solar cell module	Solar cell recycling method	A kind of method reclaiming aluminum silver from useless crystal silicon cell sheet	Recovery method of high-purity silicon in waste solar cells	Method for recycling crystalline silicon solar cell module	Method and apparatus for detaching glass form a mono- or polycrystalline silicon-based photovoltaic panel
January 5, 2016	January 29, 2015				Septemb er 27, 2016				Decemb er 23, 2015						
10-1584174 B1	10-1490088 B1				9455367 B2				204893371 U						
May 16, 2014	November 28, 2014	April 10, 2014	April 10, 2014	December 18, 2014	October 1, 2014	May 9, 2014	December 18, 2014	April 21, 2015	July 26, 2015	October 16, 2015	October 23, 2015	December 14, 2015	December 14, 2015	December 31, 2015	September 16, 2015
2014- 0058817	2014- 0168474	PCT- DE2014- 100127	14/783111	15/105332	2014- 503412	pct-it2014- 000124	pct- ib2014- 067071	2015- 10189864	2015- 20543842	2015- 10667835	2015- 10695951	2015- 10921908	2015- 10925076	2015- 11013607	2015- 185389
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2014	2014	2014	2014	2014	2014	2014	2014	2015	2015	2015	2015	2015	2015	2015	2015

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Shinshu Univ.	Shinshu Univ.	Dongying Yuhaolong Photoelectric Technology Co., Ltd.	Gree Electric Appliances, Inc. of Zhuhai	National Institute of Advanced Industrial Science and Technology
Method of recovering valuable material from solar cell module and processing equipment for recovering the same	Method of recovering valuable material from solar cell module and processing equipment for recovering the same	Special extracting tool of solar cell panel frame	Waste and old photovoltaic module recycling equipment	Method for solubilizing crosslinked EVA, and method for recovering resource from used solar cell by employing solubilization method
		June 29, 2016	Novemb er 23, 2016	
		205342359 U	205702871 U	
March 31, 2015	October 28, 2015	February 29, 2016	June 20, 2016	April 8, 2016
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plication Filing date Patent number	Filing date Patent number	Patent number		Date of patent	Title of invention	Assignee	Legal status
97- 5873		May 12, 1997	5897685 A	April 27, 1999	Recycling of CdTe photovoltaic waste	Drinkard Metalox, Inc.	Abandoned
97- May 12, 4851 1997	May 12, 1997		5779877 A	July 14, 1998	Recycling of CIS photovoltaic waste	Drinkard Metalox, Inc.	Expired
98- July 20, 3527 1998	July 20, 1998		0893250 B1	June 4, 2003	Method for separating the components of a laminated glazing	Deutsche Solar AG	Abandoned
98- May 12, 3191 1998	May 12, 1998		6129779 A	October 10, 2000	Reclaiming metallic material from an article comprising a non-metallic friable substrate	First Solar, LLC	Granted
98- June 16, 7630 1998	June 16, 1998		5997718 A	Decemb er 7, 1999	Recycling of CdTe photovoltaic waste	Drinkard Metalox, Inc.	Abandoned
99- February 2294 5, 1999	February 5, 1999				Semiconductor device, solar cell module and methods for their dismantlement	Canon Kabushiki Kaisha	Abandoned
00- September 3751 11, 2000	September 11, 2000		1187224 B1	March 22, 2006	Recycling method for CdTe/CdS thin film solar cell modules	Antec Solar AG	Abandoned
00- May 17, 3100 2000	May 17, 2000		6391165 B1	May 21, 2002	Reclaiming metallic material from an article comprising a non-metallic friable substrate	First Solar, LLC	Granted
01- September 7298 4, 2001	September 4, 2001		4790171 B2	July 29, 2011	Reproduction method of CdTe/Cds thin film solar cell module	Antec Solar GmbH	Abandoned
01- August 24, 3390 2001	August 24, 2001		6572782 B2	June 3, 2003	Process for recycling CdTe/Cds thin film solar cell modules	Antec Solar GmbH	Abandoned
02- December 3666 5, 2002	December 5, 2002		4271433 B2	March 6, 2009	Method for recovering component of CIS thin-film solar cell module	Showa Shell Sekiyu KK	Granted
04- June 28, 3666 2004	June 28, 2004		6940008 B2	Septemb er 6, 2005	Semiconductor device, solar cell module, and methods for their dismantlement	Canon Kabushiki Kaisha	Abandoned
05- August 26 5918 2005	August 26 2005	ý.	4602872 B2	October 8, 2010	Method of recovering structural component of CIS system thin film solar cell module	Showa Shell Sekiyu KK	Granted
:T- 2006- June 1, 1153 2006	June 1, 2006				System and method for separating tellurium waste	Brookhaven Science Associates	Abandoned

