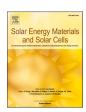
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# A review of end-of-life crystalline silicon solar photovoltaic panel recycling technology

Xiaopu Wang <sup>a,b</sup>, Xinyi Tian <sup>c</sup>, Xiaodong Chen <sup>d</sup>, Lingling Ren <sup>c</sup>, Chunxiang Geng <sup>c,\*</sup>

- <sup>a</sup> Shandong Key Laboratory of Oilfield Chemistry, China University of Petroleum (East China), Qingdao, China
- <sup>b</sup> School of Petroleum Engineering, China University of Petroleum (East China), Qingdao, China
- <sup>c</sup> School of Chemistry and Chemical Engineering, China University of Petroleum (East China), Qingdao, China
- d Guangdong Zocen Solar Energy Company Ltd, Guangdong, China

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#### ABSTRACT

With the goal of Net-Zero emissions, photovoltaic (PV) technology is rapidly developing and the global installation is increasing exponentially. Meanwhile, the world is coping with a surge in the number of end-of-life (EOL) solar PV panels, of which crystalline silicon (c-Si) PV panels are the main type. Recycling EOL solar PV panels for reuse is an effective way to improve economic returns and more researchers focus on studies on solar PV panels recycling. Most recent recycling technology studies stay at the experimental stage, and problems of high cost, low recycling value, and secondary pollution are usually ignored. In this review, to establish an efficient, economic, and environmentally friendly recycling technology system, we systematically summarized the EOL c-Si PV panel module recycling technologies and condition parameters in three sections: module disassembly, module delamination, and material recycling and reuse. We discussed current technology strengths and weaknesses and research development directions in each section. This review aimed to provide a technical reference for the upcoming recycling surge of EOL PV modules all over the world.

#### 1. Introduction

The climate crisis is a great challenge of the 21st century, and an appropriate adjustment in the current energy structure may be the key to solving the climate problem [1,2]. Since the signing of the Paris Agreement, Low Carbon Emission Reduction and Net-Zero Emission have been important issues to discuss and study for all countries. The development and exploration of renewable energy is an important research direction, among which solar photovoltaic (PV) is the fastest-growing renewable energy, and its installed capacity is growing exponentially under the promotion of energy policies and PV power generation technologies [3,4]. As shown in Fig. 1, the global solar PV panels reach an installed capacity of 707.5 GW and electricity generation of 855.7 TWh by 2020 [5], with Asia-Pacific, Europe, and North America as the major markets. According to the International Energy Agency (IEA) reports, the cumulative installed PV capacity was predicted to increase to 1.826 TW by 2026 [6] and 14.5 TW by 2050 [7], with the largest market share growth potential in China, Europe, the United States, and India [6]. The average lifetime of PV panels is 25–30 years. According to the early-loss scenario and regular-loss scenario, the cumulative waste volumes of end-of-life (EOL) PV panels will reach 1.7–8 million tons by 2030 and 60–78 million tons by 2050 [8] (see Fig. 2(a)), and in 2050 the top five PV panel waste countries are expected to include China, United States, Japan, Germany, and India (see Fig. 2(b)). This massive EOL volume will become a global burden on the environment and the economy [9]. According to the manufacturing technology of silicon wafers, solar PV panels can be classified into three categories [10] (see Table 1), and crystalline silicon (c-Si) PV panels are currently the most widely used type of commercial PV panels [11]. C–Si PV technology accounted for about 95% of the total production in 2020 and has maintained a market share of around 90% for the past 20 years [11,12]. At the end of the operating period, c-Si solar PV panels will be the dominant force in PV waste modules.

Although PV power generation technology is more environmentally friendly than traditional energy industries and can achieve zero  $\mathrm{CO}_2$  emissions during the operation phase, the waste generated during the production process and after the EOL hurts the environment and cannot be ignored [13]. Lead (Pb), tin (Sn), cadmium (Cd), silicon (Si), and copper (Cu), which are major ingredients in solar cells, are harmful to the ecosystem and human health if discharged from broken products in

E-mail address: chxgeng@upc.deu.cn (C. Geng).

<sup>\*</sup> Corresponding author.

landfills or after environmental disasters [4,14]. Through ecotoxicological experiments, Tammaro et al. [15] found that the leachate of some c-Si and thin-film PV panels could release Pb, Chromium (Cr), Cd, nickel (Ni) in amounts exceeding the local legal limits for soil and water, where the presence of Pb, Sn and Cd could adversely affect aquatic organisms, especially algae, and concluded that PV panels were a potential environmental risk as a waste. Zhi et al. [16] found that semiconductors doped with boron or phosphorus were significantly toxic to the model microorganism, Shewanella oneidensis MR-1. Using a life cycle analysis of EOL PV modules, Daniela-Abigail et al. [17] found that recycled PV modules reduce the toxicity to humans and freshwater ecology by 10-70% compared to not recycled PV modules and concluded that recycling solar panels is feasible from an environmental point of view. Therefore, it is necessary to establish a PV waste management system. Europe revised the Waste Electrical and Electronic Equipment (WEEE) regulation in 2012 to make relevant regulations on the recycling of PV panels, requiring Europe to achieve a recycling rate of 85%/80% mass recovery rate/recycling rate) of waste PV panels in 2018 [18]. South Korea's Ministry of Environment released the Electrical and Electronic Equipment and Vehicle Resource Recycling Act in 2019, applying the Extended Producer Responsibility System to 23 items including PV panel waste, effective from 2023 [19]. In contrast, countries with rapidly developing PV markets such as the United States, China, Japan, and India still lack regulations for the disposal of EOL PV modules.

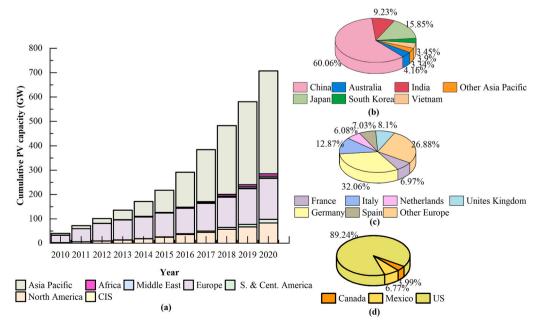
In addition to the environmental and social benefits of PV panel recycling. From the various life cycle evaluation studies conducted so far, the recycling of EOL PV panels is guaranteed by recycling technologies that can reduce the environmental burden. To promote recycling, it is important to ensure that there are sufficient value-added opportunities [19]. Therefore, it is particularly important to develop low-cost, environmentally friendly and efficient recycling technologies to improve the performance of materials recovered from EOL PV modules for recycling and to ensure their competitiveness in the market for economic benefits.

Countries urgently need viable recycling technology systems under the pressure of the surge in the number of EOL PV panels, especially c-Si PV panels. Therefore, in this paper, we focused on the structural composition and recycling value of c-Si PV panels, to provide a more specific technical reference for the current PV panel recycling. Current recycling methods and main technical parameters were also summarized in three aspects, including module disassembly, module delamination, and material recovery.

