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BROADER PERSPECTIVES

PROGRESS IN PHOTOVOLTAICS WILEY

Major challenges and opportunities in silicon solar module recycling

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Abstract

This article examines some of the basic questions about silicon module recycling: (1) What can be recovered from silicon modules? (2) What recycling technologies are needed? (3) What are the potential revenues for different recycling scenarios? And (4) what are the major challenges for different recycling scenarios? Three recycling scenarios are considered: module reuse, component extraction, and material extraction. Recycling process sequences for different scenarios are outlined. The discussions conclude that module reuse generates the highest revenue with the fewest processing steps, while material extraction leads to the lowest revenue with the most processing steps. It is suggested that gentle and clean separation of silicon solar cells from the glass pane is a critical technology for silicon module recycling. It is also argued that two low-concentration metals must be recovered from silicon modules: silver as a scarce material and lead as a toxic material. Their recovery requires chemical methods, while bulky materials including glass cullet, aluminum frame, and copper wiring can be recovered with physical methods. The silicon in the cells can be extracted with different qualities: ferro-silicon, metallurgical-grade silicon, or solar-grade silicon, with a higher revenue and more complicated recycling process for purer silicon. Markets outside the solar industry for the recovered silicon should be explored. The biggest challenge for module reuse is to find a large and sustained market for hundreds of gigawatts peak of decommissioned modules a year, and the biggest challenge for component extraction is the many different module and cell structures on the market and cell efficiency variability. For all the three scenarios, the cost of collecting and processing waste modules is a common challenge.

KEYWORDS

module standardization, recyclability, recycling processes, recycling technologies, silicon modules

Abbreviations: AM, air mass; BSF, back-surface field; EU, European Union; EVA, ethylene vinyl acetate; GWp, gigawatt peak; PET, polyethylene terephthalate; PVF, polyvinyl fluoride; PVDF, polyvinylidene fluoride; SEIA, Solar Energy Industries Association; WEEE, Waste Electrical and Electronic Equipment Directive; Wp, watt peak.

1 | INTRODUCTION

A major obstacle on the horizon to sustainable solar photovoltaic technologies is waste modules. As the deployment of solar modules expands rapidly, so will their wastes. According to the International Renewable Energy Agency,[1] waste modules are projected to total up to 78 million metric tons cumulative by 2050 or 6 million metric tons a year in 2050. As a typical 60-cell silicon (Si) module weighs 18–18.5 kg, the number of waste modules will be on the order of 4.3 billion cumulative by 2050 or 330 million a year in 2050. In the last 2 years (2018 and 2019), about 230 gigawatts peak (GWp) of solar modules were installed bringing the cumulative solar capacity to 630 GWp.[2] With a typical manufacturer guaranteed lifetime of 25 years, they would become waste in 2043–2044. It is possible that many modules will exceed their expected 25-year lifetime. Nevertheless, an increasing number of modules will reach their end-of-life earlier than expected because of damage during installation or storms, because of component failures, or simply because of the economic incentive of replacing older modules with higher-efficiency ones.

There are four commercial solar module technologies today: Si, cadmium telluride (CdTe), copper indium gallium selenide ($CuIn_xGa_{1-x}Se_2$ or CIGS), and amorphous Si (a-Si). Currently, Si modules account for 95.4% of the solar market, while CdTe possesses a 2.4% market share, CIGS 1.9%, and a-Si 0.3%.[3] Si modules, including multicrystalline Si and monocrystalline Si, have always been the dominant module technology with a market share hovering around 90% for the last 25 years.[3] Having established a global recycling program, First Solar recycles CdTe modules to recover 90% of the materials for reuse in new modules.[4] With a 95% market share, Si module recycling presents a more pressing need.

Efforts to develop recycling technologies for Si modules started in early 1990s.[5–7] Commercial recycling of solar modules started in the European Union (EU) about 10 years ago, with the mandate from the Waste Electrical and Electronic Equipment (WEEE) Directive.[8] PV CYCLE was established to manage solar module recycling in the EU.[9] In the United States, the Solar Energy Industries Association (SEIA) initiated a national voluntary solar module recycling program in 2016.[10] Both PV CYCLE and SEIA contract electronic waste and glass recyclers for solar module recycling. Most of these recyclers do not have dedicated facilities for solar modules but use or modify existing facilities established for general electronics or glass recycling. They usually recover only the bulky materials in Si modules including glass cullet, aluminum (Al) frame, and Cu wiring. Veolia built the first facility dedicated to Si module recycling in France in 2018 with an initial capacity of 2000 metric tons a year.[11] They shred then grind the modules and use an optical method to separate and recover Si from glass cullet. In the United States, two companies dedicated to solar module recycling started their services in 2019, Recycle PV Solar[12] and We Recycle Solar.[13] Recycle PV Solar charges a fee of $25/module for their service, excluding the costs to decommission, package, and ship waste modules.[12]

While more and more attention is drawn to this emerging issue of waste solar modules, there are lingering questions about how exactly Si module recycling should be done. Some of the first questions for solar module recycling are what to recover from waste modules:

1. Can waste modules be refurbished and then reused?
2. If not, what components can be extracted from waste modules for reuse?
3. If component extraction is not possible, what materials can be extracted for reuse?

On the business side, the questions include the following:

4. To whom do the recyclers sell the recovered modules, components, and/or materials?
5. What are the potential revenues for different recycling scenarios?
6. What are the costs for different recycling scenarios?
7. What is the most cost-effective approach to decommission solar modules?
8. How should waste modules be packaged to minimize damage during shipping?
9. What are the lowest-cost shipping methods for waste modules?
10. Where should the recycling facilities be located?
11. Would mobile recycling facilities make more sense over centralized ones?
12. What infrastructure should be established for waste module collection?

On the policy side, the main questions are the following:

13. Who should pay for waste module recycling?
14. How can we promote solar module recycling without a WEEE-type legislation?

In this article, we attempt to answer some of these questions, in particular Questions 1–5 and to some extent Questions 13 and 14. Three recycling scenarios are considered: module reuse, component extraction, and material extraction. By examining the structures of Si modules and cells, we can determine what components or materials are worth recovery. The recycling process sequence for each scenario is outlined, along with the technologies needed and potential revenue. Finally, some of the challenges for each recycling scenario are discussed. It is noted that the cost for any of the recycling processes is highly uncertain until they are fully developed, and prototype recycling facilities are up and running.

