Strategy and Technology to Recycle Wafer-Silicon Solar Modules

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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. Over 95% of a module by weight can be recovered with this process. 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 over \$12/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 2030's 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 over 230 million modules, as wafer-Si modules are typically ~250 W_p each. With a lifetime of 25 years, these modules would be decommissioned in 2040.

Figure 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 ~0.5 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 backsheets 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. An organization, PV CYCLE, manages 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. 1(b)). As a rule of thumb, shredding or milling Si modules does not effectively separate the various materials in them (Dias et al., 2016, b; Granata et al., 2014). To finance PV CYCLE's operation, the European Union imposes a fee on module manufacturers. This fee is ultimately passed onto consumers.

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

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 HNO₃ (Bruton et al., 1994). This is a long process taking ~24 hrs, and HNO₃ 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., 2016, a). It can be carried out in a quartz-tube furnace, conveyor-belt furnace or fluidized-bed furnace in air or N₂. 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, a; Klugmann-Radziemska et al., 2010, b; Park and Park, 2014). The chemicals for this purpose include HF for SiN_x and Al, HNO₃ for Ag, NaOH for Si, a mixture of HF and HNO₃ for Si and SiN_x, KOH for Al, or H₃PO₄ 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, b; 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 HNO₃ and extracting it through electrowinning (Klugmann-Radziemska and Ostrowski, 2010, a; Muller et al., 2007), but the Ag electrode in Si modules is actually 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. The process recovers over 95% of the module by weight. 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 over \$12/module from the recovered solar-grade Si and Ag, 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. 1(a), 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 $\sim 1 \times 10^{16} \text{ cm}^{-3}$. Once the cells are soldered for modules (Fig. 1(b)), 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, b; Tammara 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 little values as raw materials (Fthenakis, 2000, a), but their recovery is environmentally sound.

A typical 60-cell Si module contains $\sim 0.65 \text{ kg}$ of Si. If 85% of the Si is recovered as solar-grade Si, it is worth \$8.20/module at \$15/kg for solar-grade Si. The module also contains $\sim 6.5 \text{ g}$ of Ag. If 95% of the Ag is recovered, it is another \$4.30/module at \$20/oz for Ag. As a result, the valuable materials in a typical Si module add to over \$12, which 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 $\sim$ \$45 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, a). 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 solar-grade Si and Ag 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.

Figure 2. A collection network for solar module recycling based on the current distribution network.

There are more incentives to recycle Si modules. The availability of Ag is limited. The worldwide known reserve of Ag is ~530,000 tonnes (U.S. Geological Survey, 2015). At the current mining rate of 26,100 tonnes/year, the Ag reserve would be depleted in 20 years. Recovering Ag from waste Si modules is mandatory to sustain the current 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). Recovering Si from Si modules bypasses the Siemens process. It is suggested that the energy input to produce a wafer-Si module is 400 kWh with freshly-produced Si, but only 186 kWh with recycled Si (Muller et al., 2005). This is a ~55% energy saving.

3. OUR PROCESS TO RECYCLE Si MODULES

Figure 3 is our proposed process to break down wafer-Si modules and recover various materials. It involves three steps, module recycling, cell recycling and waste handling. In the first step, the junction box and Al frame are mechanically removed from a module. The polymer sheets (EVA and PVF) are then burned off to separate the cells from the glass in a furnace (Wang et al., 2012), which serve as a heat source for the furnace. This is different from the report on peeling off the PVF (Bruton et al., 1994), as PVF wastes can be either burned or buried. The glass is recycled and what is left is a string of interconnected cells. In cell recycling, interconnected cells are first immersed into a leaching solution to dissolve four metals, Ag, Pb, Cu and Sn. These metals are then recovered from the leaching solution one by one through electrowinning. The remaining cells are immersed into an etching solution to remove the SiN_x layer and Al back electrode. Finally the cells are immersed into another etching solution to remove the emitter and back-surface field and to recover the base as solar-grade Si. The remaining sludge goes to landfill.

Figure 3. A proposed process to break down wafer-Si solar modules and recover various materials.

The chemicals selected for cell recycling are critical as they determine the waste chemicals we have to deal with. On the other hand, it is desirable to employ selective, self-limited chemistries for cell recycling (Fig. 4). We have purposely chosen HNO_3 which dissolves only Ag, Pb, Sn and Cu from the cells (Fig. 4(a)), and HF which etches only Al and SiN_x on the cells (Fig. 4(b)). With self-limited chemistry, process control becomes simpler as there is no over-etch to worry about. Finally NaOH is used to remove emitter and back-surface field. This is not a self-limited process, so a method to monitor the Si etch process is needed to maximize the amount of solar-grade Si recovered.