#### 2. Structure of crystalline silicon solar PV panel

The c-Si PV module is similar in structure to a sandwich (see Fig. 3 (a)), with an Al alloy frame at the outermost part protecting the internal structure and a junction box at the bottom to convert, store and transmit the collected energy. The internal sandwich sections are, from top to bottom, tempered glass, polymeric encapsulant, silicon solar cell, polymeric encapsulant and backsheet. The encapsulating material, which is generally ethylene vinyl acetate (EVA), helps adhere the solar cells to the tempered glass and backsheet to prevent thermal, mechanical, ultraviolet, and moisture damages [4]. The backsheet is often laminates made from a range of different polymer materials [20]. Many of the backsheets wholly or partially consist of fluorinated polymers such as polyvinyl fluoride (Tedlar®, a DuPont product), polyvinylidene fluoride or ethylene chlorotrifluoroethy [21-23]. The c-Si PV power generating component of a PV module is the solar cell, which is typically 200 um thick (see Fig. 3(b)). The silicon wafer is doped with boron or phosphorus to form an n-p junction to create the photovoltage, and the upper layer of the wafer has an anti-reflective (AR) layer used to reduce the reflection of light from the silicon and increase the utilisation and conversion rate of the PV panel, mainly consisting of SiO, SiO2, Si3N4 and Al<sub>2</sub>O<sub>3</sub> [24]. The top of the solar cell layer is screen printed silver wire as electrodes and the bottom electrode is a full area of the aluminium coating [25]. The c-Si cells are connected by solder ribbon and consist mainly of Cu cores and tin (Sn)-lead (Pb) plating (see Fig. 3

From an economic point of view, junction boxes, glass, silicon and metals (Cu, Ag, Al) in PV modules are of interest to recycling, with Ag, Si, Cu and glass having a high recycling value, according to the price determined by market supply and demand (see Table 2) [4,26,27]. The manufacturing cost of PV cells accounts for 60% of the total cost of PV modules, and the manufacturing cost of Si wafers accounts for more than 65% of the manufacturing cost of PV cells. Effective recycling of Si wafers for remanufacturing into PV cells can reduce manufacturing costs and 42% of greenhouse gas emissions during the production of PV



**Fig. 1.** Global cumulative installed PV panel capacity by region. **(a)** Global cumulative installed solar PV panel capacity growth by region from 2010 to 2020, **(b)** Share of installed PV panels in Asia-Pacific in 2020, **(c)** Share of installed PV panels in Europe in 2020, **(d)** Share of installed PV panels in North America in 2020. Data source: Statistical Review of World Energy 2021/70th edition [5].

panels [28]. Ag accounts for only about 0.08% of the total module weight, and just 600 g of Ag can be separated per tonne of EOL PV panels [29]. However, Ag has a high recovery value, with 92.5% silver priced at US\$0.578/g, depending on the purity of the silver and market conditions [30]. Silver is a metal with limited availability and future Ag supplies will soon be at risk in 2075 due to its product set to peak in 2030 [31]. It's necessary to recycle Ag for both economically and sustainable resource use.

## 3. Overview of crystalline silicon PV module recycling technology

The recycling technology for EOL c-Si PV modules is shown in Fig. 4 [4]. Disassembly is generally used as a pre-treatment process for PV module recycling by the manual or mechanical removal of the junction box and cables, while the Al frame can be mechanically and pyrolytically separated for secondary metallurgical recovery [11,32]. After disassembly of the Al frame, junction box and cables, the module is a "glass-EVA-solar cell -EVA-backsheet" sandwich structure. Disposal technologies for surplus components can be divided into three forms: upcycling (i.e. high-value recycling), recycling (i.e. medium-value recycling) and downcycling (i.e. low value recycling) [4].

#### 3.1. Downcycling and recycling

Many companies in Europe used downcycling to dispose of waste PV modules, using mechanical processes to separate the module materials; processes included crushing, sieving, and metal separation. The obtained glass cullet feedstock could be used for foam or fibreglass production, while the metals extracted during the process could be sold to metal recyclers and smelters. The remaining fraction was incinerated or landfilled [33]. This simple recycling method avoids most masses being landfilled with relatively low energy input and processing costs. However, it should be noted that the materials recovered in the recycling process are of varying quality which might not be suitable for all secondary markets. Kokul et al. [34] proposed a recycling method that after mechanical removal of the Al frame, outer glass and junction box, the remaining c-Si PV module waste was powdered and blended with polypropylene and low-density polyethene to make compressed moulded tiles instead of landfilling them directly. This method of recycling PV modules is inexpensive and the recycling process is simple but does not allow for economic recycling.

Table 1 Solar PV panel types.

Generations of Solar PV Panel	Solar PV Panel Types
1st Generation (Crystalline silicon)	(a) Monocrystalline
	(b) Multi-crystalline
2nd Generation (Thin film)	(a) Cadmium telluride ( CdTe )
	(b) Copper indium gallium selenide ( CIGS )
	(c) Amorphous silicon ( a-Si )
3rd Generation	(a) CPV solar panels
	(b) Dye-sensitized solar panels
	(c) Organic solar panels
	(d) Hybrid panels

#### 3.2. Upcycling

Upcycling aims to recover high-grade glass, silicon wafers and valuable metals including Ag, Cu and Al from EOL c-Si PV panels. After mechanical or manual removal of Al frames, junction boxes and cables, the economic cycle is facilitated by a two-step process: (1) module delamination and (2) recovery of silicon wafers and valuable metals. Here we provide a review of the upcycling techniques in the order of processing sequence.

#### 3.2.1. First step: module delamination

Technologies for module delamination can be divided into thermal, mechanical and chemical delamination (see Table 3). The focus of module delamination is on how to effectively remove EVA from EOL PV panels, contributing to the recovery of high-grade glass, silicon wafers and valuable metals.

3.2.1.1. Thermal delamination. Doni et al. [35] applied the technology of radio-frequency heating to the delamination of PV modules and can easily remove broken glass from PV panels by treating them at 400 W for 15 min. However, there was still glass adhering to the PV panels and the effect of separating the remaining modules was unknown. Some scholars used the method of burning [36,37]. Riech et al. [37] used a quartz halogen lamp to soften the EVA at 90-120 °C and scrapes out the backsheet. The EVA was then removed by complete combustion at 600 °C for 30 min. To remove EVA efficiently and consume less energy, many scholars studied the pyrolysis operating conditions, including temperature, operating time, heating rate, inert environment, and the thermal treatment by-products in the operating conditions chosen. Using TGA-FTIR analysis, Wang et al. [38] concluded that the pyrolysis of the EVA binder could be divided into two stages: deacetylation of EVA to produce acetic acid in the low-temperature zone (300–400 °C) and a series of olefins were generated in the high-temperature zone (above

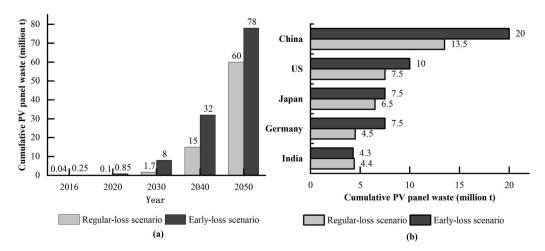


Fig. 2. Estimated cumulative waste volume of EOL PV panels. (a) Estimated cumulative global waste volumes (million t) of EOL PV panels, (b) Estimated cumulative waste volumes of EOL PV panels by the top five countries in 2050. Date source: End-of-Life Management: Solar Photovoltaic Panels (IRENA) [8].

