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CURRENT AND FUTURE PRIORITIES FOR MASS AND MATERIAL IN SILICON PV MODULE RECYCLING

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ABSTRACT: A full description of the state-of-the-art PV recycling methods and their rationale is presented, which discusses the quality of the recycled materials and the fate of the substances which end up in the landfill. The aim is to flag the PV module components currently not recycled, which may have a priority in terms of their embedded energy, chemical nature or scarcity, for the next evolution of recycling. The sustainability of different recycling options, emerging in the literature on electronic waste recycling, and the possible improvement of the environmental footprint of silicon PV modules, will be discussed.
Keywords: PV module recycling,

1 INTRODUCTION

In anticipation of the numbers of PV modules that will come to the end of their life in the next decades, and to answer legal responsibilities, the PV industry has set up recycling logistics and processes. These state-of-the-art recycling processes focus on recovery of the predominant materials of a mixed-material product, as prioritized in the current WEEE directive for electronic waste, which now also includes PV modules. Therefore, PV modules will be affected by the evolution of the regulations on waste electrical and electronic equipment (WEEE). [1] Some industrial ecologists think it is likely that the current prioritization will be revised so as to compel the recovery of less concentrated quantities of valuable metals. [2] In looking forward to the evolution of recycling, an analysis of priorities and methods is necessary, based on the cost, technical feasibility, embedded energy, materials depletion and potential hazardousness of certain PV module materials.

In aiming to make further strides towards a sustainable closed-loop product trajectory, it is essential to analyze the role that materials play along the lifetime of the product. In this work, a broad integrated view of the recycling possibilities and of the fate of the PV materials is presented. The savings in embedded energy which is gained by recycling is calculated. Through analyzing the energy, environmental impact and scarcity of the PV module material components, the priorities are outlined for the evolution of recycling, with implications for product design.

2 METHODS

The recoverable module materials are analyzed using life cycle assessment (LCA) methods, performed using Simapro software (version 7.3.3) in conjunction with the Ecoinvent database (version 2.2). The environmental impacts were assessed using the RECIPE methodology. The emissions of greenhouse gases (in kg of CO_2 equivalents), were calculated using the GWP100a method as defined by the Intergovernmental Panel on Climate Change (IPCC) in 2007. The trends for the recent price evolution metals is presented, based on information from the US Geologic Survey (USGS).

3 STATE-OF-THE-ART PV RECYCLING

The current state-of-the-art recycling process aims to recycle more than 80% of the PV module by weight. The process flow begins with the disassembly of the aluminum frame and junction box. Because the size, profiles and fastening of frames varies between manufacturers, the disassembly of the frames is frequently done manually. The frameless PV module consists of the active silicon cell encapsulated in a layer of EVA polymer, which allows the cell to be laminated to the tough polymer back sheets as well as the glass front sheet. Under the hammer mill, it will fall apart into glass fragments, back sheet fragments, wiring and silicon solar cells (wafer with small amounts of metal) still