The last step is waste handling. Our recycling process generates three waste solutions, NaOH, HNO_3 and HF. NaOH and HNO_3 can neutralize each other to form a solution of NaNO_3 , which is a fertilizer (U.S. Department of Agriculture, 2011). There is a well-established practice to treat HF wastes, i.e. $\text{Ca}(\text{OH})_2$ is added to HF to precipitate fluorine out as CaF_2 (van den Broeck et al., 2003). There are also two gaseous exhausts from the recycling process. One is the exhaust from the polymer-burning furnace, which contains fluorine. The other is the exhaust from metal dissolution in HNO_3 , which contains NO and/or NO_2 . Scrubbers are required to trap fluorine in water as HF and to trap NO and NO_2 in water as HNO_3 . It is possible to use the acids from the scrubbers in the recycling process.

Figure 4. Self-limited chemistries for cell recycling: after HNO_3 (a); after HF (b) and after NaOH (c).

It is estimated that over 95% of the module by weight can be recovered through our recycling process, as it can recover all the glass, Al frame, junction box, polymers (as heat source), 85–90% of the Si and 90–95% of the metals. On top of 95% recovery, this process can generate over \$12/module in revenue by selling the recovered solar-grade Si and Ag to the solar industry.

4. ENABLING TECHNOLOGY 1: SEQUENTIAL ELECTROWINNING

For the proposed recycling process in Fig. 3, the technologies for module recycling and waste handling have been more or less developed or at least explored. However, the technology for cell recycling is not ready yet. In particular, the technology to recover multiple metals from Si modules and the technology to maximize the amount of solar-grade Si recovered need to be developed, which are circled in Fig. 3. Here we report our recent progress in multiple metal recovery (Huang et al., 2016). In the next section we will report our progress in solar-grade Si recovery (Huang and Tao, 2015).

After module recycling, interconnected cells are separated from the glass. These cells, intact or broken, are first immersed in HNO_3 to dissolve four metals from the cells, Ag, Pb, Sn and Cu. Although there has been no report on recovering multiple metals from Si modules, there are reports on recovering three of the four metals from printed circuit boards by leaching them in HNO_3 (Yoo et al., 2012; Mecucci and Scott, 2002). Yoo et al. (Yoo et al., 2012) added NaCl to the leaching solution to precipitate Ag out as AgCl. This

requires an extra step to convert AgCl to metallic Ag. Mecucci et al. (Mecucci and Scott, 2002) used electrowinning to recover Cu and Pb from the leaching solution. We believe that electrowinning is a more cost-effective approach as it can recover metals in their pure metallic forms. Furthermore, sequential electrowinning can recover multiple metals one by one from the leaching solution.

4.1 Experimental

To measure the metal recovery rate in electrowinning, a simulated leaching solution is utilized for the experiment. Metal contents in typical wafer-Si modules are listed in Table 1 (Bine Information Service, 2010). As Table 1 does not specify the Sn content in Si modules, it is assumed that the Sn content is the same as Pb. Al does not dissolve in HNO₃ and its reduction potential is too negative to allow recovery by electrowinning from an aqueous solution. As a result, Al is not included in this study. 0.0431 g of Ag, 0.72 g of Sn, 0.72 g of Pb and 4.31 g of Cu pellets are added to a 100-ml beaker. Their weight ratios follow Table 1. An aqueous solution of 11.4% HNO₃ is poured into the beaker to dissolve the Ag, Pb, Sn and Cu pellets. The pH of the solution is between 0 and 1. If the pH is less than 0, it is found that Ag does not deposit on the Ti working electrode in electrowinning. The beaker is heated on a hotplate to 60°C. After the metal pellets are completely dissolved, the solution is cooled down to 25°C. The leaching solution after metal dissolution is shown in Fig. 5. The blue color is due to Cu²⁺ ions in the solution. The white precipitate at the bottom is SnO₂, as observed in previous studies (Yoo et al., 2012; Mecucci and Scott, 2002). The precipitated SnO₂ is recovered by filtration, but can be recovered by sedimentation as well.

Table I

Metal contents in wafer-Si solar modules by weight (Bine Information Service, 2010).