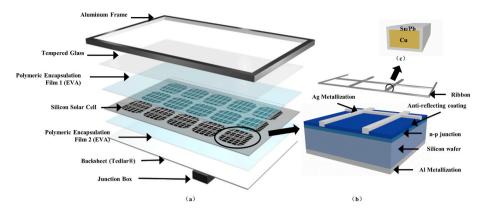


Fig. 3. Structural composition of c-Si PV panels.

(a) Schematic diagram of the solar PV panel structure, (b) PV cells Composition diagram, (c) Solder ribbon construction diagram.

Table 2

The relationship between the weight share of crystalline silicon solar panel materials and economic value.

Material	Weight percentage in a module (%)	Relative economic value	Of interest to recycling?	
Silicon	2–3	High	Yes	
Silver	0.006 ~ 0.08	High	Yes	
Copper	4.4–7	High	Yes	
Aluminium	10~20	Medium	Yes	
Glass	69~75	Low	Yes	
Junction box	2	Low	Yes	
Polymers (EVA, PVF)	7	-	No	
Boron	< 0.1	_	No	
Phosphorus	< 0.1	_	No	
Tin Dioxide	< 0.1	_	No	
Lead	< 0.1	-	No	

410 °C). Choi et al. [39] found that major pyrolysis products of the deacetylated EVA were n-alkanes, 1-alkenes, α,ω-alkadienes, and ring compounds. Bohland et al. [40] proposed the pyrolysis of EVA in an inert environment (e.g. nitrogen) so that no impurities remained on the surface of the silicon wafer. While Fiandra et al. [41] believed that organic compounds could not be completely degraded in an inert environment and recommended pyrolysis under weakly oxidising conditions so that the volatile organic compounds in the pyrolysis products were significantly reduced and oxidised to CO2. To improve the recycling rate and circular economy value during the pyrolysis process, Farrel et al. [42]. found that the calorific values of virgin and used grades of EVA encapsulants in EOL c-Si PV modules were 39.87 and 39.51 MJ kg<sup>-1</sup>, respectively, which means that the calorific value of EVA remains almost the same after the usage, and is comparable to that of biodiesel. This result indicated the energy recovery potential within the used polymers found in c-Si PV modules. However, further research is needed on how to specifically achieve energy recovery during the pyrolysis process.

Based on the pyrolysis conditions above, the pyrolysis technology is shown in Table 3 and can be divided into direct pyrolysis and two-stage pyrolysis. Dias et al. [43] found that 30 min pyrolysis at 500 °C removes >99% of the polymers present in PV modules. Frisson et al. [44] achieved 80% recovery of glass under optimal operating conditions by direct pyrolysis of PV modules in a fluidised bed under a nitrogen atmosphere. However, direct pyrolysis of the backsheet (e.g. Tedlar®) at high temperatures decomposed to form dangerous fluorinated by-products requiring special abatement systems [45,46]. Research into pyrolysis technology has therefore favoured two-stage pyrolysis [37,38, 41,47,48]. The first stage is the softening of the EVA at low temperatures followed by mechanical or manual stripping of the backsheet or direct mechanical milling to remove the backsheet. The second stage is the

pyrolysis of EVA under high-temperature conditions. To reduce the cost of energy consumption during the first stage of the pyrolysis process, Fiandra et al. [47] used machine milling with an accuracy of 0.0012 mm instead of heat treatment to remove the backing. The two-stage pyrolysis to remove the backsheet reduces the production of fluorinated by-products, but EVA still produces significant amounts of volatile organic compounds in the second stage of pyrolysis. Fiandra et al. [41] improved conditions for second stage pyrolysis that maximised CO2 yield compared to the produced VOCs when performed at a temperature of 500 °C, in an air atmosphere, with an equivalent combustion ratio (φ) < 1. Dobra et al. [48] investigated the effect of pre-stripping backsheet on the pyrolytic delamination of PV modules and found that samples without stripped backsheet would have a white powder residue (TiO<sub>2</sub>), derived from the pigment additive in the backsheet and that backsheet (containing PVF) would release large amounts of fluorine (mostly in the form of hydrofluoric acid) after heat treatment, with the emissions expected to have environmental and human health impacts if not handled properly. Pre-peeling the backsheet has none of these problems and reduces the separation time of the subsequent components by more than 45%. The process of stripping the backing plate in advance is therefore considered to be superior.

3.2.1.2. Mechanical delamination. Mechanical delamination is divided into milling/shredding [27,49-52], high-pressure pulse [53-56], hot knife [57,58] and laser irradiation delamination [59] (see Table 3). Due to the complex composition of the particles after mechanical crushing, it is often necessary to combine this with a suitable sorting method. Mechanical crushing does not result in complete separation of the PV modules and further pyrolysis or chemical treatment is required depending on the composition of the different fractions. Granata et al. [49] crushed the EOL PV modules successively by using two-blade rotors crushing and hammer crushing, recovering 80-85% of the glass. After two-blade rotors crushing 70% of the sample made by a d > 8 mm fraction was still kept together by the EVA polymer. While hammer crushing determined the separation between glass, EVA-Tedlar® and powder. After sieving, d > 8 mm and 5 < d < 8 mm fractions contain the most EVA cut sheets and backsheet, while glass is mainly distributed in the 1<d < 5 mm fraction. Glass is recovered by pyrolysis of fractions with d > 1 mm to remove the polymer, or directly from fractions with d < 1 mm. To improve glass recovery and reduce the amount of pyrolysis processed, Pagnanelli et al. [50] used multiple hammer crushing to reduce the size of the panel fragments. The coarse fraction (d > 1 mm)was pyrolyzed, the middle fraction (0.4<d < 1 mm) recovered glass directly and the fine fraction (d < 0.4 mm) recovered glass after chemical leaching of the metal, giving an overall recovery of 91%. Azeumo et al. [51] used heavy media separation methods to sort glass and metals. The sink was milled and sieved, the under-screen contained 76% of the glass of the panel at a grade of about 100%, while the

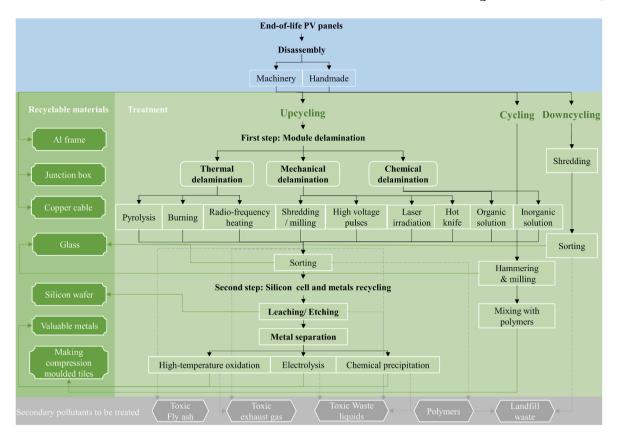


Fig. 4. Feasible recycling technologies for EOL crystalline silicon solar PV panels. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

over-screen contained 100% of the initial metal at a grade of 67%. Dias et al. [27] used electrostatic separation to enrich metals from crushed PV debris with up to 95% enrichment. However, electrostatic separation does not work with polymers and the presence of polymers may cause metal enrichment to fail.