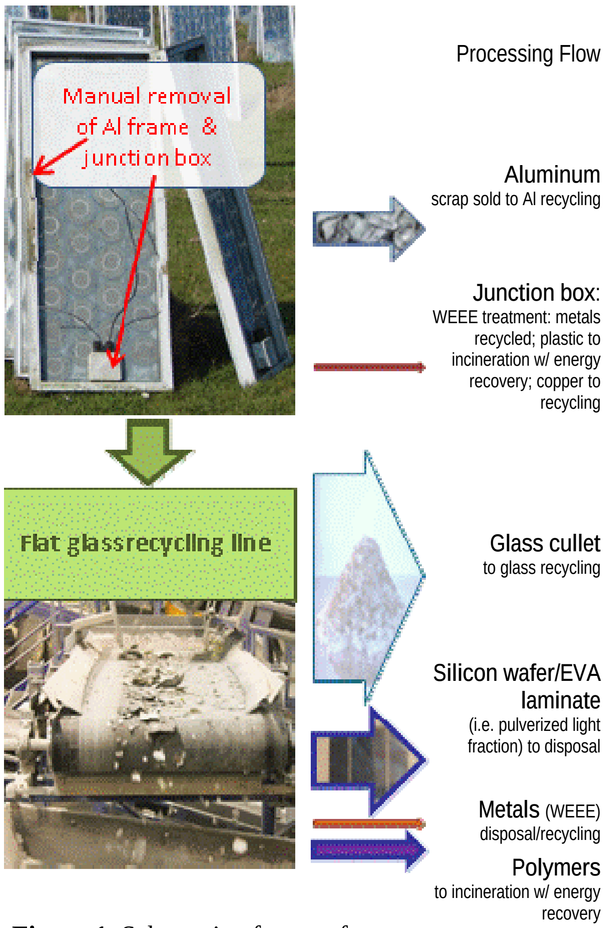


Figure 1. Schematic of state-of-the-art PV recycling process flow

embedded in the EVA, as a shredded laminate. The pulverization results in both larger fragments which may be sorted for recycling, as appropriate, and a fraction of smaller particles which is referred to as the lighter fraction which consists of dust, fibers, and very small fragments of the materials undergoing pulverization. The light fraction, also referred to as 'fluff', has not typically been subject to separation procedures. In recycling of automobiles, 'fluff' contains a high percentage of fibers which may be incorporated in some composite materials. [3]

The 2012 update to the WEEE directive includes photovoltaic panels. The directive frames the recycling targets in terms of the product's weight, and the current process flow is compatible with these targets. The WEEE directive also expresses the intent that collection rates and processes will evolve over time to enable progressively more material to be recycled and less to be landfilled. With the current recycling of over 80% of the weight of a PV module , and with targets aiming for 65% product weight recycling, the current method is in compliance, as long as the criteria remains weight-based.

In this paper, the components of a typical PV module, manufactured in 2011, is analyzed by weight, embedded energy and selected environmental impact indicators. These results are discussed in terms of the possible driving forces for future evolution of the state-of-the-art PV recycling process.

It is important to note that presently "the principal difficulty encountered regarding the recycling of photovoltaic modules is financial. The recycling processes are costly and the waste volumes are still fairly low with regards to industrializing these processes." [4] The recovery of materials which have high embedded energy and/or value, but which are currently not recoverable with existing methods, requires research and development funding and support on a societal scale.

3 RESULTS AND DISCUSSION

3.1 Analysis of components by weight, embedded energy and environmental impact.

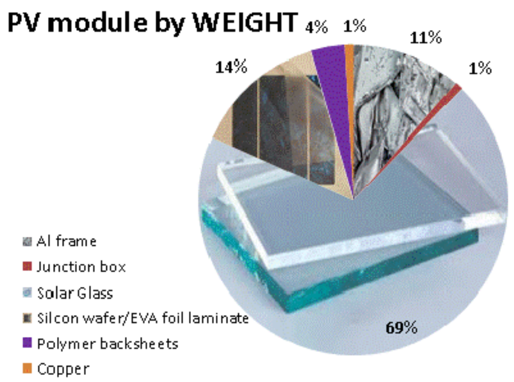


Figure 2. Weight breakdown of main components of a typical (2011) crystalline silicon PV module.

The silicon wafer and the EVA contribute 11% and 3%, respectively, to the weight, but account for a respective 76% and 7% of the embedded energy. (Figures 3 and 4).

The silicon wafer and EVA encapsulant also account for the lion share of the environmental impact

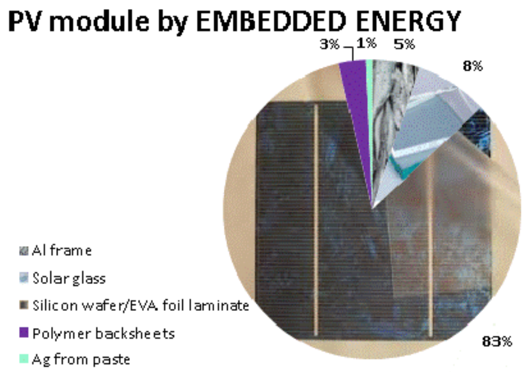


Figure 3. Breakdown by the embedded energy of the components of a typical (2011) x-Si PV module (excluding junction box).

among the indicators calculated here. (Figures 4-6) The impacts are shown as relative contributors (in %) to the overall impact of environmental impact of a PV module in perspective, PV electricity contributes 96–98% less greenhouse gases than electricity from 100% coal, and 92–96% less compared with the European electricity mix. Furthermore, compared with coal electricity, PV electricity over its lifetime uses 89–86% less water, occupies or transforms over 80% less land, and presents ~95% lower toxicity to humans; it also contributes 92–97% less to terrestrial acidification and 97–98% less to marine eutrophication. [1]