Metal in wafer-Si module	Content (weight%)
Al	10%
Si	~3%
Pb	<0.1%
Cu	0.6%
Ag	<0.006%

Figure 5. The HNO₃ leaching solution after dissolution of four metals, Ag, Pb, Sn and Cu.

The leaching solution undergoes sequential electrowinning to recover the remaining metals, Ag, Cu and Pb. Fig. 6 illustrates the setup for sequential electrowinning, which involves three electrodes, a working electrode (W.E.), a counter electrode (C.E.) and a reference electrode (R.E.). Pt and Ti foils are used as the counter electrode and working electrode, respectively, since they are stable in concentrated HNO_3 . An Ag/AgCl electrode is used as the reference electrode. A Gamry Reference 3000 potentiostat is used for electrowinning. Voltammetry is performed on the leaching solution to measure the reduction potential for each of the three remaining metals, Ag, Pb and Cu. The scan rate is 10 mV/s. A progressively more negative voltage is then applied to the Ti working electrode to recover the metals one at a time. Each voltage is applied for 7,000 s. The deposit on the working electrode for each voltage is characterized by energy-dispersive x-ray spectroscopy (EDX). For maximum recovery rates, the time for Ag recovery is increased to 20,000 s and the time for Cu to 24 hrs. The solution is stirred to speed up the diffusion of Ag^+ and Cu^{2+} ions.

4.2 Results and Discussions

Figure 7(a) is the voltammetry of the leaching solution. There is a large cathodic current at ~ 0.1 V vs. the Ag/AgCl reference electrode, indicating that something is reduced. If Fig. 7(a) is zoomed in between 0.45 V and 0 V as shown in Fig. 7(b), it shows two reduction reactions. The first reduction reaction begins at ~ 0.43 V and reaches a peak at ~ 0.35 V. The second reduction reaction occurs at ~ 0.1 V. Since Ag is the noblest metal and Cu is the second noblest in the solution, the first and second reduction reactions are attributed to Ag and Cu reduction, respectively. The window to separate Ag from Cu is between 0.43 V and 0.25 V from Fig. 7(b).

Figure 6. Schematic of the three-electrode electrolyzer for sequential electrowinning of multiple metals.

The Nernst equation defines the equilibrium reduction potential:

$$E_{red} = E^{\circ} + \frac{RT}{nF} \ln[M] \quad (1)$$

where E_{red} is the reduction potential under nonstandard conditions, E° the standard reduction potential, R the gas constant, T the absolute temperature, n the number of electron involved in the reaction, F the Faraday constant and $[M]$ the concentration of the metal ion. The concentrations of Ag^+ , Cu^{2+} and Pb^{2+} in the simulated leaching solution are 5×10^{-3} M, 0.85 M and 0.04 M, respectively. Their reduction potentials from

the Nernst equation are 0.45 V, 0.128 V and -0.38 V vs Ag/AgCl. The theoretical reduction potentials for Ag and Cu are very close to those from the voltammetry. Since the concentration of Cu^{2+} is much higher than Pb^{2+} , its large reduction current shadows the reduction reaction of Pb^{2+} in the voltammetry.

Figure 8 shows EDX analysis of the deposits under different voltages on the Ti working electrode. Ti peaks show up due to the Ti electrode. Between 0.35 V and 0.25 V, the deposits contain only Ag. However, when the voltage is less than 0.2 V, Cu starts to show up in the EDX spectra. As a result, the window to recover 99% pure Ag is between 0.45 V and 0.25 V vs. Ag/AgCl since the detection limit of EDX is typically below 1%. The concentration of Ag in the solution decreases with time. The Nernst equation states that, when the concentration decreases, the reduction potential becomes more negative. Although the minimum voltage before Cu^{2+} reduction is 0.25 V, 0.3 V vs. Ag/AgCl is chosen for Ag recovery.

Figure 7. Voltammetry of the leaching solution (a) and zoom-in of (a) between 0.5 V and 0 V vs. Ag/AgCl (b).

Figure 8. EDX spectra of the deposits on the Ti working electrode under different voltages vs. Ag/AgCl.

Figure 9 is the current vs. time plot for Ag recovery with the voltage on the Ti working electrode at 0.3 V vs. Ag/AgCl. The total electrowinning time is 20,000 s. The reduction current decreases with time as the concentration of Ag^+ decreases over time. It does not reach zero, suggesting a kinetic limit to Ag recovery. Fig. 10 is EDX analysis of the deposit at 0.3 V vs. Ag/AgCl for 20,000 s. It shows only Ag peaks from the recovered Ag and Ti peaks from the Ti electrode. The purity of the recovered Ag is at least 99%. The recovery rate of Ag in this experiment is 74%. This is obtained by measuring the weight gain of the Ti electrode and comparing it with the amount of Ag in the solution. By minimizing kinetic factors, the recovery rate of Ag can be significantly improved. The current efficiency for Ag recovery is 99.7%.