Granted	Abandoned	Granted	Granted	Granted	Abandoned	Abandoned	Granted	Abandoned	Granted	Granted	Granted	Granted	Granted	Granted
Brookhaven Science Associates	Showa Shell Sekiyu K. K.	Loser Ulrich Palitzsch Wolfram	S & D KK	Jenoptik Automatisierungstechnik GmbH	Calyxo GmbH	Calyxo GmbH	General Electric Company	General Electric Company	Neo Material Technologies INC.	Molycorp Minerals Canada ULC.	Shenzhen GEM High-Tech Co., Ltd.	Advanced Solar Power (Hangzhou) Inc.	Lobbe Industrieservice GmbH & Co. KG	Terumu KK
System and method for separating tellurium from cadmium waste	Method of recovering constituent member of CIS type thin- film solar cell module	Method for recycling a thin layer solar module during simultaneous recovering of recyclable material, by loading photovoltaic cells to be processed so that the plastic portion is separated from remaining components of the module	Apparatus and method of recovering film	Recycling process for thin film solar cell modules	Photovoltaic module recycling	Photovoltaic module recycling	Method and system for respectively recycling tellurium and cadmium from module containing cadmium telluride	Method for recovering tellurium from module comprising cadmium telluride	Treatment of indium gallium alloys and recovery of indium and gallium	Treatment of indium gallium alloys and recovery of indium and gallium	Method for recycling gallium, indium and germanium from wasted thin-film solar cells	Recovery processing method of cadmium telluride thin-film solar cell	Method and assembly for the recovery of metals from composite materials, in particular from silicon solar modules, thin film solar modules, LCD displays or the like	Recycling apparatus and recycle method for solar battery panel
June 8, 2010		October 31, 2012	March 12, 2010	March 24, 2016			March 30, 2016			Septemb er 16, 2014	October 21, 2015	March 16, 2016	February 13, 2013	May 20, 2016
7731920 B2		10-2008-058530 B4	4472014 B2	10-1607706 B1			102953081 B			8834818 B2	103199148 B	103199147 B	2556893 A3	5938309 B2
May 31, 2006	February 2, 2007	November 21, 2008	January 30, 2009	June 4, 2009	August 13, 2009	August 13, 2009	August 31, 2011	April 29, 2011	November 22, 2011	November 22, 2011	January 9, 2012	January 10, 2012	August 7, 2012	September 12, 2012
2006- 421343	PCT- JP2007- 053848	10-2008- 058530	2009- 020329	10-2009- 0049461	PCT- US2009- 053705	2009- 058959	2011- 10255648	PCT- US2011- 034410	PCT- CA2011- 001276	2011- 989740	2012- 10009187	2012- 10006584	2012- 179513	2012- 200257
SU	РСТ	DE	٩	KR	РСТ	SU	CN	РСТ	РСТ	NS	CN	CN	EP	Ъ
2006	2007	2008	2009	2009	2009	2009	2011	2011	2011	2011	2012	2012	2012	2012