In the methods of milling and shredding above, glass is predominantly recovered, while metals are difficult to enrich and recover. High-Voltage Pulse Crushing was introduced in the 1960s and has been widely used in rock mining [60]. Compared to conventional mechanical crushing, it released metal more efficiently [61]. Nevala et al. [56] compared high-voltage pulse technology with conventional crushing and found that the highest amounts of metals were present in the >4 mm and <0.5 mm fractions after high-voltage pulse crushing, and 100% of Cu, Pb, Sn, Al and 90% of Ag were recovered after further processing. While higher metal content was found in each fraction after conventional crushing. This proved that the high-voltage pulse technology had the same high crushing selectivity for metals in the field of PV panel recovery. Akimoto et al. [53] used a two-stage high-voltage pulse technique and found a more than 30-fold increase in silver enrichment after heavy media separation and purification. Furthermore, processing costs in the high-voltage pulse crushing were estimated to be around US \$0.0019/W, and the technique was considered to be potentially commercially viable. Song et al. [54] obtained more than 95% of Cu and 96% of Ag enriched in the fraction of particle size <1 mm, 85% of Al enriched in the 0.25-2 mm fraction, 85% of Pb and 87% of Sn concentrated in the small particles below 0.5 mm under the optimal experimental conditions of high-voltage pulse crushing. Zhao et al. [55] studied the selective crushing law of high voltage pulse crushing on EOL PV modules and found that differences in the selectivity of 20 different components during high-voltage pulse crushing (selectivity: Ag > Si > glass) and appropriate increasing of electrode gap could improve the recovery of Ag.

Full Recovery End of Life Photovoltaic project (FRELP), funded by the EU Life Programme, used infrared radiation heating and controlled pulsating knife frequencies to soften and cut EVA to peel glass [57,62]. NPC Incorporated in Japan has manufactured a glass/EVA separation machine that uses a 180–200 °C heated cutter to separate the glass from the EVA/cell layer [63]. This technology, called the "hot knife method", maintains the integrity of the glass and has a short operating time of just 50s [58]. Li et al. [59] proposed a laser irradiation method to recycle the back EVA layer on the solar cell in the c-Si PV module. The laser treatment undamaged both the stripped EVA and the solar cells, and no  $\rm CO_2$  was generated during the process. However, the remaining components still adhere together and other methods are combined to recover the valuable material.

3.2.1.3. Chemical delamination. The dissolution process of EVA follows the normal dissolution model of polymers, in which the solvent results in the plasticization of the polymer leading to the formation of a swollen gel-like polymer layer [64]. The different swelling pressures within EVA, on the other hand, can easily lead to the shattering of the silicon wafer [65]. Many academics studying chemical layering methods consider the effects of reagent type, concentration, temperature, time, solid-to-liquid ratio, and solubilisation on component separation and wafer recovery. Chemical delamination is divided into organic and inorganic reagents according to the type of solvents (see Table 3).

In the organic approach, Doi et al. [66] found that trichloroethylene (TCE) could dissolve cross-linked EVA samples kept at 80 °C, requiring 10 days. While Pang et al. [67] proposed a new method of microwave-enhanced EVA film also using TCE under optimal experimental conditions, only 2 h to completely separate the PV modules. This showed that microwaves could significantly accelerate the separation of PV modules. Kim et al. [68] used probe-type ultrasonic irradiation to investigate the effect of organic reagents on the dissolution of EVA. It