Figure 9. Current-time plot for Ag recovery at 0.3 V on the Ti working electrode vs. Ag/AgCl.

Figure 10. EDX spectrum of the deposit on the Ti working electrode at 0.3 V vs. Ag/AgCl for 20,000 s.

Figure 11 compares the voltammetry of the leaching solution before and after Ag recovery. After Ag recovery, the Ag^+ reduction reaction at ~ 0.35 V disappears and only the reduction reaction of Cu^{2+} is still present. This further proves that only Ag is removed from the solution during Ag recovery.

Cu recovery is performed after Ag recovery. -0.3 V vs. Ag/AgCl is applied to the Ti electrode. The reduction reaction of Pb^{2+} is shadowed by the reduction reaction of Cu^{2+} in Figs. 7 and 11, and the theoretical reduction potential of Pb^{2+} from Eq. (1) is -0.38 V vs. Ag/AgCl. Fig. 12 shows EDX analysis of the deposit on the Ti electrode at -0.3 V for 24 hrs. There are Cu peaks but there is no Pb peak in EDX, indicating that Cu with 99% purity is recovered from the Pb^{2+} -containing solution. The Ti peaks are not present as the Cu deposit is thick. The oxygen peak is due to oxidation of Cu on the Ti working electrode. The recovery rate of Cu is currently 83%.

Figure 11. Comparison of voltammetry of the leaching solution before and after Ag recovery.

Figure 12. EDX spectrum of the deposit on the Ti working electrode at -0.3 V vs. Ag/AgCl for 24 hrs.

It is found that Pb^{2+} ions deposit on the Pt counter electrode as PbO_2 during Cu recovery, which is observed in a previous study (Mecucci and Scott, 2002). Fig. 13 is EDX analysis of the Pt electrode after Cu recovery. Pb peaks are present, indicating that when Cu is recovered on the Ti working electrode, Pb is also recovered on the Pt counter electrode from the solution. The oxygen peak is small, maybe due to the nonstoichiometric PbO_x ($x < 2$) on the Pt counter electrode. The solution after Cu recovery for 48 hrs is investigated by inductively coupled plasma optical emission spectroscopy (ICP-OES). The results are listed in Table 2. Ag and Cu are largely removed. The Sn concentration is high because the filtration of SnO_2 was done only with a simple filter paper. With the Pb concentration at 92 ppm and the volume of the solution at 60 ml, the amount of Pb in the solution is ~ 5.5 mg. This is only 0.76% of the Pb in the starting solution, i.e. over 99% of the Pb^{2+} ions are removed from the solution during Cu recovery and the solution is almost free of toxic Pb.

Figure 13. EDX spectrum of the deposit on the Pt counter electrode after Cu recovery for 24 hrs.

Table II

Metal contents in leaching solution after Cu recovery for 48 hours.

Metal	Content (ppm)
Ag	0.034
Cu	3.38
Pb	92.1
Sn	426

5. ENABLING TECHNOLOGY 2: SHEET RESISTANCE MONITORING

The cells after metal dissolution have the structure in Fig. 4(a). They are immersed into an aqueous solution of 10% HF for 15 min to remove the SiN_x layer and Al back electrode. The structure of the remaining cells is shown in Fig. 4(b), and the purpose of solar-grade Si recovery is to etch off the front emitter and back-surface field and to recover the base. We have carried out two studies for Si recovery (Huang and Tao, 2015). The first study is to optimize the conditions of NaOH etch for the highest etch rate of Si. The second study is to maximize the amount of solar-grade Si recovered.

5.1 Experimental

To optimize the NaOH etch conditions, Si wafers are immersed into aqueous NaOH solutions of various concentrations from 1% to 50% at 25°C, as the saturated NaOH concentration in water is ~50% at 25°C. The weight of the Si wafers is measured every 15 min and then converted to wafer thickness by the following equation:

$$\text{Thickness} = \frac{\text{Weight}}{\text{Area} \times \text{Density}} \quad (2)$$

It is assumed that the area of the Si wafer does not change after etch. Once the NaOH concentration for the highest etch rate is determined, the temperature of the NaOH solution is raised to 50°C to further increase the etch rate.