12	٩	2012- 263172	November 30, 2012			Method of recovering constituent material of solar cell element	Shinryo Corp.	Pending
12	٩	2012- 070522	March 27, 2012			Method for recovering glass material	Showa Shell Sekiyu KK	Abandoned
112	٩	2012- 227542	October 13, 2012			Method of recovering valuables from CIS thin film solar cell	Miyazaki Prefecture	Pending
012	РСТ	PCT- SE2012- 051396	December 14, 2012			Recycling of copper indium gallium diselenide	Midsummer AB	Granted
012	SU	2012- 364454	December 14, 2012			Recycling of copper indium gallium diselenide	MIDSUMMER AB	Pending
012	NS	13/527841	June 20, 2012	8821711 B2	Septemb er 2, 2014	Process to recycle end of life CdTe modules and manufacturing scrap	Colorado School of Mines	Granted
014	CN	2014- 10466337	September 12, 2014	104201248 B	July 6, 2016	Recovery method of thin-film solar cells	Chengdu Cryostech Equipment Co., Ltd.	Granted
014	CN	2014- 10090916	March 12, 2014	103866129 B	January 20, 2016	Recycling method of CdTe solar cell module	Institute of Electrical Engineering, Chinese Academy of Sciences	Granted
014	DE	11-2014- 004689	September 16, 2014			Method for the separating detachment of layers of a composite component formed from at least two layers	Loser Chemie GmbH	Pending
014	ЕР	2014- 739960	May 9, 2014			Process for treating spent photovoltaic panels	Eco Recycling S.R.L	Abandoned
014	РСТ	PCT- IT2014- 000124	May 9, 2014			Process for treating spent photovoltaic panels	Eco Recycling S.R.L.	Abandoned
014	MO	PCT- EP2014- 069691	September 16, 2014			Method for the separating detachment of layers of a composite component formed from at least two layers	Loser chemie GmbH	Pending
015	CN	2015- 10104365	March 11, 2015			A kind of recovery method of copper-indium-gallium- selenium photovoltaic assembly	Hanergy New materials Technology Co., Ltd.	Pending
015	CN	2015- 10393356	July 8, 2015			Copper-indium-gallium-selenium flexible thin film solar battery recycling method	Changde Hanneng Film Solar Energy Technology Co., Ltd.	Pending
015	٩Ļ	2015- 029492	February 18, 2015			Recycling method for substrate type thin film solar cell and recycling method for substrate with transition metal	Solar Frontier KK	Pending

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Filing year	Country	Application number	Filing date	Patent number	Date of patent	Title of invention	Assignee	Legal status
2008	CN	2008- 10093635	April 18, 2008			Method for recycling transparent conducting glass substrate of solar cell	Contrel Technology Co., Ltd.	Abandoned
2011	КК	2011- 0115076	November 7, 2011			Method for recycling the dye of a dye-sensitized solar cell module capable of improving a dye absorption speed	Dongjin Semichem Co., Ltd.	Pending
2012	РСТ	PCT- KR2012- 009171	November 2, 2012			Method for recycling dye of dye-sensitized solar cell module	Dongjin Semichem Co., Ltd.	Abandoned
2014	KR	10-2014- 0065359	May 29, 2014			Method of separating and purifying natural dye for dye-sensitized solar cells	Gyeongbuk Natural Color Industry Institute	Abandoned
2014	КК	10-2014- 0065378	May 29, 2014			Sorbent of separating and purifying natural dye for dye-sensitized solar cells	Gyeongbuk Natural Color Industry Institute	Abandoned
2015	CN	2015- 10580867	September 14, 2015			Method for recycling and reusing a transparent conducting glass substrate of a thin-film solar cell	Shandong Province Yucheng City Hanergy Thin Film Solar Energy Co., Ltd.	Pending

Appendix B: Examples of R&D projects on PV module recycling

Country/region	Project title	Targeted PV module
Japan	Development of recycling technology for	crystalline Si
	crystalline Si PV modules	
	Development of high-level recycling technology	crystalline Si
	of crystalline Si solar cell module by the wet	
	processing	
	Development of complete recycling technology	crystalline Si
	of glass and metals by separating with heated	
	cutter	
	Low cost disassembling technology	CIGS
	demonstration of laminated glass PV modules	
	Research and development of PV system	crystalline Si, thin-film Si, CIGS
	low-cost general-purpose recycling processing	
	method	
Korea	Recovery and purification of rare metal from	crystalline Si
	end-of-life c-Si solar module	
	Technology for recovering silicon and valuable	crystalline Si
	metals from end-of-life solar modules	
	Technology for recycling photovoltaic modules	crystalline Si
	Technology to recover valuable materials from	crystalline Si
	end-of-life photovoltaic modules	
	Low-cost/highly efficient recycling processing	crystalline Si
	system of c-Si PV module and processing	
	technology for materialization	
China	Thermal method of PV module recycling	crystalline Si
	Mechanical method of PV module recycling	crystalline Si
Europe	Photolife	crystalline Si, thin-film
	Full Recovery End-of-Life Photovoltaic (FRELP)	crystalline Si
	Photovoltaic panels Mobile Recycling Device	crystalline Si
	(PV Morede)	
	Reclamation of Gallium, Indium and Rare-earth	CIGS
	Elements from Photovoltaics, Solid-State	
	Lighting and Electronics Waste (Reclaim)	