2 | COMMERCIAL RECYCLING PROCESSES FOR Si MODULES

Figure 1 shows the structure of the most common commercial Si modules today. The Al frame seals, in conjunction with a silicone adhesive, the edges of and provides mechanical support for the module. A junction box, which is not shown in the figure, is attached to the backside of the module. It has a plastic case containing Cu wiring,

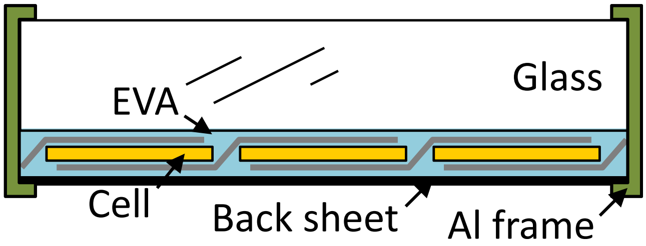

FIGURE 1 Schematic structure of today's most common commercial Si modules [Colour figure can be viewed at wileyonlinelibrary.com]

usually protected with silicone potting. Some modules also contain a Si bypass diode in the junction box. The glass is about 3 mm thick with a high transmittance. The Si solar cells are laminated to the glass pane through an encapsulant layer of ethylene vinyl acetate ($(C_2H_4)_n(C_4H_6O_2)_m$) or EVA). There is another layer of EVA between cells and backsheet. The backsheet typically consists of an electrically insulating layer of polyethylene terephthalate ($(C_{10}H_8O_4)_n$ or PET) protected on the outer surface with a thinner layer of polyvinyl fluoride ($(C_2H_3F)_n$ or PVF) or polyvinylidene fluoride $(CH_2CF_2)_n$ or PVDF). The EVA layers and backsheet are each about 0.3 mm thick.

Table 1 shows the weight distribution for various materials in a typical Si module.[14] Glass accounts for about 75% of the module weight and Al frame another 10%. These are the bulky materials in Si modules, along with the Cu wiring in the junction box.

Today, most recyclers recover only the bulky materials in Si modules: glass cullet, Al frame, and Cu wiring. They utilize mechanical methods to strip materials from modules (Figure 2):

1. Removal of junction box from the modules;
2. Extraction of Cu wiring from the junction box;
3. Removal of Al frame from the modules;
4. Shredding of remaining modules for glass cullet.

The glass cullet recovered contains EVA, Si cells, and backsheet as they are still laminated to the glass after Step 3. Therefore, the glass recovered is not high-transmittance solar glass but lower-quality impure glass. Some recyclers do not remove the Al frame or junction box but shred the entire module. This approach makes use of existing facilities but is less desirable because it does not allow effective separation and reuse of materials.

TABLE 1 Composition of Si modules by weight percent[14]

Material	Weight%
Glass	74
Al	10
Si	~3%
Polymers	~6.5%
Sn	0.12
Pb	<0.1
Cu	0.6
Ag	<0.006

Veolia, in their facility in France, added two more steps in order to recover Si from the modules (Figure 2)[11]:

1. Grinding of the shredded modules;
2. Separation of Si from glass cullet.

Veolia's glass cullet has a slightly better quality but is still not high-transmittance solar glass as it contains EVA and pieces of Si cells. As discussed later in this article, the Si they recover is low-quality impure ferro-Si, not high-purity solar-grade Si which is used to produce Si cells. On the other hand, these processing steps are all mechanical so they do not produce chemical wastes, except that the backsheet releases hydrogen fluoride (HF) from PVF or PVDF when the glass cullet is melted for new glass products. Therefore, a scrubber is needed to capture HF. PVF contains approximately 43% by weight of HF. As a result, assuming a mass of PVF of 30–100 g per module depending on the backsheet construction, the mass of HF generated during thermal treatment would be 13–43 g/module.

The revenue generated by the recovered glass, Al, and Cu is on the order of \$3 for a 60-cell Si module (Table 2). \$3/module is the basis for the projection of \$15 billion cumulative by 2050 in recovered materials from waste modules by the International Renewable Energy Agency,[1] but it is far below the actual cost to collect and process waste modules. Therefore, today's recyclers always require government subsidies or fees from module owners to be profitable.

3 | WHAT TO RECOVER FROM Si MODULES

With the revenue far below the cost for Si module recycling, it is worthwhile to rethink about what to recover from waste Si modules in an attempt to increase the revenue and offset the cost. There are three potential recycling scenarios for waste Si modules[17]:

1. Refurbish and reuse waste modules;
2. Extract and reuse components from waste modules;
3. Extract and reuse materials from waste modules.

Each scenario requires a different recycling process sequence with a different cost and revenue associated with it. This section analyzes these different recycling scenarios.

3.1 | Reuse of waste modules

Many decommissioned modules are still functioning but at lower efficiencies, typically at 80% of the original efficiencies as guaranteed by the manufacturers. They can be in principle refurbished and reused as a lower-quality product to secondary markets at maybe 50% of the price for new modules. Reuse of decommissioned modules is the first

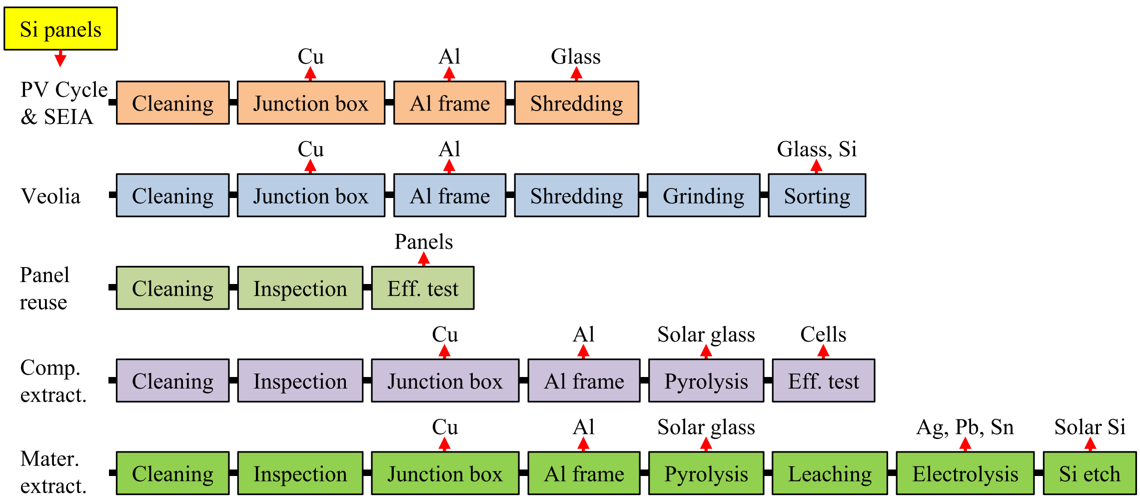

FIGURE 2 Comparison of two commercial recycling processes with three proposed recycling processes for Si modules [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Revenue of commercial recycling processes for Si modules as of 30 October 2019

