Solar Energy 144 (2017) 22–31

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Strategy and technology to recycle wafer-silicon solar modules

Wen-Hsi Huang [a], Woo Jung Shin [a], Laidong Wang [b], Wen-Cheng Sun [b], Meng Tao [b,*]

[a] School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ 85287, USA
[b] School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, AZ 85287, USA

ARTICLE INFO

Article history:
Received 26 November 2016
Received in revised form 21 December 2016
Accepted 3 January 2017

Keywords:
Wafer-Si solar modules
End-of-life Si solar modules
End-of-life management
Recycling

ABSTRACT

A major obstacle to sustainable solar technologies is end-of-life solar modules. In this paper, a recycling process is proposed for wafer-Si modules. It is a three-step process to break down Si modules and recover various materials, leaving behind almost nothing for landfill. Two new technologies are demonstrated to enable the proposed recycling process. One is sequential electrowinning which allows multiple metals to be recovered one by one from Si modules, Ag, Pb, Sn and Cu. The other is sheet resistance monitoring which maximizes the amount of solar-grade Si recovered from Si modules. The purity of the recovered metals is above 99% and the recovered Si meets the specifications for solar-grade Si. The recovered Si and metals are new feedstocks to the solar industry and generate $11–12.10/module in revenue. This revenue enables a profitable recycling business for Si modules without any government support. The chemicals for recycling are carefully selected to minimize their environmental impact. A network for collecting end-of-life solar modules is proposed based on the current distribution network for solar modules to contain the collection cost. As a result, the proposed recycling process for wafer-Si modules is technically, environmentally and financially sustainable.

1. Introduction

A major obstacle on the horizon to sustainable solar technologies is end-of-life solar modules. As module deployment expands rapidly, so will module waste. The International Renewable Energy Agency estimates that waste modules will appear in large quantities by the early 2030s and by 2050, they will total 78 million tonnes (International Renewable Energy Agency, 2016). Among the different module technologies on the market, wafer-Si modules have always been the dominant technology with a ~90% market share (Fraunhofer Institute, 2016). In 2015, the production of wafer-Si modules reached 59 GW_p (Fraunhofer Institute, 2016). This is equal to ~220 million modules, as wafer-Si modules are typically ~270 W_p each. With a lifetime of 25 years, these modules would be decommissioned in 2040.

Fig. 1 illustrates the structures of the most common commercial wafer-Si solar cell and module. The Si wafer in the cell is 180–200 µm thick. The front emitter is ~0.3 µm thick and heavily n-type. The back-surface field (BSF) is ~10 µm thick and heavily p-type. The SiN_x antireflection layer is 75 nm thick. The front electrode is Ag and the back electrode Al. In a module, the cells are interconnected by soldering Cu wires onto them. The solder is made of Sn and Pb. The interconnected cells, two sheets of ethylene vinyl acetate (EVA) and a backsheet of polyvinyl fluoride (PVF) are laminated to the front glass. An Al frame seals the edges of the module. A junction box (not shown in Fig. 1) is attached to the backside of the module for electrical connection.

Recycling is rarely practiced for Si modules. As of today, only the European Union enforces solar module recycling. PV CYCLE is one of the organizations which manage module recycling in Europe. The technology practiced by PV CYCLE for Si module recycling involves first stripping the Al frame and junction box from a module and then shredding the remaining module for glass (PV CYCLE). Si modules have a complex structure (Fig. 1b). As a rule of thumb, shredding or milling Si modules does not effectively separate the various materials in them (Dias et al., 2016b; Granata et al., 2014). To finance module recycling, the European Union imposes a fee on module manufacturers. This fee is ultimately passed onto consumers.

Three approaches have been reported to recycle the Si cells from the modules. Before 2005, the focus was on recovering the cells from the modules and then reusing the reclaimed cells in new modules. The key for this approach is a gentle method to separate the cells from the modules, so the cells remain intact. After the removal of the Al frame and junction box by mechanical measures, the backsheet can be peeled off (Bruton et al., 1994). There are three methods to detach the cells from the glass. The first method is to dissolve EVA in HNO_3 (Bruton et al., 1994). This is a

* Corresponding author at: PO Box 875706, Tempe, AZ 85287-5706, USA.
E-mail address: meng.tao@asu.edu (M. Tao).

http://dx.doi.org/10.1016/j.solener.2017.01.001
0038-092X/

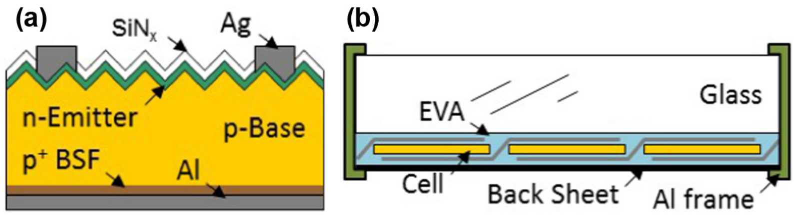

Fig. 1. Schematics of the most common commercial wafer-Si solar cell (a) and module (b).