Country/region	Japan
Project title	Development of recycling technology for crystalline Si PV modules
Granting agency	NEDO (New Energy & Industrial Technology Development Organization)
Implementing organization	Mitsubishi Materials Corporation
Project period	FY2015-2018
Targeted PV module	c-Si
Project target	5 JPY/W (as supposed capacity: 200MW/year)
Technology type	Mechanical
Targeted and recovered subjects	Frame, glass, Ag containing material
Technical description	- Removal of Al frame and terminal box by machine
	- Scraping cover glass, and recovering remaining sheet consisting of
	EVA and metals containing Ag concentrated
	- Sorting and separating glass scraped for glass cullet and other
	particles containing Ag
	Crystalline Si PV module Scraping glass Scraping glass Scraping glass Scraping blass Glass for recycling Glass for recycling Giass for recycling
	[Courtesy of Mitsubishi Materials Corporation]
Reference	Mitsubishi Material Corporation: Development of recycling technology for
	crystalline Si PV modules, FY2015 NEDO debriefing session, Oct. 2016
	(in Japanese)

Country/region	Japan
Project title	Development of high-level recycling technology of crystalline Si solar cell
	module by the wet processing
Granting agency	NEDO
Implementing organization	Toho Kasei Co., Ltd.
Project period	FY2015-2016
Targeted PV module	c-Si
Project target	5 JPY/W (as supposed capacity: 200MW/year)
Technology type	Mechanical & chemical
Targeted and recovered subjects	Glass (full-scale), metals
Technical description	- Removal of Al frame and terminal box
	- Scraping back sheet
	- Scraping layer consisting of EVA and cells
	- Removal of adhering EVA layer from glass by remover, and recovery
	of 'full-scale glass' without breakage
	- Separating EVA and cells by another remover (organic liquid)
	Removal of Alframe and terminal box Scraping backsheet Soraping layer consisting of EVA and Si cells Removal of EVA layer from cover glass Removal of EVA and recovery of Si and metals
	Toronkollow Backbert V/A Voregleo Altane
	[Courtesy of Toho Kasei Co., Ltd.]
Reference	Toho Kasei Co., Ltd.: Development of high-performance recycling
	technology using wet-method for crystalline Si PV modules, FY2015
	NEDO debriefing session, Oct. 2016 (in Japanese)

Country/region	Japan
Project title	Development of complete recycling technology of glass and metals by
	separating with heated cutter
Granting agency	NEDO
Implementing organization	Hamada Corporation, NPC Incorporated
Project period	FY2015-2018
Targeted PV module	c-Si
Project target	5 JPY/W (as supposed capacity: 200MW/year)
Technology type	Mechanical & chemical (under discussion)
Targeted and recovered subjects	Glass, metals
Technical description	- Removal of Al frame and terminal box by machine
	- Cutting adherend between glass and EVA by heated cutter
	- Scraping EVA adhering glass, and recovery of glass without breakage
	- Separation of metals, EVA and backsheet from remaining sheet.
	Remove aluminum frames Separate EVA from glass
	Aluminum Cell EVA Glass Back sheet Heated cutter
	Collecting metal (aluminum)
	[Courtesy of NPC Incorprated]
Reference	Hamada Corporation and NPC Incorporated: Development of recycling
	technology of glass and metals from photovoltaic panels by separation with
	a heated cutter, FY2015 NEDO debriefing session, Oct. 2016 (in Japanese)
	NPC Incorporated: Development of recycling technology of glass and
	metals from photovoltaic panels by separation with a heated cutter,
	NEDO-ADEME joint workshop on circular economy and recycling, Dec.
	2016

Country/region	Japan
Project title	Low cost disassembling technology demonstration of laminated glass PV
	modules
Granting agency	NEDO
Implementing organization	Solar Frontier K.K.
Project period	FY2015-2018
Targeted PV module	CIS
Project target	5 JPY/W (as supposed capacity: 200MW/year)
Technology type	Mechanical & chemical
Targeted and recovered subjects	Glass, semiconductor metals (CIS layer, Mo)
Technical description	 Cutting EVA layer between cover glass without circuit and substrate glass with circuit by heated cutter Removal of EVA layer adhering glass by chemical treatment, and recovery of cover glass Removal of EVA and recovery of CIS layer from the substrate glass by alkali solution Recovery of Mo layer by acid. Cutting EVA layer between cover glass and substrate glass Produles Cutting EVA layer between cover glass and substrate glass
Reference	Solar Frontier K.K.: Development of low-cost cover-glass separation
	techniques for laminated glass-glass PV modules, FY2015 NEDO
	debriefing session, Oct. 2016 (in Japanese)