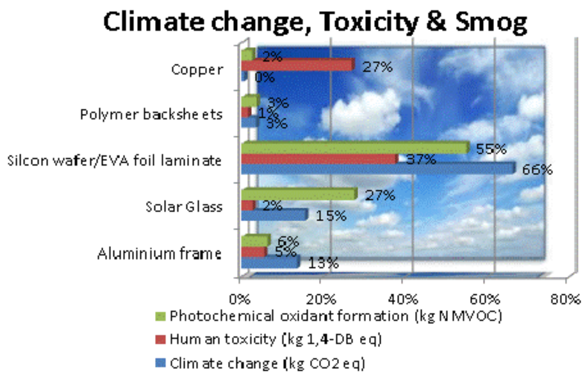


Figure 4. The relative impact of PV module components, over their life cycle, on climate change (kg CO_2 eq), human toxicity (kg 1,4 dichlorobenzene equivalents(1,4-DB eq)), and photochemical oxidant formation (kg non-methane volatile organic compounds (NMVOC)).

The savings in cumulative energy and greenhouse gas emissions per process step in the current recycling approach may be estimated by comparing the calculations in Ecoinvent for primary and secondary module components.

The original Al frame is modeled using the Ecoinvent Al production mix (32% recycled) which is extruded and machined into a frame. By considering the savings in energy and emissions by replacing the production mix with 100% secondary Al, an upper estimate of the savings due to recycling can be made. The low-iron solar glass was considered to be produced into 100% recycled white packaging glass. The original copper was taken to be a production mix of 20% recycled material and compared to 100% recycled copper. It is an upper estimate because it refers only to the material. It doesn't include the energy and emission costs of the recycling process itself, nor the material losses. Mechanical recycling produces, as a rule, less secondary waste streams as compared to chemical processes or incineration.

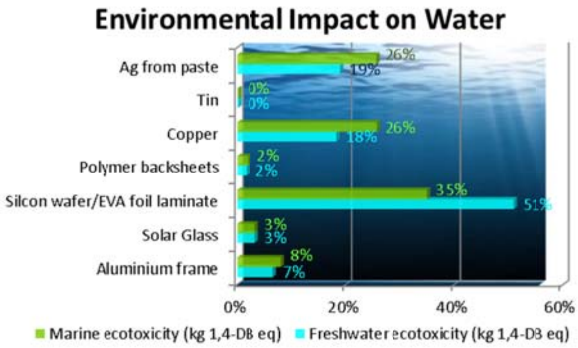


Figure 5. Relative impact of PV module components, over their lifetime, on marine and freshwater toxicity (kg 1,4-DB eq).

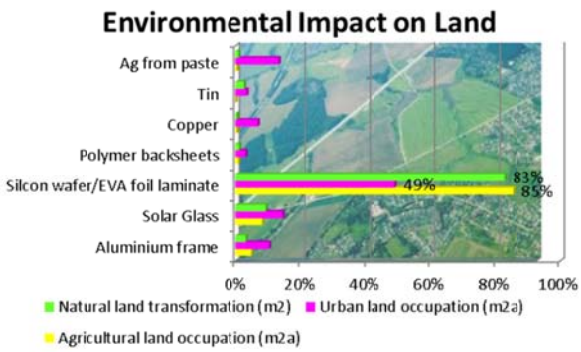


Figure 6. Relative impact of PV module components, over their lifetime, on natural land transformation (m^2) , urban and agricultural land occupation (m^2 per year (m^2a)).

The polymer backsheets which include a fluorinated polymer layer (e.g. PVDF) and a PET polymer layer are currently incinerated, due to a lack of other feasible options for their separation and/or marketing When burned, fluorinated polymers release hydrofluoric acid (HF), fluoroalkanes and alkenes, oxidation products (epoxides, aldehydes and acids), and fluoro-polymer particulates. [3] Compounds containing a carbon-fluoride bond are potent greenhouse gases. Incinerators in Europe are required by the Waste Incineration Directive to remove acids such as HF, and other toxic alkenes, such as dioxin. [4] However, as the emissions of fluoropolymers during incineration are largely not yet characterized, they may not yet be entirely well controlled. [3] This should be viewed as an area for more research.