**Table 3**Module delamination method and technical parameters for crystalline silicon solar PV panels.

Technology	Methods	Key parameters	Separation rate (%)	Comment	Year	Ref
Thermal Radio- delamination frequency heating Direct pyrolysis  Two-stage pyrolysis	frequency	400 W, 15 min	N/A	➤ No secondary contaminants and green ➤ Partial glass peeling only	2012	[35
	· ·	Fluidised bed angle(60°), particle diameter (100 $\mu$ m), fluidisation velocity (1 cm s $^{-1}$ ), 450 °C, 15 min	N/A	<ul><li>➤ The glass recovery rate of 80%</li><li>➤ High energy consumption</li></ul>	2000	[44
		500 °C, 30 min, 600 °C•h <sup>-1</sup> , N <sub>2</sub>	>99	<ul> <li>➤ Complete removal of polymers</li> <li>➤ High energy consumption and toxic gas production</li> </ul>	2017	[43
	U	1st stage: 150 °C, 5 min, $N_2$ 2nd stage: 500 °C, 60min, $N_2$	>99	<ul><li>➤ Avoidance of fluorinated gases</li><li>➤ Still generating VOCs</li></ul>	2019	[38
		1st t stage: 200 °C, 30 min, 450 °C•h <sup>-1</sup> , $\varphi$ < 1, 24L•h <sup>-1</sup>	100	➤ Avoidance of fluorinated gases	2019	[41
		2nd stage: 500 °C, 60min, 450 °C•h <sup>-1</sup> , $\phi$ < 1, 24L•h <sup>-1</sup> 1st t stage: machine milling	100	<ul> <li>➤ Highest oxidation of VOCs to CO2 and green</li> <li>➤ Avoidance of fluorinated gases</li> </ul>	2019	[47
		2nd stage: 500 °C, 60 min, 450 °C•h $^{-1}$ , $\phi$ =0.5, 24L•h $^{-1}$		➤ Less energy consumption and green		2
	Burning	1st stage: quartz halogen lamp (90–120 °C), Flexible sheet scraping backsheet 2nd stage: 600 °C, 30min	100	➤ Complete combustion of polymers	2021	[37
Mechanical delamination	Milling/ Shredding	Two blade rotors crushing + Hammer crushing + Sieving	Glass: 80-85	<ul> <li>Reduction of pyrolysis and hydrometallurgy throughput</li> </ul>	2014	[49
		Two blade rotors crushing + Sieving Knife mill + Electrostatic Separation	Overall: 91 Metals: 95	<ul> <li>➤ Improving the recycling rate of glass</li> <li>➤ Enrichment for metals, but Polymers may lead to a failure of metal enrichment</li> </ul>	2017 2018	[50
		Knife mill + Heavy medium separation + Magnetic separation	Glass: 76 Metals: 100	<ul> <li>▶ Best parameters not found</li> <li>▶ Low energy consumption</li> <li>▶ Low purity of recycled material</li> </ul>	2019	[5]
		Liquid nitrogen modification (5 min) +Three- blade rotors crushing (8s) + Sieving	Glass: 70	<ul> <li>➤ EVA is less viscous, more brittle and more prone to breakage</li> <li>➤ Costs need to be considered</li> </ul>	2021	[5
High-voltage pulse Hot knife		1st stage: 110 kV, 20 pulses	N/A	➤ More than a 30-fold increase in silver enrichment	2018	[5
	•	2nd stage: 90 kV, 250 pulses Heavy medium separation		<ul> <li>Low estimated cost and economic viability</li> <li>High difficulty in industrial batch processing</li> </ul>		
	Hot knife	169 kV, 300 pulses, 192.99 J $\rm g^{-1}+$ Sieving Infrared radiation heating, pulsating knife	N/A Glass: 100	<ul><li>➤ High metal enrichment rate</li><li>➤ More economical</li></ul>	2020 2014	[5 <sup>-</sup>
		180–200 °C heated cutter, 50 s	Glass: 100	<ul> <li>➤ Reduced CO2 emissions</li> <li>➤ Keeping peeled glass intact</li> <li>➤ Reduced CO2 emissions</li> </ul>	2016	[5
	Laser irradiation	hot air gun (500 °C) $+1064$ nm near-infrared optical-fibre pulsed laser (2.1 MW cm $^2$ , 50 kHz)	N/A	<ul> <li>➤ Complete peeling of the EVA (film 2)</li> <li>➤ Reduced CO2 emissions</li> <li>➤ No effect on PV cells</li> </ul>	2022	[5
Chemical delamination	Organic reagents	TCE, 80 °C, 10 days	N/A	<ul> <li>Mechanical pressure is applied to maintain the integrity of the wafer</li> <li>Highly toxic reagents and long processing time</li> </ul>	2001	[6
		Probe-type ultrasonic (400 W), O-DCB (3 mol $L^{-1}),70^{\circ}\text{C},30\text{min}$	N/A	<ul> <li>➤ Silicon cells return to normal without cracks</li> <li>➤ Short processing time and low reagent</li> </ul>	2012	[6
		Ultrasonic (200 W), Toluene, 60 $^{\circ}$ C, 50min	95	concentration under ultrasound  ➤ Low temperatures and short processing times  ➤ Toxic waste liquids require further treatment	2019	[5
		Ultrasonic, Hexane, 70 °C, 24 h	92.4	<ul> <li>► Low toxicity reagents</li> <li>► Long processing times and low separation rates</li> </ul>	2021	[7
		$\text{ScCO}_2$ (7.5 $\times$ $10^6$ Pa), Toluene, 180 °C, 45min,	N/A	<ul> <li>➤ Short separation times and good separation result</li> <li>➤ Some EVA is still adhering to the</li> </ul>	2021	[6
		Microwave, TCE (4 mol $\rm L^{-1}$ ), 70 °C, 2 h, 50 g/L	100	components s  ➤ Microwave enhances the swelling capacity of EVA  ➤ Short separation times and good separation	2021	[6
	Inorganic reagents	Nitric acid, 24 h	N/A	results ➤ Dangerous emissions	1994	[7
	1 CagCIIIS	KOH (0.2 mol $L^{-1})\text{-ethanol}$ solution, 200 °C, 3 h, 55 g/L	100	<ul> <li>Non-toxic reagents and environmentally friendly</li> <li>High treatment temperature and energy consumption</li> </ul>	2020	[7

was found that in the presence of 450 W of ultrasonic radiation, o-dichlorobenzene (O-DCB) at optimal experimental conditions for 30 min resulted in complete dissolution of EVA and no cracks in the silicon wafers, whereas the selected benzene, toluene, and TCE resulted in cracks in the wafers. Azeumo et al. [51] experimentally concluded that toluene was the best organic reagent for separation, with up to 95% separation of the PV module at 60 °C and 200 W with sonication for 50 min. Lovato et al. [69] proposed a new method for facilitating the separation of PV modules from toluene using supercritical carbon dioxide technology. Experiments have demonstrated that the delamination time of modules using supercritical carbon dioxide (ScCO2) is reduced by a factor of about 3.5-fold compared to the time at atmospheric pressure. Under optimal experimental conditions, 100% recovery of glass, metal solder tape and backsheet were achieved. Tembo et al. [70] used hexane as a pure solvent to separate the PV modules and achieved a separation rate of 92.4% after 24 h under optimal experimental conditions, with little damage to the wafers. Compared to TCE, toluene and O-DCB, hexane is much less toxic. Among the inorganic methods, Bruton et al. [71] proposed the use of hot nitric acid leaching to separate EOL PV modules, which is effective but requires large amounts of nitric acid and produces toxic gases such as nitrogen dioxide during the leaching process, making recovery more difficult. It was not adopted by the industry due to the high cost and difficulty of treatment. Yan et al. [72] proposed the separation of PV modules with KOH-ethanol solution, and the separation rate of the modules could reach 100% when treated at 200  $^{\circ}\text{C}$  for 3 h in a muffle furnace. Compared to organic reagents, KOH-ethanol solution is a green reagent with low environmental toxicity and low secondary pollution; the surface oxidation rate of recovered silicon cells is lower compared to the pyrolysis method.

There are three main research directions for the chemical separation of PV components, replacing highly toxic organic reagents with less toxic organic reagents, replacing toxic organic reagents with non-toxic inorganic reagents, and reducing the concentration, processing temperature and treating time of reagents through auxiliary solubilisation techniques (e. g. ultrasound, microwave, ScCO<sub>2</sub>, etc.) to reduce energy consumption and secondary pollution.

#### 3.2.2. Second step: silicon wafers and valuable metals recycling

3.2.2.1. Recovery of pure silicon wafers from PV cell. Table 4 provides an overview of the methods and technical parameters for the recovery of silicon wafers by chemical etching to remove the Ag electrode, AR layer, n-p junctions and Al coating from the PV cell layers. The solution composition, ratio, temperature and treatment time of etching solution all have an important influence on the purity and thickness of the wafers. The recycling methods can be divided into two categories according to the use of recycled silicon wafers. One category recovers low-grade silicon powder by simple etching as a raw material for production in other industries, such as making anode materials for lithium-ion batteries, where the key step is to convert the recycled silicon wafers into nano-scale or porous silicon powder. Eshraghi et al. [73] leached the recovered silicon wafers in critically tuned alkali-acid leaching baths to remove Ag, Al and Pb. The ultrapure Si was then nanosized via milling routes to meet the requirements of expansion-tolerant Si anodes for Li-ion batteries (LIBs) delivering capacities as high as 1400 mAh $\bullet$ g<sup>-1</sup>. Zhang et al. [74] converted recycled silicon powder into porous silicon for the preparation of LIBs by chemical etching to remove Ag and Al electrodes and AR layers from PV cells, and the corresponding LIBs can provide a capacity of 2427.7 mAh•g<sup>-1</sup>.