Country/region	Japan
Project title	Research and development of PV system low-cost general-purpose
	recycling processing method
Granting agency	NEDO
Implementing organization	Shinryo Corporation
Project period	FY2015-2017
Targeted PV module	c-Si, thin-film Si, CIS
Project target	5 JPY/W (as supposed capacity: 200MW/year)
Technology type	Thermal (and mechanical for CIS)
Targeted and recovered subjects	Glass (full-scale), metals
Technical description	Following processes are operated automatically;
	- Removal of Al frame
	- Scraping back sheet
	- Combusting EVA with recovering combustion heat
	After the processes above:
	- Retrieving full-scale cover glass without breakage and metals
	In case of CIS:
	- Retrieving CIS layer from substrate glass by scraping.
	Euroro 15 12/4 Euroro
Reference	M. Noda, K. Kushiya, H. Saito, K. Komoto, and T. Matsumoto:
	Development of the PV Recycling System for Various Kinds of PV
	Modules, 6th WCPEC, Kyoto, Japan, November 2014
	Shinryo Corporation: Development of low-cost recycling technology for
	various kinds of PV modules, FY2015 NEDO debriefing session, Oct.
	2016 (in Japanese)

Country/region	Korea
Project title	Recovery and purification of rare metal from end-of-life c-Si solar module
Granting agency	Currently, Ministry of Trade, Industry and Energy (MOTIE)
Implementing organization	Korea Research Institute of Chemical Technology (KRICT), Kangwon
	National University
Project period	June 1, 2009 - May 31, 2012
Targeted PV module	c-Si
Project target	Recovery/recycling rates, purity
Technology type	Chemical
Targeted and recovered subjects	Only Si
Technical description	- Dissolving EVA by submerging modules in an organic solvent with
	additional ultrasound irradiation to overcome the shortcomings of
	chemical separation, which typically requires long duration treatment.
Reference	Sukmin Kang, et al.: Experimental investigations for recycling of silicon
	and glass from waste photovoltaic modules, Renewable Energy 47
	(152-159) 2012.

Country/region	Korea
Project title	Technology for recovering silicon and valuable metals from end-of-life
	solar modules
Granting agency	Ministry of Environment (ME)
Implementing organization	Symphony Energy Co., Chonnam National University, Renew Energy Co.
Project period	May 1, 2011 - March 31, 2013
Targeted PV module	c-Si
Project target	Recovery/recycling rates, purity
Technology type	Thermal & chemical
Targeted and recovered subjects	Mainly Si, Ag, Cu
Technical description	- Decomposition of encapsulant using a thermal treatment furnace
	- Chemical method to recover silicone, silver and copper from cell
	scrap and ribbon mixture
Reference	Youn-Kyu Yi, et al.: Recovering Valuable Metals from Recycled
	Photovoltaic Modules, J. of Air & Waste Management Association 64
	(797-807), 2014

Country/region	Korea
Project title	Technology for recycling photovoltaic modules
Granting agency	Ministry of Trade, Industry and Energy (MOTIE)
Implementing organization	DSM Co., JSPV Co., Korea Interfacial Science and Engineering Institute
	(KISEI), Korea Electronics Technology Institute (KETI)
Project period	June 1, 2013 - May 31, 2016
Targeted PV module	c-Si
Project target	Recovery/recycling rates, purity
Technology type	Thermal & chemical
Targeted and recovered subjects	Mainly Si, Al, Ag, Cu
Technical description	A jig that can be applicable to modules to thermally recover cells without
	damaging the cells. Additional wet recovery technology to recover
	valuable metals from the recovered cell scrap and ribbon mixture.
Reference	Jongsung Park, et al.: An Eco-Friendly Method for Reclaimed Silicon
	Wafers from a Photovoltaic Module: from Separation to Cell Fabrication,
	Green Chem. 18 (1706-1714), 2016