Material	Weight (kg)	Price ($/kg)	Value ($/module)
Glass	13.5	0.06[15]	0.81
Al	1.83	0.95[16]	1.74
Cu	0.11	5.00[16]	0.55
Total			3.10

option for recyclers as it requires the fewest processing steps (Figure 2):

1. Cleaning of the modules to remove dust and other deposits on the modules;
2. Visual inspection for damage such as broken glass, punctured backsheet, bubbles in backsheet, burned out wiring, and hot spot;
3. Efficiency test to recertify the modules.

If half of the waste modules are functional, there would be 51 GWp of modules in 2043 for reuse out of 102 GWp installed in 2018.[2] The question is whether there will be a large and sustained market to absorb hundreds of gigawatts peak of reused modules a year while the spot price for new modules is only $0.20/Wp today for multicrystalline Al back-surface field (BSF) modules.[18] It is noted that there are other challenges for module reuse,[19] in addition to finding a market. Those challenges include lower-efficiency, shorter-lifetime, and unmatched modules with quality and safety issues. Today, the markets for refurbished modules are largely in developing countries where electronic wastes are not regulated. On the other hand, reused modules will eventually cease functioning and will need to be recycled. As a result, it is important to also consider methods for component and material extraction from waste modules.

3.2 | Component extraction from waste modules

If modules come in with damage or low efficiency, they cannot be reused. However, some of the components in those modules may be extracted for reuse in remanufactured modules if their performance is comparable with newly produced components. These are the inorganic components of the modules, namely,

1. The glass pane if it is extracted intact and clean;
2. The Si cells if they are extracted intact with good efficiency and solderability.

Inorganic components suffer less degradation than organic components and typically maintain their good performance far longer than the modules they are in. The Al frame and plastic case of the junction box are forcefully removed from the module, so they are damaged during the removal and cannot be reused. The EVA encapsulant, silicone adhesives, and backsheet cannot easily be removed and reused because they have been adhered or cross-linked during the original application process.

To extract components for reuse, the EVA layers and backsheet must be removed gently and cleanly in order to have the glass pane and Si cells recovered clean and intact. Component extraction requires more processing steps as compared with module reuse (Figure 2):

1. Cleaning of the modules;
2. Visual inspection for damaged modules;
3. Removal of junction box from the modules;
4. Extraction of Cu wiring from the junction box;
5. Removal of Al frame from the modules;
6. Separation of Si cells from the glass pane and polymers;
7. Efficiency test to sort the recovered cells.

A major concern for cell extraction is that 25-year-old cells have too low efficiencies to be economically feasible for reuse. This concern is expected to be short term. Today's Si cell efficiencies are very close to the Shockley–Queisser limit, so the pace at which cell efficiency improves will slow down and eventually level out unless inexpensive Si-based tandem cells are developed; that is, sometime into the future 25-year-old Si cells could have similar efficiencies to newly produced cells, and cell reuse could become an option. On the other hand, the technology to separate cells from glass should impact neither the efficiency nor the solderability of the cells. As discussed in Section 3.3, the first step in module production is interconnection of cells by soldering Cu ribbons onto the Ag pads and lines on the cells, so the Ag must be solderable after separation from glass.

3.3 | Material extraction from waste modules

If none of the components in a waste module can be reused due to damage or poor performance, our last option is to extract the materials for reuse. Figure 3 shows the structure of the most-common commercial Si cells today, the Al BSF cell. The Si wafer is a square of 157 × 157 mm^2 with a thickness of 180 μm. With a density of 2.32 g/cm^3, it weighs 10.3 g. It is high-purity solar-grade Si with a boron (B) doping level of 1 × 10^{16} $atoms/cm^3$ in the base, which makes it p-type. On the front side of the wafer, there is a 0.3 μm thick emitter of heavy phosphorus (P) doping in the 10^{19} $atoms/cm^3$ range. On the backside, there is a 10 μm thick BSF of heavy Al doping also in the 10^{19} $atoms/cm^3$ range. These heavily doped regions are out of the specifications for solar-grade Si. Other parts of the Si cell include a Si nitride (SiN_x) layer on the front side for antireflection, which is 80 nm thick. The front electrode is Ag, which is about 10 μm thick but in a grid pattern to let sunlight through. The back electrode is Al, which is also about 10 μm thick. There are also Ag pads on the backside to add solderability to the back Al electrode.

There is currently a major shift in the industry to move from the Al BSF cell to the passivated emitter rear contact (PERC) cell, but large

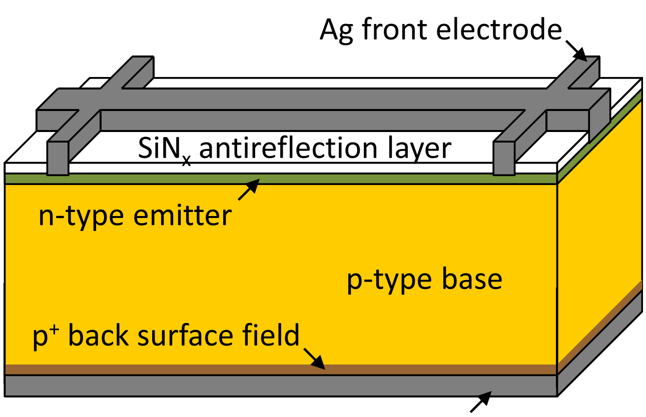

FIGURE 3 Schematic structure of today's most common commercial Si cell, the Al BSF cell [Colour figure can be viewed at wileyonlinelibrary.com]

quantities of waste PERC modules will not appear until 2040s. On the other hand, the structure of the PERC cell is similar to the Al BSF cell, except that the back electrode in the PERC cell is confined with a stack of thin Al oxide (Al_2O_3) and SiN_x layers sandwiched between Si and Al. Therefore, most of the analysis in this article is also applicable to the PERC cell.