The other category aims to increase the value of recycled wafers by recovering intact, high purity silicon wafers of a certain thickness for refabrication into solar grade cells. PV module delamination methods have a significant impact on the integrity of the silicon wafer. During the thermal delamination process, the gases generated by the decomposition of EVA result in uneven internal pressure, which can easily lead to the

shattering of silicon cells. Mechanical shredding causes the wafers to shatter completely, making it impossible to recover intact wafers. The integrity of the wafers is better preserved with chemical treatment, but the EVA remains on the surface of the silicon cell and needs to be removed by pyrolysis. Xu et al. [75] developed a novel method of coupling solvothermal swelling with thermal decomposition for structure-intact Si- wafers recovery. under the optimized laboratory-scale conditions (190 °C, 2 h and 0.2 mol  $\rm L^{-1}$  toluene), structure-intact Si-wafers were reclaimed. An average integrity rate of 86.11%, which was nearly 10-fold higher than that of thermal decomposition alone (9.26%), was obtained by using a scaling up facility.

To recover silicon wafers with high purity and a certain thickness, it is important to select the precise etching conditions. Depending on the composition of the etching solution, it can be divided into etching solutions containing hydrofluoric acid and etching solutions without hydrofluoric acid. Most etching mixtures contain hydrofluoric acid (HF) as the oxidation product solvent and nitric acid (HNO<sub>3</sub>) as the oxidising agent. Ostrowski et al. [24] used KOH to remove the Al coating, followed by an etchant consisting of HNO<sub>3</sub>/HF/CH<sub>3</sub>COOH/Br<sub>2</sub> to remove the Ag coating, AR coating and n-p junction, with 5% of the regenerated wafers not meeting the solar cell quality requirements. Kang et al. [76] used a mixture of HF/HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>/CH<sub>3</sub>COOH/H<sub>2</sub>O etchant and achieved 86% recovery of silicon. Huang et al. [36] recovered 90% of the silicon using an HNO<sub>3</sub>/HF/NaOH etchant. Xu et al. [77] used HCI/HNO<sub>3</sub>/HF etchant to remove the Al coating, Ag electrode and AR layer and fabricated recycled wafers by the Metal-Assisted Chemical Etching (MACE) process with the addition of Cu<sup>2+</sup> and Ag<sup>+</sup>, which was an excellent choice for PV module production due to its ultra-low reflectivity (5-15%). Wang et al. [78] used hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as the oxidant. The Al electrode was removed with HCl/H2O2/H2O etchant. The antireflection layer, Ag electrode and n-p linkage layer were removed in 5% HF and 25% NaOH successively. A recovery of 62% of silicon was achieved.

HF is a highly toxic and corrosive chemical that requires special equipment to handle and is harmful to humans and the environment. Some scholars replaced HF with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) to make the etching process greener. Jung et al. [32] used HNO<sub>3</sub>/H<sub>3</sub>PO<sub>4</sub>/KOH etchant to remove the Al coating, Ag electrode, AR layer and n-p linkage layer with a recovery of 80% for silicon. Shin et al. [79] investigated an etching paste containing H<sub>3</sub>PO<sub>4</sub>. In the first step, the Ag electrode and Al coating were dissolved with HNO3 and KOH. In the second step the etching paste containing H<sub>3</sub>PO<sub>4</sub> was applied to the silicon wafer at 320 °C to remove the AR layer and n-p junction, followed by immersion in an aqueous KOH solution to recover the wafers. The recovered wafers were 180  $\mu m$  thick and the resistivity was maintained at 0.5 to 4  $\Omega$ -cm, close to the carrier lifetime of a polysilicon wafer. Punathil et al. [80] used a KOH/HNO<sub>3</sub>/H<sub>3</sub>PO<sub>4</sub> etchant to achieve 99.999%(5 N) purity of silicon after etching. Park et al. [81] used mechanical grinding to remove the AR layer, the n-p connecting layer, after removing the metal electrode, which can reduce the number of chemical reagents used by more than one and a half.

There are still problems with recycling silicon wafers from PV cell layers: (1) The high cost of chemical etching reagents and the complexity of the etching process are yet to be studied for economic sustainability. (2) The secondary pollutants produced by etching, such as nitrogen oxides, can be harmful to the environment if they are not properly disposed of. (3) The most common commercial wafer thickness is  $180\text{--}200~\mu\text{m}$  [36]. Etching results in the loss of silicon, and as technology advances wafer thickness is further reduced, it is more likely to result in wafers that are prone to breakage and cannot meet the requirements of solar-grade cells. (4) Solar cells regenerated from recycled wafers tend to exhibit lower conversion efficiencies than commercial wafers [79], which is disadvantageous in the highly competitive PV market. However, after years of research, the performance of the recycled silicon wafers under study is gradually approaching that of commercial silicon wafers and has a good certain market promise.