Country/region	Korea
Project title	Technology to recover valuable materials from end-of-life photovoltaic
	modules
Granting agency	Ministry of Science, ICT and Future Planning (MSIP)
Implementing organization	Korea Institute of Energy Research (KIER), Chungnam National
	University, Pukyong National University
Project period	January 1, 2013 - December 31, 2015
Targeted PV module	c-Si
Project target	Recovery rate: Si(90%), Ag(95%)
	Purity: Si(7N), Ag(4N)
Technology type	Thermal & chemical
Targeted and recovered subjects	Si, Al, glass, Ag, Cu, Sn, Pb
Technical description	- Pre-treatment of the module surface, e.g., patterning
	- Thermal decomposition and retrieving cells without damages
	- Retrieving all valuable metals from the cell scrap and ribbons by wet
	and dry methods, respectively
Reference	Jun-Kyu Lee, Jin-Seok Lee, et al .:: Low-cost Recovery Process of
	Unbroken Solar Cell from PV Module, 25th PVSEC, Busan, Korea,
	November 2015

Country/region	Korea
Project title	Low-cost/highly efficient recycling processing system of c-Si PV module
	and processing technology for materialization
Granting agency	Ministry of Trade, Industry and Energy (MOTIE)
Implementing organization	Pretech Co., Korea Institute of Energy Research (KIER), Pukyong
	National Univeristy, Hapdong Hightechglass Co., Chungbuk Technopark
Project period	May 1, 2016 - April 30, 2019
Targeted PV module	c-Si
Project target	Technology demonstration
	- Facility capability: 2ton/day
	- Recovery rate: wafer(70%), glass(98%), Si(90%), Ag(98%), other
	metals(95%)
	- Purity: Si(6N), Ag(4N), other metals(3N)
Technology type	Thermal & chemical
Targeted and recovered subjects	Si(incl. unbroken wafer), Al, glass, Ag, Cu, Sn-Pb alloy
Technical description	Implementing technology to recover over 70% of undamaged cells from
	EoL modules based on continuous thermal treatment, in a 2 ton/day output
	grade facility. Developing technologies and equipment to recover
	re-sellable materials from glass, cells and ribbons, respectively.
	(a) Glass cracking
	(b) EVA patterning
	(c) Glass cracking EVA patterning EVA Gisss Gisss Gass escape through crack of glass
Reference	Jin-Seok Lee: Recovery Technology of Intact Wafer from End-of-life c-Si
	PV Module, 26th PVSEC, Singapore, October 2016

Country/region	China
Project title	Thermal method of PV module recycling
Framework	National High-tech R&D Program "PV Recycling & Safety Disposal
	Research"
Implementing organization	Chinese Research Academy of Environmental Sciences, Institute of
	Electrical Engineering
Project period	2012 - 2015
Targeted PV module	c-Si
Technology type	Thermal & chemical
Targeted and recovered subjects	Glass and metals
Technical description	- Recovery of glass and metals such as Si cells by combustion process
	- Separation and recovery of metals contained in Si cells by chemical
	processes.
	The initial PV module Put in muffle furnace PV module after heating
	Clean cell debris Cell debris
Reference	J. Liu: Experimental Study on Recycling of Waste Crystal Silicon PV
	Modules Technology, PV Environmental Health and Safety Workshop,
	Beijing, China, March 2014

Country/region	China
Project title	Mechanical method of PV module recycling
Framework	National High-tech R&D Program "PV Recycling & Safety Disposal
	Research"
Implementing organization	YingLi Solar, Institute of Electrical Engineering
Project period	2012 - 2015
Targeted PV module	c-Si
Technology type	Mechanical
Targeted and recovered subjects	Glass, metals and plastics
Technical description	- Removal of Al frame and terminal box
	- Crushing and refrigerating to -197 degree C by using liquid nitrogen
	- Grinding module refrigerated
	- Separating particles of encapsulation (EVA), glass and mixed powder
	of Si, Ag, Cu, etc. physically
	Modules Artificial dismantling Box, aluminium Glass particle and copper Mixed power Back of Si, Ag, Sheet A, etc.
Reference	Z. Wang: China PV Recycling technology -Physical method, PV Environmental Health and Safety Workshop, Beijing, China, March 2014