Table 1. Energy & Emissions savings estimate

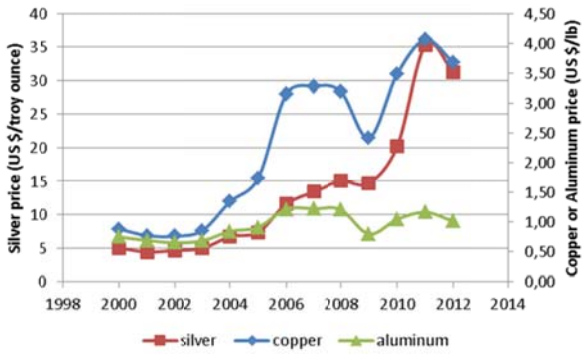
	Primary/kg		Secondary/kg		Savings to module	
	CED (MJ)	GWP (kg)	CED (MJ)	GWP (kg)	CED (%)	GWP (%)
Al frame	189,1	11,4	76,9	4,3	3,0%	8,1%
glass	14,6	1,1	11,3	0,7	1,8%	5,2%
copper	34,5	1,9	28,1	1,79	0,03%	0,01%
Total					4,8%	13,4%

3.2 Driving forces for recycling evolution

Rising prices for metal and energy, and scarcity of supply, may apply pressure to create targets that are based on the nature of the material components. The development of commodity prices as recorded by the US Geological Survey (USGS) for primary copper, silver and aluminum are shown in Figure 7.

As there are 14.6 troy ounces to a pound, the price of silver is significantly higher than the other 2 metals. By 2011, the cost of silver was becoming an issue for PV manufacturers. It was estimated then that metal added ~11 ¢/W to the cost of a panel (~$23.50/panel, about 2% in 2011). [1] [2] This drove the research to strive to either reduce the amount of silver or replace it, with copper as the leading candidate. Recovery of silver has not been considered to be worth the effort because it contributes only ~0.08% to the weight and is relatively dispersed throughout the solar cell, which is securely encapsulated in the EVA polymer. The recycling business case for any component is relative to the volume of the PV module waste stream, which will only begin to come into maturity in the next decades.

Cumulative global installed PV amounted to just over 71 GW in 2011, including about 53 GW located in Europe. [3] Estimating each panel at 200W, 22 kg, and with 18g of silver apiece leads to the rough calculation that roughly 5000 metric



ary Cu, Ag,

tons of silver are in the European installed PV capacity as of the end of 2011. These kinds of calculations are motivating a reflection on how the current recycling methods are dealing with low weight concentrations of valuable metals in increasing amounts of electronic consumer products, even though feasible solutions for their recovery are not yet available.

Electric and electronic waste (e-waste) is a global problem. Current estimates say that about 40 million tons of e-waste were disposed of worldwide, in 2011 alone, and the annual amount is growing. [8] E-waste contains low concentrations of specialty and/or precious metals that are highly mixed with other components, so that separation is challenging. The business case for their recovery is not yet a sufficient motivator. Despite existing regulations, only 20-40% of e-waste in the EU is collected and treated in the existing recycling lines, but low concentration metals are often not recovered, and have significant environmental impacts when disposed of in landfills or incinerators. [9] Many of these materials are also characterized by EU as ‘critical materials’ – i.e. economically important materials, that enable technology development and markets, but which are subject to insecurities, either political or physical, in their supply to the EU. [10] For these reasons, industrial ecologists who have evaluated the current WEEE legislation express the opinion that recycling should change to prioritize a material-related approach over a mass-related one. [9]

The silicon wafer accounts for 76% of the embedded energy, and can contribute ~60% to the costs of the module. [8]. A long-standing aim of European PV research has been to lower PV module costs. It has been articulated in the goals of the Strategic Research Agendas and the Solar Europe Industry Initiative (SEII) PV Implementation Plans since 2007. [9] [10] The cost issue has been tackled by improving efficiencies, device design and manufacturing processes. In the most recent SEII plan, improvement of recycling is also taken on as a research goal, for the aim of improving the sustainability and competitiveness of EU PV products. It is conceivable that the cost issue might also be addressed by re-using silicon wafers. After a lifetime of 25 to 30 years, it has often been observed that the failure of a PV panel is due to de-lamination or other module architecture issues, and not due to the silicon solar cell itself. The reuse of silicon wafers, however, depends on the ability to de-manufacture the PV module so as to recover the solar cells intact and liberated from the cross-linked EVA polymer encapsulant.

Current research on ways to recover the intact silicon wafer include thermal and chemical methods. In one approach, the glass/EVA/silicon cell/EVA/back sheet laminate undergoes pyrolysis to vaporize the EVA polymer at about 500 °C. The solar cell is then subjected to various etching steps to remove the metal contacts, the anti-reflection coating and diffusion layers. [14] [15] Another approach, which claims to avoid damage to the cell at temperatures greater than 450 °C, is liberation of the laminate components by chemical dissolution of the EVA using *O*-dichlorobenzene, in combination with ultrasonic irradiation to speed up the dissolution time from 7 days to 30 minutes. [15]

Emerging strategies for silicon wafer recycling may come from the hydrometallurgical techniques used to recycle batteries, and from the physical chemistry approaches of surfactant-based emulsions for delamination of the silicon wafer laminate.