**Table 4**Recycling technology of silicon wafers from PV cells.

Etching process and key	Recovery rate% (Purity	Comment	Year	Ref.
parameters	%) of Si			
Removal of Al coating: KOH (30%), 60–80 °C, 2 ~ 3 min Removal of Ag electrodes, AR layer and n-p junctions: HNO <sub>3</sub> (65%), HF (40%), CH <sub>3</sub> COOH (99.5%) +Br <sub>2</sub> , 40 °C, 9 s	N/A	➤ Etching solutions need to be modified by the type of PV cells to be recycled.	2010	[24]
Removal of Al coating: HCl: H <sub>2</sub> O <sub>2</sub> : H <sub>2</sub> O (1:1:5), 80 °C Removal of Ag electrodes, AR layer and n-p junctions: HF (5%), NaOH (25%)	62 (8 N)	➤ The 38% silicon loses during NaOH etching.	2012	[78]
Removal of all: HNO <sub>3</sub> (70%), HF (48%), H <sub>2</sub> SO <sub>4</sub> (97%), CH <sub>3</sub> COOH (99%) Removal of oxidised impurities from silicon wafer surfaces: Surfactants (20% by weight)	86 (8 N)	➤ The addition of surfactants improves the recovery of silicon.	2012	[76]
Removal of Al coating and $\overline{AR}$ layer: $H_3PO_4$ (90%), $160$ °C, $60$ min Removal of Ag electrodes and n-p	N/A	➤ The recycled wafers are thick enough to be used in the solar cell production process and perform the same as commercial virgin wafers.	2014	[87]
junctions: HF, HNO <sub>3</sub> , 60 s Removal of Ag electrodes: HNO <sub>3</sub> (60%), RT, 120s Removal of AR layer and n-p junctions: Mechanical grinding Removal of Al coating: KOH (45%), 80 °C, 10 min	N/A	> Recycled wafers meet solar cell manufacturing requirements and HF free.	2016	[81]
Removal of Al coating: HNO <sub>3</sub> (5 mol L <sup>-1</sup> ), RT, 1 h Removal of Ag electrodes, AR layer and n-p junctions: H <sub>3</sub> PO <sub>4</sub> (90%), 160 °C, 60 min, KOH (45%), 80 °C, 10 min	80	➤ Partial silicon loss during etching and HF free.	2016	[32]
Removal of all: HNO <sub>3</sub> , HF (10%), 15 min, NaOH (3%), 50 °C, 20 min	90	➤ The recovered Si meets the specifications for solar-grade Si.	2017	[36]
Removal of Ag electrodes: HNO <sub>3</sub> (60%), RT, 5 min Removal of Al coating: KOH (45%), 80 °C, 8 min Removal of AR layer and n-p junctions: Etching paste containing H <sub>3</sub> PO <sub>4</sub> , 320 °C, 2 min Removal of oxidised impurities	N/A	➤ Solar cells made from recycled wafers are comparable in efficiency to commercial solar cells and HF free.	2017	[79]
from silicon wafer surfaces: KOH (0.05%)	NI /A	> Described more efficient mosts the assuring mosts of supersign assistant efficient and on far LIDs	2020	[70]
Removal of Al coating: KOH (8 mol L <sup>-1</sup> ), 60 °C, 5 min Removal of Ag electrodes: HNO <sub>3</sub> (8 mol L <sup>-1</sup> ), 80 °C, 15 min Ball milling	N/A	➤ Recycled nano-silicon meets the requirements of expansion-resistant silicon anodes for LIBs, providing 1400 mAh•g <sup>-1</sup> capacity, and HF free.	2020	[73]
Removal of Al coating: NaOH (10 mol L <sup>-1</sup> ), 63 °C, 5 min Removal of Ag electrodes: HNO <sub>3</sub> (6 mol L <sup>-1</sup> ), 70 °C, 5 min Removal of AR layer and n-p junctions: H <sub>3</sub> PO <sub>4</sub> (90%), 70 °C, 45 min	(4 N)	➤ NaOH instead of KOH is more economical and HF free.	2021	[80]
Removal of Ag electrodes: $HNO_3$ (5 mol $L^{-1}$ ), 80 °C, 1 h, 25 mL $g^{-1}$ Removal of Al electrodes, AR layer and n-p junctions: $KOH$ (2 mol	99.9 (nearly 3 N)	➤ HF free, but more reaction time than the treatment with HF.	2021	[86]
L <sup>-1</sup> ), 80 °C, 1 h, 50 mL g <sup>-1</sup> Removal of Ag electrodes: HNO <sub>3</sub> (60%), RT, 10 min Removal of AR layer: H <sub>3</sub> PO <sub>4</sub> (90%), 180 °C, 30 min, Magnetic stirring Removal of Al coating: NaOH (45%), 80 °C, 5 min	N/A	<ul> <li>▶ HF free and LIBs made to provide a capacity of 2427.7 mAh•g<sup>-1</sup>.</li> <li>▶ Alleviate greenhouse gas emissions caused by Si production.</li> </ul>	2021	[74]

(continued on next page)

Table 4 (continued)

Etching process and key parameters	Recovery rate% (Purity %) of Si	Comment	Year	Ref.
Ball milling and alloying/ dealloying approach convert Si wafers to porous Si				
Removal of Ag and Al: HNO <sub>3</sub> (3 mol L <sup>-1</sup> ), Ultrasonic (150 W), ultrasonic cleaner, 60 °C, 90 min	98.9 (2 N) 99.24 (2 N)	> The cavitation effect of an ultrasonic cleaner improves silicon recovery and purity and HF free.	2022	[88]
Removal of Ag and Al: HCl (3 mol L <sup>-1</sup> ), Ultrasonic (150 W), ultrasonic cleaner, 60 °C, 90 min				
Removal of Ag electrodes, Al electrodes, AR layer: HCl (18- 24 wt%, RT, 10–15 min), HNO <sub>3</sub> (30 wt%, 50 °C, 10 min), HF (20-30 wt%, RT, 5 min)	N/A	➤ Solar cells made from recycled wafers have higher conversion efficiency than commercial solar cells	2022	[77]
Removal of n-p junctions and anti- reflection texture fabrication processes: MACE (Cu <sup>2+</sup> , Ag <sup>+</sup> ), HF, H <sub>2</sub> O <sub>2</sub> , RT, 5 min				
Removal of residual nanoparticles: HNO <sub>3</sub> (30 wt%, RT, 15 min), HCl: H <sub>2</sub> O <sub>2</sub> : H <sub>2</sub> O (1:1:6), 80 °C, 20 min				
Modified rough surface structure: KOH (0.2 mol L <sup>-1</sup> ), IPA (10 vol %), 50 °C, 90 s				

Note: RT (Room temperature), MACE (Metal-Assisted Chemical Etching), IPA (Isopropyl alcohol), LIBs (Li-ion batteries).

3.2.2.2. Recovery of valuable metals from PV modules. EOL c-Si PV panels contain valuable metals such as Ag, Al and Cu that have recycling value. Table 5 provides an overview of the methods and technical parameters for the recovery of valuable metals. The effectiveness of silver recovery is influenced by two factors: the effect of the PV module delamination methods on silver enrichment, and the effect of processes such as hydrometallurgy and electrolysis on the purity of silver recovery.

Savvilotidou et al. [82] compared the effect of three different PV models separation methods, pyrolysis, conventional mechanical crushing and the combination of organic reagents and pyrolysis, on silver enrichment recovery. Pyrolysis was proposed to be the most effective Ag pre-enrichment route, achieving 91% enrichment. Akimoto, Song, Zhao et al. [53–55] proposed the use of high-voltage pulse crushing to improve the silver enrichment. Many scholars used hydrometallurgical

**Table 5**Recycling technology of valuable metals from PV cell layers.

Chemical leaching solutions	Leaching rate (%)	Separation and purification methods	Metal recovery rate% (Purity %)	Comment	Year	Ref.
NHO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub>	N/A	Cu: Removal of tin-lead coating	copper wire: 85	➤Cu loss is due to the acid etching process for remove the Pb/Sn alloy	2012	[78]
NHO <sub>3</sub> (64%)	N/A	Ag <sup>+</sup> : NaCl (99%)	N/A	➤ Ag enrichment of 94%  ➤ Pyrolysis did not assist in silver extraction from PV modules.	2016	[22]
$NHO_3(5 \text{ mol } L^{-1})$	N/A	Ag <sup>+</sup> : HCl, NaOH, N <sub>2</sub> H <sub>4</sub> ·H <sub>2</sub> O, Electrorefining	Ag: 90 (4 N)	➤ Removing Pb via a neutralization and sulfurization process.	2016	[32]
		Al <sup>3+</sup> : KOH, Calcination Cu <sup>2+</sup> : LIX84-I Extractants, H <sub>2</sub> SO <sub>4</sub> , Electrolytic Removal of Pb <sup>2+</sup> : NaOH,	Al: 94 Cu: 79			
MSA: H <sub>2</sub> O <sub>2</sub> (90:10)	N/A	Ag <sup>+</sup> : HCl, NaOH, H <sub>2</sub> O <sub>2</sub> , Electrorefining	Ag: (4N5)	≻MSA is Environmentally friendly and reusable	2017	[83]
NHO <sub>3</sub>	N/A	Electrowinning	Al: 74(>99)	➤Part of the metal is lost at the working electrode during transfer and rinse.	2017	[36]
			Cu: 83			
I <sub>2</sub> -KI	Ag <sup>+</sup> : >95	Ag <sup>+</sup> : Acetate and borate, NaBH <sub>4</sub> ,	Ag: 4.36 mg/g	<ul> <li>➤ Reducing environmental impact (acidification &amp; eutrophication)</li> <li>➤ The high cost of reagent</li> </ul>	2021	[84]
NHO <sub>3</sub> (5 mol L <sup>-1</sup> )	Ag+: 99.4	Ag+: NaCl, NaOH, Glucose	Ag:99.7(98.85)	≻Ag, Sn, Cu, and Pb recovered from PV cells, while	2021	[86]
, , ,	Sn <sup>2+</sup> :99.3	Sn <sup>2+</sup> : TBP Extractants, NH <sub>4</sub> OH,	CuO:98.5(99.7)	Al was not considered.		[]
	Cu <sup>2+</sup> : 10	Cu2+: LIX84-I Extractants, NH <sub>4</sub> OH, Calcination	SnO <sub>2</sub> :96.5(99.47)			
	Pb <sup>2+</sup> : 99.9	Removal of Pb2+: NH4OH	copper wire:99.57			
$H_2SO_4(5 \text{ mol } L^{-1})$	N/A	BDD electrode, H <sub>2</sub> SO <sub>4</sub> as an oxidising agent,250 mA	Ag:88 Cu:99	►No additional hazardous and volatile chemicals	2021	[85]
-	-	Wire explosion (High-voltage pulsed discharge), 15 kV	Ag:69%	➤No chemical reagents and green. ➤Low recovery rate	2021	[29]