The first step in module production is to electrically interconnect Si cells in series by soldering Cu ribbons onto them. The solder contains tin (Sn) and lead (Pb). Typical modules contain 60 cells in a 6 × 10 configuration, but there are also modules with 72 cells in a 6 × 12 configuration.

The materials that should be recovered from Si cells include valuable materials (Ag and solar-grade Si), toxic material (Pb), Cu from the ribbons, and Sn from the solder. The Al and SiN_x in the cells are unlikely to be recovered. They are difficult to recover, and they have little value. The processing steps for material extraction include the following (Figure 2)[20]:

1. Cleaning of the modules;
2. Visual inspection for damaged modules;
3. Removal of junction box from the modules;
4. Extraction of Cu wiring from the junction box;
5. Removal of Al frame from the modules;
6. Separation of Si cells from the glass and polymers;
7. Dissolution of metals from the cells;
8. Extraction of metals from the leachate;
9. Removal of SiN_x, emitter, and BSF for the Si base.

It is noted that material extraction requires chemical methods, as physical methods are incapable of extracting low-concentration materials from Si modules such as Ag, Pb, and Sn. Chemical methods typically have higher costs than physical methods and generate chemical wastes, so an important question is whether we should incorporate chemical methods into Si module recycling.

We argue that chemical methods are necessary as two of the metals in Si modules must be recovered: Ag and Pb. The known reserve of Ag on our planet, according to the United States Geological Survey,[21] is 560 000 metric tons. At the current mining rate of 27 000 metric tons per year, the known Ag reserve would be depleted in 21 years. We must recover Ag from waste Si modules to sustain the Si solar industry until a competitive Ag-free module technology emerges. Pb is toxic and makes the recycling sludge hazardous if not removed. Extraction of these two metals from Si modules requires chemical methods.

Another important question in material extraction is what quality of Si is to be recovered: ferro-Si, metallurgical-grade Si, or solar-grade Si? They have different purity levels. Purer materials generate higher values, but they also require more processing steps. This is a financial decision the recyclers will have to make. The Si recovered by Veolia contains Al, Ag, SiN_x, EVA, and backsheet, so it can be sold only as ferro-Si with a minimum Si content of 75% for \$0.45/kg (Table 3); that is, physical methods generate a mere \$0.31/module from the Si cells. By removing all the non-Si materials from the cells, the recovered Si is

TABLE 3 Revenues from Si of different qualities as of 30 October 2019

Si quality	Purity (%)	Weight (kg)	Price ($/kg)	Value ($/module)
Ferro-Si	75	0.68	0.45[23]	0.31
Metallurgical-grade Si	99	0.62	1.50[23]	0.93
Solar-grade Si	99.9999	0.56	7.58[18]	4.24
Second-grade Si	99.9999	0.56	5.52[18]	3.09

upgraded to metallurgical-grade Si with a minimum of 99% purity for $1.50/kg. Chemical methods are typically needed to remove the non-Si materials from the cells such as dissolving metals in nitric acid (HNO_3).[20,22] The remaining impurities are now B, P, and Al, which are about 0.05% or less in concentration in the Si wafer. If the emitter and BSF are removed and only the base is recovered, the Si becomes solar-grade Si. Prime-grade solar Si has a price of $7.58/kg today,[18] but the recovered Si base may be forced to sell as second-grade solar Si for $5.52/kg. Table 3 lists the revenues for different Si qualities. Step 9 in the process sequence above determines whether the recovered Si is metallurgical-grade Si or solar-grade Si.

4 | TECHNOLOGIES FOR COMPONENT/MATERIAL EXTRACTION

There are three recycling scenarios for Si modules, and the recycling process becomes more and more complicated as we move from module reuse to component extraction to material extraction (Figure 2). Ideally, all the waste Si modules should begin with the same processing steps. If module reuse is not possible, we add a few more steps for component extraction. If component reuse is impossible, we add even more steps for material extraction. This is feasible as Si modules have a largely layered structure except the junction box and Al frame (Figure 1), and Si cells have a completely layered structure (Figure 3). With layered structures, we can start from the outermost layer first and then move to the next layer(s) inside. This is implied in the recycling process sequences outlined in Figure 2. Several reviews of reported recycling technologies are provided in Deng et al. and Komoto and Lee.[24,25]

4.1 | Technologies for component extraction

The first components to be removed from a Si module should be the junction box and Al frame. Their removal allows access to the layered structure of the module (Figure 4). There are commercial tools to mechanically strip the Al frame off the module without breaking the glass pane. When the junction box is stripped off the module, there is a chance that the glass pane is shattered, which is less desirable. Figure 4A shows the structure of the module after junction box removal, and Figure 4B is the remaining module after Al frame removal.

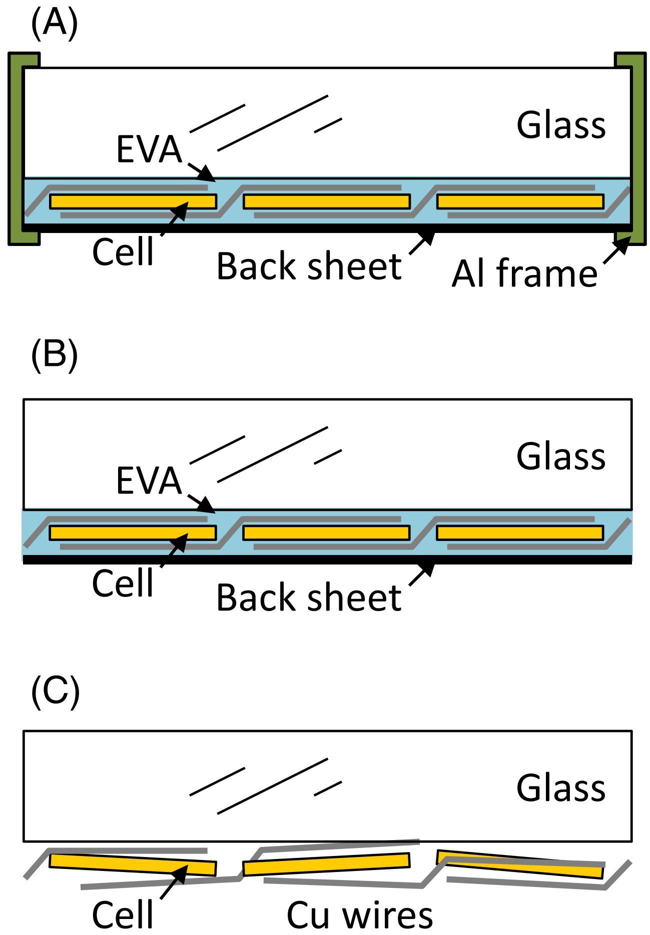

FIGURE 4 Sequence of Si module recycling: (A) junction box removed; (B) Al frame removed; and (C) cells separated from glass [Colour figure can be viewed at wileyonlinelibrary.com]

Most recyclers today shred the remaining module in Figure 4B for glass, but the EVA layers, Si cells, and backsheet are still attached to the glass. This impure glass cullet currently generates only $0.81/module (Table 2). Moreover, when this glass cullet is melted for new glass products, the backsheet releases toxic HF. Any glass manufacturer taking in this glass cullet must have a scrubber on their furnace in order to trap the fluorine and then deal with the HF waste.