Country/region	Europe
Project title	Photolife
Framework	EU Life+ program
Implementing organization	Eco recycling (Italy), High-Tech Recycling Centre (Italy), Eco Power,
	Green Engineering
Project period	June 2014 – August 2017
Targeted PV module	c-Si, thin-film
Targeted and recovered subjects	To demonstrate the technical feasibility of an innovative process for the
	recovery of different types of PV components through
	The realization of an automated pilot plant with a capacity of 200t/year.
Technology type	(Mechanical, thermal and) chemical
Targeted and recovered subjects	Glass, metals
Technical description	The process involves the following steps: the target of this project is a
	hydrometallurgical treatment of shredded PV modules.
	- Manual dismantling of PV frames for Al recovery
	- Automatic shredding of PV
	- Sieving giving three fractions (coarse, intermediate and fine) and first
	glass separation
	- Solvent treatment of the coarse fraction to give other recoverable glass
	fraction
	- Sieving separating glass from plastic residual (Tedlar+EVA)
	- Hydrometallurgical treatment of fine fraction for metal recovery
	PVP → Multiple Crushing PVP → Multiple Crushing PVP → Crushing Course fraction (d < 0.08-0.4 mm) Sieving Course fraction (d > 1mm) Course fraction (d > 1mm) (d
Reference	http://www.photolifeproject.eu
	G. Granata, et al: Recycling of Photovoltaic Panels by Physical
	Operations, Solar Energy Materials & Solar Cells 123 (239–248), 2014

Country/region	Europe
Project title	Full Recovery End-of-Life Photovoltaic (FRELP)
Framework	EU Life program
Implementing organization	Sasil, S.p.A. (Italy), Stazione Sperimentale del Vetro (Italy), PV CYCLE
	(Belgium)
Project period	July 2013 – June 2017
Targeted PV module	c-Si
Targeted and recovered subjects	Recovery rate:100% for glass & metals
	Development of prototype for 1 ton/hour treatment
Technology type	Laser/IR, mechanical, thermal and chemical
Targeted and recovered subjects	Glass, metals
Technical description	- Automatic removal of frames and terminal box
	- Heating and separating glass by IR, laser and knife
	- Pyrolysis of reminded structure (EVA/cell/EVA/back sheet (PET))
	- Chemical (acid) treatment of Si cells recovered and electrochemical
	treatment for retrieving metals
	FIRE PRODUCTION O,24 KW O,12
Reference	 L. Ramon, Full Recovery End of Life Photovoltaic, Workshop on PV Life Cycle Management and Recycling at the 29th EU-PVSEC, Amsterdam, the Netherlands, September 2014 P. Ercole: FRELP 2 Project - Full Recovery End of Life Photovoltaic, 32nd EU-PVSEC, Munich, Germany, June 2016



Country/region	Europe
Project title	Reclamation of Gallium, Indium and Rare-earth Elements from
	Photovoltaics, Solid-State Lighting and Electronics Waste (Reclaim)
Framework	EU FP7 program
Implementing organization	Nederlandse Organisatie voor Toegepast Natuurwetenschappelijk
	Onderzoek (the Netherlands), CogVis Software and Consulting GmbH
	(Austria), Optoelectronica – 2001 SA (Romania), Indumetal Recycling
	(Spain), Relight (Italy), Coolrec (the Netherlands), Técnicas Reunidas
	(Spain), Ondeo Industrial Solutions (the Netherlands), Francisco Albero
	(Spain), Österreichische Gesellschaft für System und
	Automatisierungstechnik (Austria), Technische Universität Wien (Austria)
Project period	January 2013 – December 2016
Targeted PV module	CIGS
Targeted and recovered subjects	To develop technological solutions for recycling gallium, indium and rare
	earth elements. To implement the technologies in a pilot plant in an
	industrial setting to demonstrate its application.
Technology type	Mechanical and chemical
Targeted and recovered subjects	Glass and metals
	Recovery rate of rare metals: 95%
	Purification (In, Ga): 99.99%
Technical description	- Crushing and sorting PV modules
	- Recovering cover glass and substrate glass containing CIGS layer
	- Chemical treatment of substrate glass and recovery of metals (In and
	Ga)
	- Purification of recovered metals (In and Ga)
Reference	http://www.re-claim.eu/
	W. Steeghs, Suez Water: Recovery of Indium and Gallium from Flat Panel
	Displays and Photovoltaic (CIGS) modules, RECLAIM Workshop on
	Reclamation of key metals from Energy Efficient Lighting, Flat Panel
	Displays and Photovoltaic modules, June 2016