7 CONCLUSIONS

The silicon wafer carries most of the embedded energy and environmental impact associated with producing a PV module. Therefore, it is conceivable that it will eventually be desirable, also in terms of cost, to recycle them (either as feedstock, wafer, or even cell) in the next decades when the volumes of PV waste increase. The cost, materials depletion and risks associated with the production of silver, copper and tin prioritize their recovery for reuse. An outlook on the emerging possibilities for dismantling a PV module is mentioned.

8 ACKNOWLEDGEMENTS

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8 REFERENCES

[1] European Commission, "DIRECTIVE 2012/19/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL on waste electrical and electronic equipment (WEEE)of 4 July 2012," 24 July 2012. [Online]. Available: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2012:197:0038:0071:EN:PDF. [Accessed 20 September 2013].

[2] C. Olson, "In the balance: the social costs and benefits of PV," *Photovoltaics International,* 2013.

[3] S. Huber , M. K. Moe, N. Schmidbauer, G. H. Hansen and D. Herzke, "Emissions from incineration of fluoropolymer materials," 12 2009. [Online]. Available: http://www.nilu.no/Publikasjoner/tabid/62/ctl/PublicationDetails/mid/764/publicationid/24739/language/en-GB/Default.aspx. [Accessed 20 September 2013].

[4] European Commission, "The Waste Incineration Directive," 30 11 2012. [Online]. Available: http://ec.europa.eu/environment/air/pollutants/stationary/wid/legislation.htm. [Accessed 22 September 2013].

[5] R. Michaelson, "The PV race to replace silver," pv magazine, 15 August 2011. [Online]. Available: http://www.pv-magazine.com/news/details/beitrag/the-pv-race-to-replace-silver_100003885/#axzz2fRAmjLpu. [Accessed 20 September 2013].

[6] E. Goossens, "Silver surge makes headwind for solar in fossil fuel rivalry," Bloomberg, 23 June 2011. [Online]. Available: http://www.bloomberg.com/news/2011-06-22/silver-surge-makes-headwind-for-solar-in-fossil-fuel-rivalry.html. [Accessed 20 September 2013].

[7] European Photovoltaic Industry Association (EPIA), "Global Market Outlook for Photovoltaics 2013-2017," 8 May 2013. [Online]. Available: http://www.epia.org/news/publications/global-market-outlook-for-photovoltaics-2013-2017/. [Accessed 4 August 2013].

[8] Step. Initiative, "What is e-waste?," Step Initiative - Solving the e-waste problem, 2013. [Online]. Available: http://www.step-initiative.org/index.php/Initiative_WhatIsEwaste.html. [Accessed 22 Spetember 2013].

[9] B. Reck and T. Graedel, "Challenges in Metal Recycling," *Science,* vol. 337, p. 690, 2012.

[10] EU, "Critical raw materials," European Commission, 2011. [Online]. Available: http://ec.europa.eu/enterprise/policies/raw-materials/critical/. [Accessed 22 September 2013].

[11] NREL, "Rationale for the Silicon Wafer Replacement Tool," NREL, February 2012. [Online]. Available: http://www.nrel.gov/pv/pdil/swr_rationale.html. [Accessed 22 September 2013].

[12] E. P. Platform, "Strategic Resarch Agenda," 5 September 2011. [Online]. Available: http://www.eupvplatform.org/publications/strategic-research-agenda-implementation-plan.html. [Accessed 22 September 2013].

[13] S. E. I. I. (SEII), "Solar Europe Industry Initiative Plan 2013-2015," 22 May 2013. [Online]. Available: http://www.epia.org/fileadmin/user_upload/News/SEII_IP__2013-2015___22_May_2013.pdf. [Accessed 22 September 2013].

[14] E. Klugmann-Radziemska, "Current trends in recycling of Photovoltaic solar cells and modules waste," *Chem Didact Ecol metrol,* vol. 17, no. 1-2, pp. 89-95, 2012.

[15] T.-Y. Wang, J.-C. Hsiao and C.-H. Du, "Recycling of Materials from Silicon Base Solar Cell Module," *IEEE,* no. 978-1-4673-0066-7, pp. 2355-2358, 2011.

[16] Y. Kim and J. Lee, "Dissolution of ethylene vinyl acetate in crystalline silicon PV modules using ultrasonic irradiation and organic solvent," *Solar Energy Materials & Solar Cells,* vol. 98, pp. 317-322, 2012.