To remove the emitter and back-surface field, commercial monocrystalline-Si (mono-Si) solar cells are used. They go through HNO_3 and HF to remove the front electrode, back electrode and SiN_x layer. The remaining cells have the structure in Fig. 4(b). They are etched in an aqueous NaOH solution under the conditions identified above. Every 15 min, the cells are lifted from the NaOH solution and their sheet resistances are measured by a four-point probe on both the front and back sides. The reciprocal sheet resistances are then plotted against etch time to determine the precise moment when the heavily-doped emitter and back-surface field are just removed.

5.2 Results and Discussion

Figure 14(a) shows the thickness loss of Si wafers as a function of etch time at 25°C under different NaOH concentrations from 10% to 50%. Etch of Si starts after 15 min with stable slopes, i.e. constant etch rates, for all concentrations. The slow etch during the first 15 min suggests the presence of native oxide which hinders the etch rate. This assumption is verified in Fig. 14(b), which shows the thickness loss of two Si wafers in 10% NaOH, one with and the other without 10% HF pretreatment for 15 min. With HF pretreatment, the wafer shows a stable slope from the beginning, while the other wafer initially has little etch and then a stable slope after 15 min. The etch rate of native oxide by NaOH is lower than that of Si. With native oxide, there are two stages in the etch: (1) an oxide etch stage (first 15 min) and (2) a Si etch stage (dashed circle). It is noted that the etch rate, i.e. the slope, for the HF-treated wafer is the same as the wafer without HF pretreatment after 15 min. This is clearly the Si etch stage.

From Fig. 14(a), the etch rate in the Si etch stage increases when the NaOH concentration decreases. In order to increase the etch rate, the NaOH concentration is reduced below 10%. Fig. 15 is the thickness loss of Si wafers as a function of etch time in 1%, 3%, 5% and 10% NaOH aqueous solutions at 25°C. None of these wafers goes through HF pretreatment, so they all have the oxide etch stage. The time for oxide etch is 15 min, 30 min, 45 min and 60 min for 10%, 5%, 3% and 1% NaOH, respectively. After oxide etch, all the wafers show stable slopes indicative of Si etch. From the slopes the etch rate of Si is determined, as shown in Fig. 16. The 3% NaOH solution shows the highest Si etch rate, which is 0.082 $\mu\text{m}/\text{min}$.

Figure 14. Thickness loss of Si in NaOH solutions of various concentrations at 25°C (a) and with or without HF pretreatment (b).

The back-surface field is $\sim 10 \mu\text{m}$ thick. Even at 0.082 $\mu\text{m}/\text{min}$, the etch rate is still too low for the back-surface field. In order to increase the etch rates of native oxide and Si, the 3% NaOH solution is heated to 50°C. This temperature can be achieved by exposing the NaOH solution under sunlight. Fig. 17 shows the thickness loss of a Si wafer as a function of etch time in a 3% NaOH aqueous solution at 50°C. There is no oxide etch stage at 50°C and the Si etch rate is around 0.53 $\mu\text{m}/\text{min}$. At this etch rate, the back-surface field can be removed in ~ 20 min. 3% NaOH at 50°C are the conditions used for actual cell etch.

Commercial mono-Si cells with the structure in Fig. 4(b) are immersed into a 3% NaOH aqueous solution at 50°C. Every 15 min, the cells are lifted out of the NaOH solution and their sheet resistances are measured from both the front and back sides by a four-point probe. Fig. 18 plots the reciprocal sheet resistance of a cell as a function of etch time. Initially, the sheet resistances from the two sides are different because the

sheet resistance from the front side is that of the n^+ emitter, and the sheet resistance from the backside is that of the p^+ back-surface field in parallel with the p-type base. After 15 min, the two sheet resistances become identical. This happens when the n^+ emitter is completely removed. As a result, no matter which side the sheet resistance is measured from, it is always the sheet resistance of the p^+ back-surface field in parallel with the p-type base. After 30 min, the plot changes its slope. This indicates the complete removal of the p^+ back-surface field and only the lightly-doped p-type base is left. As soon as the slope changes, the etch should be stopped to recover the maximum possible amount of solar-grade Si from the cell.

Figure 15. Thickness loss of Si in 1%, 3%, 5% and 10% NaOH aqueous solutions at 25°C.

Figure 16. Si etch rate in 1%, 3%, 5% and 10% NaOH aqueous solutions at 25°C.