A better approach, if it can be done cost-effectively, would be to cleanly separate the cells from the glass pane (Figure 4C). This is a critical technology for Si module recycling as it enables the reuse of both the cells and glass pane. It also enables material extraction from the cells if reuse of cells or glass pane is not possible. The extracted glass pane and cells should be intact and completely free of EVA or backsheet. In addition, cell efficiency and solderability should not suffer during the separation process, or they are not reusable.

It has long been concluded that pyrolysis is a feasible method to cleanly and gently separate Si cells from the glass pane.[6,7,22] Other methods to separate cells from glass such as dissolving EVA in an organic solvent or HNO_3 either take a long time to release the cells[26] or erode the Ag and Al electrodes on the cells,[5] in addition to generating significant wastes. A Japanese company developed a hot-knife method in which a steel blade heated to about 300°C slices through the EVA to separate the cells from the glass.[27] This method is particularly suitable for mobile applications, but at 300°C, the EVA does not decompose so there is residual EVA on the cells and glass necessitating pyrolysis after the hot-knife step. For pyrolysis, the fluorine-containing backsheet can be peeled off by softening the EVA at 200°C,[5] and the exposed EVA can then be thermally decomposed in air or an inert ambient.[6,7,22] Recently, a collaboration between TG Companies, Arizona State University, and Canadian Solar demonstrated successful extraction of intact cells from glass by pyrolysis.[28] This was done with today's commercial Si cells, which are 160–180 μm thick and 157 × 157 mm^2 in size. They easily break, and the key to extract them intact is to minimize the thermal stress they experience during pyrolysis. In addition, a collaboration between Chalmers University of Technology and Arizona State University indicated that both the backsheet and EVA layers can be thermally decomposed simultaneously at 500°C, but a scrubber is needed to trap the fluorine in the exhaust.[29] The remaining issues in this pyrolytic approach include the following:

1. There is no suitable furnace big enough for an entire module, not to mention multiple stacks of modules. A Si module is about 1 × 1.6 m^2, and it is likely that the furnace needs to handle hundreds of modules in a single run for a good throughput.
2. The furnace requires a scrubber to capture the fluorine from the backsheet, as noted above. The captured HF can be used in Si cell recycling, making it a closed loop.
3. The furnace must minimize the thermal stress in glass panes and Si cells for them to be intact. This feature is not available in today's off-shelf furnaces.
4. The cells extracted must maintain good efficiency and solderability, but conventional pyrolysis that takes place at 450–500°C may result in unwanted contamination, alloying, and/or oxidation. Lower-temperature pyrolysis is desirable, for example, by developing a new encapsulant with a lower pyrolytic temperature.
5. The intact cells after pyrolysis can be picked up by automation. However, the Cu ribbons soldered to the cells are now detached from the cells. They need to be separated from the cells and glass pane.

4.2 | Technologies for material extraction

If the glass pane is broken before, during, or after pyrolysis, it can still be recovered as glass cullet. In order to recover it as pure high-transmittance solar glass cullet, an effective method is required to separate glass cullet from pieces of Si cells and Cu ribbons. If the recovered glass cullet contains any Si and/or Cu, it loses its value.

If for any reason the extracted Si cells cannot be reused, material extraction is the last option. Figure 5A shows the structure of the cells extracted from modules, broken or intact. Table 4 is the weight distribution of various materials in the extracted cells under the assumption that Si cells and Cu ribbons are not separated. It is possible to sell these cells as ferro-Si with a minimum of 75% Si content for \$0.31/module (Table 3). This approach means that all the Ag and solar-grade Si are sold at the price of ferro-Si, and toxic Pb remains in the ferro-Si.

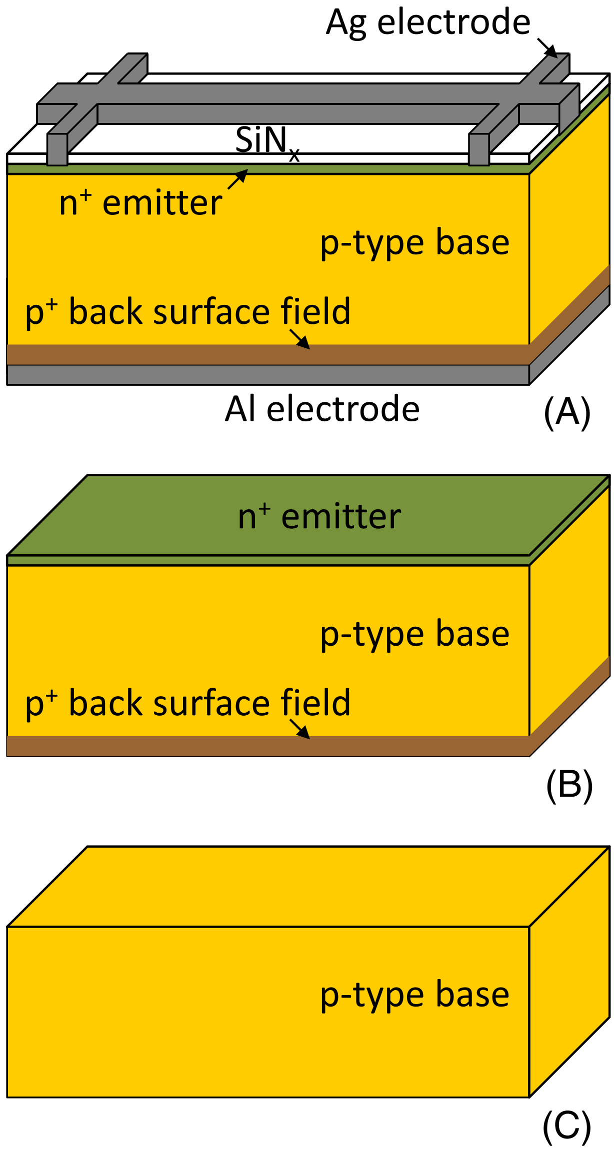

FIGURE 5 Sequence of Si cell recycling: (A) cells extracted from modules; (B) non-Si layers removed; and (C) heavily doped Si layers removed [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 4 Composition of Si cells extracted from modules by weight percent