Note: LIX84-I Extractants (A copper extraction agent), TBP (Tributyl phosphate), BDD electrode (Boron-doped diamond electrode).

methods to recover silver, using nitric acid solutions to leach out silver ions, adding chloride ions (e.g. NaCl, HCl) to precipitate enrichment in the form of silver chloride (AgCl). AgCl was then immersed in sodium hydroxide solution and converted to silver oxide (Ag<sub>2</sub>O) and then reduced using reducing agents (e.g. Hydrazine hydrate(N<sub>2</sub>H<sub>4</sub>-H<sub>2</sub>O), H<sub>2</sub>O<sub>2</sub>, glucose) to obtain the silver powder, which was then electro refined to obtain high purity silver of over 99.99% [22,32,36,82]. As nitric acid produced toxic fumes containing nitrogen oxides during use and the waste acid solution could lead to environmental eutrophication, some scholars began to investigate greener reagents to replace nitric acid solutions for silver extraction. Yang et al. [83] proposed the extraction of silver using methane sulfonic acid (MSA) and hydrogen peroxide instead of nitric acid, with a purity of 99.995% for silver recovery after electrorefining. Chung et al. [84] proposed an I<sub>2</sub>-KI leaching agent to replace nitric acid for the enrichment recovery of silver and aluminium with leaching efficiency comparable to that of nitric acid. Wet metallurgy is a well-established process for metal recovery, but the cost of reagents and the cost of waste liquid disposal need to be considered. In addition to wet metallurgical methods, Modrzynski et al. [85] proposed an electrochemically assisted leaching process using boron-doped diamond as the electrode and sulphuric acid as the oxidant to recover silver with a recovery of 88%. Lim et al. [29] proposed the direct recovery of silver wire by a wire explosion method using a high-voltage pulsed discharge, which is greener than wet metallurgy as no chemical reagents are used and no waste liquid needs to be treated, but the silver recovery rate is low at only 69%.

Al is mainly derived from the Al frame of the PV panels and the Al coating in the PV cell layer. Al frames are directly recycled by mechanical or pyrolytic removal before the separation of the PV modules [11,32]. After etching of the aluminium coating in the PV cell layer with an acidic solution, alkaline reagents (e.g. NaOH, KOH) are added to the filtrate and aluminium ions are precipitated as aluminium hydroxide, and finally, aluminium oxide is obtained by calcination [32]. Cu, Sn, and Pb are derived from the ribbon in the PV cells layer. Cu can be recovered by hydrometallurgical and physical polishing methods. Jung et al. [32] used nitric acid leaching and electrolysis to recover copper with a recovery of 79%. Chen et al. [86] oxidised the ribbon at 800 °C and polished the surface to remove the tin-lead coating layer, with a purity of 99.63% for the copper wire. Lead is a toxic metal that is harmful to the environment and the humans and is generally removed by acid leaching followed by the addition of alkaline reagents.

#### 4. Conclusion

In the upcoming surge of EOL solar PV panels, c-Si PV panel is the main type of concern. It is important to establish a systematic process for EOL PV panels recycling, in terms of environmental and resource utilisation. This paper provides an overview of c-Si solar PV panel assembly and recycling methods, and mainly introduced the module delamination and material recovery.

There are three methods of component delamination: thermal, mechanical and chemical delamination. Pyrolysis allows complete removal of the polymer and recovery of high purity glass and silicon wafers. To avoid the generation of toxic exhaust gases from the polymer during pyrolysis, two-stage pyrolysis is proposed. The backsheet of the PV panel is firstly removed at low temperature to prevent the production of fluorinated exhaust gases, followed by high-temperature pyrolysis to remove the EVA. Energy recovery should be a promising option to solve the high energy consumption problem of the pyrolysis/combustion process. However, the specific implementation of energy recovery during heat treatment and the problem of wafer brittleness need to be further researched. Mechanical delamination is simple and environmentally friendly at a low cost, and the metal enrichment rate can be increased by high-voltage pulse crushing. However, the crushed composition is complex and difficult to handle and recover, so it needs to be combined with a suitable sorting method. Moreover, the recovery

value of crushed glass and wafers is lower than that of intact glass and wafers. Chemical delamination can be achieved at low temperatures and the integrity of the wafer is well preserved, but the EVA adhering to the PV cell needs to be removed by pyrolysis. The chemical reagents studied so far are mainly organic reagents with toxicity, while less toxic, efficient and economically viable chemical reagents are yet to be studied.

The focus of material recovery is on glass, pure silicon and valuable metals. Glass is recycled through component delamination and can achieve high recovery rates and purity. Through the etching process, silicon wafers are recovered by removing impurities from PV cells. The performance of recycled silicon wafers is close to that of silicon wafers for commercial solar cells and has a high recycling value and market prospect. However, to improve the market competitiveness of the recovered wafers, the treatment of the waste solution generated by etching and the economics of recovered wafers need further study. Valuable metals (aluminium, silver, copper, etc.) in PV modules originate from PV cell layers. They can be recovered by chemical precipitation, electrostatic recycling, high-temperature oxidation polishing, etc. The metal content is a small proportion of the total PV panel and increasing the metal enrichment rate is also an important part of reducing recycling costs.

#### CRediT authorship contribution statement

Xiaopu Wang: Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition. Xinyi Tian: Writing – original draft, Investigation, Data curation. Xiaodong Chen: Resources, Conceptualization. Lingling Ren: Data curation. Chunxiang Geng: Writing – review & editing, Supervision.

#### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

No data was used for the research described in the article.

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