long process taking ~24 h, and HNO_3 damages cell components including the Ag and Al electrodes. The second method is to dissolve EVA in an organic solvent (Doi et al., 2001). A large number of organic solvents have been screened, and the process is really slow taking weeks. The process can be sped up with ultrasonic agitation (Kim and Lee, 2012), but the cost and energy input for the ultrasonic process are likely high. The third method is to thermally decompose EVA (Bohland and Anisimov, 1997; Zeng et al., 2004; Frisson et al., 2000; Dias et al., 2016a). It can be carried out in a quartz-tube furnace, conveyor-belt furnace or fluidized-bed furnace in air or N_2. The exothermic reaction of burning EVA serves as a heat source for the furnace (Frisson et al., 2000), reducing the energy input for the furnace. Since the reclaimed cells often suffer from damage (Frisson et al., 2000), the second approach is to reclaim the Si wafers from the modules. New cells are then fabricated on the reclaimed wafers. Reclaiming wafers requires the removal of the Ag and Al electrodes, SiN_x layer, emitter and back-surface field (Frisson et al., 2000; Rover et al., 2005; Klugmann-Radziemska and Ostrowski, 2010; Klugmann-Radziemska et al., 2010; Park and Park, 2014). The chemicals for this purpose include HF for SiN_x and Al, HNO_3 for Ag, NaOH for Si, a mixture of HF and HNO_3 for Si and SiN_x, KOH for Al, or H_3PO_4 for Al.

Since 2005, the thickness of the wafers has been reduced to 180–200 μm (Fraunhofer Institute, 2016). The thin wafers prevent cell or wafer reclamation since the cells will all break during separation from the glass (Kang et al., 2012). Therefore, the most recent approach focuses on recovering the solar-grade Si from the cells (Klugmann-Radziemska et al., 2010; Huang and Tao, 2015; Muller et al., 2007). On the other hand, few papers have discussed metal recovery from Si modules (Huang et al., 2016). Two papers mentioned Ag recovery from Si cells by dissolving it in HNO_3 and extracting it through electrowinning (Klugmann-Radziemska and Ostrowski, 2010; Muller et al., 2007), but the Ag electrode in Si modules is partially covered under soldered Cu. There has been no report on recovery of multiple metals from Si modules.

In this paper we report our recent progress in wafer-Si module recycling. Our objective is to develop a recycling technology for Si modules that is technically, environmentally and financially sustainable. It involves a multi-step process to break down Si modules and recover various materials including all the toxic and valuable materials, solar-grade Si, Ag, Pb, Cu and Sn. Our process leaves behind almost nothing for landfill. The chemicals for recycling are carefully chosen so their wastes have a minimum environmental impact. More importantly, this recycling process generates a revenue stream of \$16–17/module from the recovered solar-grade Si, Ag, glass, Al frame and junction box, which is more than enough to cover the cost of recycling.

2. Incentives to recycle Si modules

There are two valuable materials to recover from the Si cell in Fig. 1a, solar-grade Si and Ag. The SiN_x layer and Al back electrode are hard to recover. For the Si wafer, the front emitter and back-surface field are heavily doped. They are out of the specifications for solar-grade Si. Only the base can be recovered as solar-grade Si, which is boron doped to $\sim 1 \times 10^{16}\ cm^{-3}$. Once the cells are soldered for modules (Fig. 1b), there are three more metals to consider, Pb and Sn from the solder and Cu from the wires. While Sn and Cu may have enough values to recover, Pb is a toxic metal and should be removed from the recycling sludge (Fthenakis and Moskowitz, 2000; Tammaroa et al., 2016). Besides the valuable and toxic materials, the Al frame, junction box, front glass and polymer sheets (EVA and PVF) should be recycled as well. These components have less values as raw materials (Fthenakis, 2000), but their recovery is environmentally sound.

A typical 60-cell Si module weighs 18–18.5 kg. It contains ~0.65 kg of Si. If 85% of the Si is recovered as solar-grade Si, it is worth \$8.30/module at \$15/kg for solar-grade poly-Si or \$7.20/module at \$13/kg for 2nd grade poly-Si. The module also contains ~7 g of Ag. If 95% of the Ag is recovered, it is another \$3.80/module at \$16/oz for Ag. As a result, the valuable materials in a typical Si module add to \$11–12.10 depending on the quality of the recovered Si. Additional values come from bulky materials including the glass, Al frame and junction box, which total ~\$5/module. The total revenue a typical Si module can generate is thus \$16–17, with over 45% of the revenue from recovered Si. This revenue is more than enough to cover the cost of recycling for a profitable recycling business without any government support. Our estimation is much higher than the analysis by the International Renewable Energy Agency, which predicts \$15 billion in revenue from recycling 78 million tonnes of solar modules (International Renewable Energy Agency, 2016). Our estimation is over \$60 billion from 78 million tonnes of solar modules. This is because our process keeps high-value materials in their pure, high-value forms.

A major contributor to the cost of solar module recycling is the cost to collect and transport solar modules which are scattered around in small quantities (Fthenakis, 2000). To contain the collection cost, we propose to utilize the current distribution network of solar modules in the reverse order as a collection network (Fig. 2). Installers go to homes to perform repair and pick up waste modules. The waste modules are shipped to retailers, then to distributors and finally to recyclers who operate centralized recycling plants and generate revenues by selling the recovered materials to the solar industry. To finance the network, each party in this collection network receives monetary compensation from the next party in the value chain.

There are more incentives to recycle Si modules. The cost of Ag is a major concern for the solar industry. The price of Ag has been fluctuating between \$13/oz and \$48/oz since 2010, and currently it is ~\$16/oz (InvestmentMine). The fluctuating price makes cost control difficult for module manufacturers. Recovering Ag from waste Si modules provides another source of Ag to the solar industry. There are also significant energy savings by recovering Si from waste Si modules. One of the most energy-intensive steps in the production of wafer-Si modules is the Siemens process, which reduces $SiHCl_3$ to solar-grade Si (Tao, 2014; Tao et al., 2011).