Material	Weight%
Al	4.6
Si	82.0
Sn	2.9
Pb	2.4
Cu	7.3
Ag	0.9

The materials in Table 4 can be extracted from the cells. The methods proposed so far for material extraction from Si cells are all chemical methods.[20,22,30–33] Figure 5 shows the process for Si cell recycling. The non-Si layers should be removed first from the cells to expose the Si wafer (Figure 5B): Ag front electrode with solder, Al back electrode with Ag pads and solder, and SiN_x antireflection layer. The chemicals used to etch the various non-Si layers include the following:

1. HF for SiN_x and Al, HNO_3 for Ag[22];
2. HF for SiN_x and Al, HNO_3 for Ag, Pb, Cu, and Sn[20];
3. HF + HNO_3 mixture for Al, Ag, and SiN_x[30];
4. HNO_3 for Ag, KOH for Al, HF + HNO_3 mixture for SiN_x[31];
5. H_3PO_4 for Al and SiN_x, HF + HNO_3 mixture for Ag[32];
6. CH_3SO_3H + H_2O_2 mixture for Ag.[33]

There is no consensus on which recipe is the most cost-effective for Si cell recycling, although most studies employ HNO_3 to leach Ag out of the Si cells.[20,22,31] A mixture of HF and HNO_3 can also leach Ag out of the cells, but that leachate contains other materials from the cells: Al, SiN_x, and Si,[30,32] which make Ag extraction from the leachate more difficult.

Methods to extract metallic Ag from the HNO_3 leachate include electrowinning and metal replacement.[34] The Ag in the leachate can be precipitated out by hydrochloric acid (HCl) as Ag chloride (AgCl). The precipitate can then be separated, redissolved, and the Ag electrowon.[35] Electrowinning of Ag directly from the HNO_3 leachate is a simpler approach,[34] but the Ag recovery rate is low at about 70%.[20] This is because the electrowon Ag often detaches from the cathode and redissolves in the HNO_3 solution. TG Companies has developed a new chemistry for Ag recovery by electrowinning, and a 99% Ag recovery rate has been demonstrated.[28] Their new chemistry also allows the regeneration of the leachate during Ag electrowinning, reducing the chemical waste from Ag recovery. Metal replacement involves zinc (Zn) plates in the HNO_3 leachate[34]:

$$2Ag^{+} + Zn(s) \rightarrow Zn^{2+} + 2Ag(s).$$

This method has a high Ag recovery rate but generates a Zn nitrate ($Zn(NO_3)_2$) waste.

Of all the metals contained in Si cells (Ag, Pb, Cu, Sn, and Al), Ag and Pb must be removed from the recycling sludge due to the value of Ag and the toxicity of Pb. There are two methods in the literature that deal with multimetal recovery from the leachate. Jung et al[36] used 2-hydroxy-5-nonylacetophenone oxime to extract Cu from the HNO_3 leachate and then divided the leachate into two parts: One part contained Cu, and the other contained Ag and Pb. For the Cu-containing part, they added sulfuric acid (H_2SO_4) to form Cu sulfate ($CuSO_4$) and then performed electrowinning to recover metallic Cu. For the Ag- and Pb-containing part, they added HCl to precipitate and filter out AgCl. They reacted AgCl with sodium hydroxide (NaOH) to obtain Ag oxide (Ag_2O), which was then reduced to metallic Ag by hydrazine (N_2H_4). To obtain high-purity Ag (99.99%), they used an electrorefining process with the recovered Ag as the anode and an aqueous Ag nitrate ($AgNO_3$) solution as the electrolyte. For Pb recovery, they added NaOH to the Pb-containing part, forming Pb hydroxide ($Pb(OH)_2$) which precipitated. After filtration, $Pb(OH)_2$ was heated to obtain Pb oxide (PbO). Finally, Na sulfide (Na_2S) was added to the Pb-containing leachate to remove the remaining Pb by precipitation and filtration of Pb sulfide (PbS).

A simpler method for multimetal recovery, sequential electrowinning, was reported by Arizona State University.[20] The HNO_3 leachate contains Ag, Pb, Sn, and Cu. Sn precipitates out as Sn oxide (SnO_2), which is recovered by filtration or sedimentation. The remaining metals are electrowon out of the leachate one by one based on their redox potentials: Ag first and Cu second. When Cu is recovered, Pb further oxidizes and deposits on the anode. The recovered Ag and Cu are at least 99% pure, and the recovery rate for Ag is 74%, Pb 99%, and Cu 83%. This sequential electrowinning method is more attractive than the one in Jung et al.,[36] especially if the Ag recovery rate approaches 100%.[28]

Now what is left is the Si wafer with heavily doped emitter and BSF (Figure 5B). This Si can be sold as metallurgical-grade Si with a minimum of 99% Si content for \$0.93/module (Table 3), but it can be further processed to remove the heavily doped layers and extract the p-type base as solar-grade Si (Figure 5C). The chemicals used for Si etching include the following:

1. NaOH for Si[20,22];
2. HF + HNO_3 mixture for Si.[30–32]

To maximize the amount of solar-grade Si to be recovered, Arizona State University developed a technique to precisely pinpoint the moment when the emitter or the BSF is removed with a four-point probe.[20] It allows 90% of the Si from the wafer in Figure 5B to be recovered as solar-grade Si.

Several studies investigated the possibility of wafer reuse; that is, making new Si cells on the recovered wafers if they are not broken.[22,31] We exclude this possibility because those studies involved wafers that were 250–300 μm thick. After the removal of the emitter and BSF, they were still 220 μm thick for monocrystalline wafers and 290 μm thick for multicrystalline wafers.[31] Today's Si wafers are 160–180 μm thick. After the removal of the emitter and BSF, they would be only 140–160 μm thick. They would easily break, and expensive wafer handling tools must be developed for these thinner than normal wafers. In fact, the wafer thickness has been stable at 160–180 μm for over 10 years now,[3] and there are reasons for the stable thickness. Therefore, wafer reuse in new cells is very challenging, and the main possibilities to recycle today's commercial Si cells are either cell reuse or material extraction.