The backside of the cell contains a p layer and a p^+ layer in parallel. The reciprocal sheet resistance of the backside is:

$$\frac{1}{R_s} = \frac{\rho_{p^+} w_p + \rho_p w_{p^+}}{\rho_{p^+} \rho_p} \quad (3)$$

where R_s is the measured sheet resistance, ρ_{p^+} the resistivity of the p^+ layer, ρ_p the resistivity of the p layer, w_{p^+} the thickness of the p^+ layer and w_p the thickness of the p layer. Eq. (3) indicates that the measured sheet resistance of the backside is a function of the thicknesses of the p and p^+ layers. In Fig. 17, the thickness of the Si wafer has a linear relation with etch time in 3% NaOH at 50°C. As a result, the reciprocal sheet

resistance of the backside is a linear function of etch time. This is verified by the straight line for the backside between 0 min and 30 min in Fig. 18.

Figure 17. Thickness loss of Si in a 3% NaOH aqueous solution at 50°C.

When the p^+ layer is completely removed, the reciprocal sheet resistance of the backside becomes:

$$\frac{1}{R_s} = \frac{w_p}{\rho_p} \quad (4)$$

At this stage, the reciprocal sheet resistance is also linear with etch time because the thickness of the p layer has a linear relation with etch time. However the reciprocal sheet resistance shows a different slope. This is why the slope changes at 30 min in Fig. 18, and the point of slope change indicates that the p^+ back-surface field has just been completely removed. Since w_p decreases with etch time at a constant rate, Eq. (4) can be rewritten as:

$$\frac{1}{R_s} = -\frac{r \times t}{\rho_p} + C \quad (5)$$

where r is the Si etch rate, t the etch time and C a constant related to the initial thickness of the p-type base. With Eq. (5), one can find the resistivity of the p-type base, ρ_p , by dividing the Si etch rate with the absolute value of the slope between 30 min and 120 min in Fig. 18. The etch rate of Si is 0.53 $\mu\text{m}/\text{min}$ and the fitted slope is $-3.77 \times 10^{-5} \text{ } \square/\Omega\text{-min}$. The ρ_p calculated is thus 1.41 $\Omega\text{-cm}$, which is in agreement with the specifications of the starting Si wafer.

Figure 18. Reciprocal sheet resistance of a Si cell in a 3% NaOH solution at 50°C as a function of etch time.

Figure 19. Remaining weight of a Si cell in a 3% NaOH solution at 50°C as a function of etch time.

The remaining weight of a Si cell as a function of etch time has also been measured, as shown in Fig. 19. A 30-min etch removes all the heavily-doped layers. Fig. 19 reveals that after 30 min, the remaining weight is ~91% of the starting wafer, i.e. the amount of solar-grade Si recovered by sheet resistance monitoring is over 90%.

6. CONCLUSION

A recycling process is proposed for wafer-Si solar modules that is technically, environmentally and financially sustainable. It is a three-step process, module recycling, cell recycling and waste handling, to break down Si modules and recover various materials. Over 95% of a module by weight can be recovered by the proposed process including all the glass, Al frame, polymers (as heat source), junction box, ~90% of the Si as solar-grade Si and over 90% of the valuable and toxic metals. Two new technologies are demonstrated to enable the practice of the proposed recycling process. One is sequential electrowinning which allows multiple metals to be recovered one by one from Si modules, Ag, Pb, Cu and Sn. The recovery rates of Ag and Cu are currently 74% and 83%, respectively, but can be increased to 95%. The purity of the recovered metals is above 99%. The other technology is sheet resistance monitoring which maximizes the amount of solar-grade Si recovered from the modules. Over 90% of the Si in the original modules can be

recovered, and the recovered Si meets the specifications for solar-grade Si. The recovered metals and Si are new feedstocks to the solar industry and generate over \$12/module in revenue at today's prices for Ag and solar-grade Si. This revenue eliminates a major obstacle to Si module recycling, enabling a profitable recycling business without any government support. The chemicals for recycling are carefully selected so their wastes can neutralize each other for a minimum 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.

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A multi-step process is proposed to break down Si modules and recover almost all the materials. New technologies are demonstrated for the recycling process including sequential electrowinning to recover multiple metals one by one from Si modules, Ag, Pb, Sn and Cu, and sheet resistance monitoring to maximize the amount of solar-grade Si recovered from Si modules. The recovered Si and metals are new feedstocks to the solar industry. They generate \$11–12/module in revenue to cover the cost of recycling.