Because the recycling process for material extraction is not finalized, there are no commercial tools on the market to perform any of the processing steps described in this section, which include the following:

1. A tool to separate glass cullet from Si cells and Cu ribbons;
2. A tool to load Si cells, intact or broken, into a wafer carrier;
3. A tool to leach metals out of Si cells;
4. A tool to recover pure metals one by one from the leachate;
5. A tool to remove heavily doped layers from the Si wafer.

5 | POTENTIAL REVENUES

Different recycling scenarios are outlined above, and each scenario requires a different recycling process with a different set of recycling technologies. In this section, the potential revenue for each recycling scenario is estimated. It is shown that the simplest recycling process generates the highest revenue, and the most complicated process produces the lowest revenue.

5.1 | Potential revenue by material extraction

The materials that should be extracted from Si modules include bulky materials (glass cullet, Al frame, and Cu wiring), valuable materials (Ag and solar-grade Si), toxic material (Pb), and Sn. Table 5 shows the potential revenue if all these materials were extracted in their pure, high-value forms as of 30 October 2019, summing to $10.61/module. This is the maximum revenue if only materials are extracted from Si modules.

The extracted Si is assumed to be solar-grade Si and sold as second-grade solar Si. We could not find the price for recycled solar glass cullet, so the price used, $0.10/kg, is for high-purity recycled glass cullet.[23] The EVA layers and backsheet are not recovered, but they can serve as a heat source and reduce the energy needed for pyrolysis of the EVA and backsheet.[22] 100% recovery rates are desirable for all the materials except Si, which is limited to 90%. This is because to recover Si as solar-grade Si, the emitter and BSF in the cells must be removed (Figure 3), thus capping the solar-grade Si recovery rate to 90%.[20]

The most valuable materials from Si modules are Ag, solar-grade Si, Al, and glass. Ag and solar-grade Si account for about 65% of the potential revenue. Today's recycling processes recover only low-quality glass, Al, and Cu for $3.10/module (Table 2), so they miss 70% of the potential revenue. If recyclers decide to recover the Si as metallurgical-grade Si instead of solar-grade Si, the revenue becomes $8.45/module as the revenue from Si is reduced from $3.09/module to $0.93/module (Table 3). The demand for solar glass under high solar penetration may enable dedicated solar glass manufacturing facilities alongside recycling facilities.[38] This would improve the value of recycled solar glass in two ways: minimizing shipping costs and sharing primary and secondary glass production facilities.[39]

5.2 | Potential revenue by component extraction

Component extraction promises a higher revenue than material extraction. Table 6 shows that the potential revenue, if the glass pane and all the 60 Al BSF cells are extracted intact and reusable, is $18.14/module. This is a 71% increase in revenue from material extraction. In this table, it is assumed that the recovered glass pane and Si cells are sold for only 50% of the prices for newly produced glass pane and Si cells. The glass pane for 60-cell modules is about 1×1.6 m^2 in area. Each 157×157 mm^2 cell today produces about 4.6 Wp under standard test conditions (25°C and AM 1.5). The price for Cu ribbons is not available, so Table 6 uses the price for scrap Cu wires, $5.00/kg.[16]

5.3 | Potential revenue by module reuse

New 60-cell multicrystalline Al BSF modules produce about 275 Wp per module under standard test conditions. These new modules are sold for a spot price of $0.20/Wp[18] or $55/module today. The manufacturers guarantee 80% of the original efficiency after 25 years, which translates into 220 Wp for decommissioned modules. If the decommissioned modules are sold at 50% of the price for new modules, each such module is worth $22/module.

Table 7 shows comparisons among three recycling scenarios: module reuse, component extraction, and material extraction. It is clear that as the number of processing steps increases, the potential revenue decreases. This is an important message: Products are usually worth more than the components they are made of, and components are

TABLE 5 Potential revenue by material extraction from a 60-cell Al BSF module as of 30 October 2019, $10.61/module

Material	% Recovery	Weight	Price ($/kg)	Value ($/module)	% Total
Glass	100	13.5 kg	0.10[15]	1.35	12.7
Al	100	1.83 kg	0.95[16]	1.74	16.4
Polymers	0	1.18 kg		0	0
Si	90	0.56 kg	5.52[18]	3.09	29.1
Ag	100	6.5 g	574.23[37]	3.73	35.2
Cu	100	0.11 kg	5.00[16]	0.55	5.2
Pb	100	18.3 g	1.10[16]	0.02	0.2
Sn	100	21.9 g	6.06[16]	0.13	1.2
Total				10.61	100

TABLE 6 Potential revenue by component extraction from a 60-cell Al BSF module as of 30 October 2019, \$18.14/module

Component	% Recovery	Unit price	Quantity	Value (\$/module)	% Total
Glass pane	100	\$4.05/m^2 [23]	1.6 m^2	3.25[a]	17.9
Al	100	\$0.95/kg [16]	1.83 kg	1.74	9.6
Al BSF cells	100	\$0.42/cell [18]	60 cells	12.60[a]	69.4
Cu ribbons	100	\$5.00/kg [16]	0.11 kg	0.55	3.0
Total				18.14	100

[a]Recovered components are assumed to sell at 50% of the prices for new components.

TABLE 7 Comparison of different recycling scenarios: their potential revenue and processing steps

Scenario	No. of processing steps	Potential revenue
Module reuse	3	\$22
Component extraction	7	\$18.14
Material extraction	9	\$10.61

worth more than the materials they are made of. From a profitability point of view, module reuse should be the first option, component extraction second, and material extraction last. It is also reminded that the potential revenue estimates above do not account for any of the costs in decommissioning, shipping, and processing waste modules and in selling the recovered modules/components/materials.

6 | CHALLENGES FOR Si MODULE RECYCLING

Solar modules are not truly green until they are recycled. There are different recycling scenarios: module reuse, component extraction, or material extraction. Each requires a different recycling process with its unique challenges, but all the recycling processes also share some common challenges.

As intact modules are always worth more than damaged modules, a common requirement for Si module recycling is that waste modules should be handled as carefully as new modules. This will entail higher decommissioning, packaging, and shipping costs than bulk decommissioning of the modules designated as waste. A specially designed container is needed to prevent damages to modules during packaging and shipping. At current prices, damaged modules are worth at best \$10.61/module, whereas intact modules can generate up to \$22/module. The higher revenue would be partially offset by the increased cost from careful handling of the modules.

There are several challenges for module reuse. One is to find a large and sustained secondary market on the order of hundreds of gigawatts peak a year for reused modules. A related challenge is that as modules become a smaller portion of the system cost, there are less financial incentives to buy and install reused modules.[19] In the United States, the national median installed costs in 2018 were \$3.7/Wp for residential, \$3.0/Wp for small nonresidential, and \$2.4/Wp for large nonresidential systems.[40] With solar modules priced as low as \$0.20/Wp as of 30 October 2019, the cost of solar modules now accounts for about 10% of the system cost in the United States. There is a need to reduce the installation cost of solar systems for reused modules to remain attractive. The situation is better in the EU as the system costs are far lower, 0.70€/Wp for utility-scale systems and 1.1€/Wp for residential systems in 2018 in Germany.[41]

Some of the recovered materials from Si modules including Ag, Al, Cu, Sn, and Pb can be sold directly on the commodity market. The largest quantity of the recovered materials is the glass cullet, about 4.4 million metric tons per year in 2050, assuming 6 million metric tons of waste Si modules a year. The glass cullet needs to be free of Si cells and Cu ribbons for reuse in the solar industry. If it does not meet the requirements of the solar industry, it could saturate the secondary market for low-quality glass cullet. Another challenge for material extraction is the recovered Si. It is supposed to be a new feedstock for the growth of solar Si ingots, but the Si feedstock for ingot growth must have a high and consistent quality. This might be difficult for recyclers, not only because of process variation and quality control issues but also because of the many different types of Si modules on the market (refer to Section 6.1). If the Si ingot growers are not comfortable with the quality of the recovered Si, they will not buy it. This would leave metallurgical-grade Si as the only option for the recyclers. It should be noted that the Si in Figure 5B has a far better purity than typical metallurgical-grade Si, 99.99% versus 99%. There might be other applications for this Si outside the solar industry, such as the Si-based anode in lithium-ion batteries.[42]

Incorporating recyclability into solar module design is another important issue. Today's solar modules are designed for performance, cost, and reliability but not for recyclability. Design for circularity should be a guiding principle for all manufacturers.[43]

6.1 | Module standardization

Module reuse and component extraction suffer from the many different types of Si modules on the market. At the cell level, there are monocrystalline versus multicrystalline, n-type versus p-type, Al BSF versus PERC, whole cell versus half-cut cell, unifacial versus bifacial, different numbers of busbars, and different wafer sizes. At the module level, there are 60 cells versus 72 cells, single-glass versus double-glass, framed versus frameless, among other variations. Different cell and module structures lead to different module powers and efficiencies. Based on datasheets from different manufacturers, module power varies from 260 Wp/module to over 400 Wp/module today. Even for the same cell and module structures, there are still efficiency variations among cells and thus modules. For the same manufacturer, the efficiency variation is about 1.5% absolute for the same cell and module structures. Datasheets from different manufacturers for the same cell and module structures indicate an efficiency variation of 2.5% absolute, from slightly over 15% to nearly 18% for multi-crystalline p-type Al BSF modules. In addition, modules of different structures or from different manufacturers often have different dimensions and weights.

Modules of different power, efficiency, voltage, or current cannot be directly connected in series or parallel into a solar system due to mismatch losses. This means that the recyclers would have to have hundreds of large containers, each for a particular type of modules with a particular efficiency. They would have to accumulate a large enough number of the same modules with the same efficiency in order to make a sale, unless they deal exclusively with waste modules from large solar farms. This would significantly increase the cost for the reused modules.

The variations in cell and module structures also create problems in component extraction. For example, the glass panes extracted are not one size, so the recyclers would have to accumulate glass panes of the same dimensions. They would have to have hundreds of bins, each for a particular cell structure with a particular efficiency. They would have to process a large number of waste modules before enough cells of the same structure and same efficiency could be accumulated for a remanufactured module. They would have to sell different types of cells to different module manufacturers, as it is hard to stay profitable for a manufacturer that produces dozens of different types of modules all at small quantities. A related issue is that wafer size and, consequently, cell and module sizes have tended, and may continue, to grow over time, and 25-year-old cells and glass panes may not suit current modules.

To improve the recyclability of Si modules, module standardization would be ideal. Module standardization means that no matter which manufacturer produces the modules, they would all have the same power, efficiency, voltage, current, dimension, and weight; that is, Si modules become a true commodity. Module standardization involves three components:

1) Standardization of cell structure;
2) Standardization of cell efficiency; and
3) Standardization of module structure.

Efficiency variations during the production of Si cells can be minimized by more tightly controlling the process conditions, especially the temperature uniformity in the emitter diffusion furnace.[44] An efficiency window of 1% or even 0.5% absolute is possible. For example, multicrystalline Al BSF cells from any manufacturer would fall between 18% and 18.5%. This vision of ideal standardization as a way of facilitating Si module recycling is unlikely to occur in the near term because market-driven competition drives innovation and differentiation, particularly in the areas of cell and module structures. Eventually, as certain cell technologies mature, the efficiency of specific cell structures may converge on a standardized efficiency. This trend may facilitate the reuse of components or entire modules.

Module standardization also significantly reduces the production, installation, and maintenance costs of solar systems, but this is beyond the scope of this article.

7 | CONCLUSIONS

This article aims to answer several questions about Si module recycling: (1) What can be recovered from Si modules? (2) What recycling technologies are needed? (3) What are the potential revenues for different recycling scenarios? And (4) what are the main challenges for different recycling scenarios? These questions are answered for three recycling scenarios along with their recycling process sequences: module reuse, component extraction, and material extraction. Module reuse generates the highest revenue with the fewest processing steps, while material extraction leads to the lowest revenue with the most processing steps. Gentle and clean separation of cells from glass is a critical technology, and pyrolysis is so far the most feasible method. Two low-concentration metals must be recovered from Si modules: Ag as a scarce material and Pb as a toxic material. Their recovery requires chemical methods while bulky materials including glass cullet, Al frame, and Cu wiring can be recovered with physical methods. The Si in the cells can be extracted with different qualities, with a higher revenue and more complicated recycling process for purer Si. Markets outside the solar industry for the recovered Si should be explored. The biggest challenge for module reuse is to find a large and sustained market for hundreds of gigawatts peak of decommissioned modules a year, and the biggest challenge for component extraction is the variety of module and cell structures and cell efficiency variability. For all three scenarios, the cost of collecting and processing waste modules is a common challenge.

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