

LEAD-FREE PV MODULES: INDUSTRIAL REALIZATION AND EVALUATION OF ENVIRONMENTAL IMPACT

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ABSTRACT: With the large amount of photovoltaic (PV) modules required for a more renewable energy sector, strategies to avoid the toxic material lead, which is still present in most conventional modules today, becomes more and more relevant. This work presents the result of the government-funded research project “BermUDa”, in which the industrial realization and environmental impact of lead-free modules was investigated. The herein chosen approach was to directly replace lead-containing module materials (namely metallization paste and solder cell connectors) with lead-free alternatives, while leaving the industrial production process as unchanged as possible. For this, a large number of pre-processed silicon wafers underwent cell (PERC) and module production, where the processability was tested and compared with conventional lead-containing materials. Subsequently, the performance of the products (cells and PV modules) was tested and compared in terms of electrical performance and reliability in power measurements and accelerated aging tests, respectively. The project thereby demonstrated the feasibility to work with lead-free technologies and adapt currently established industrial processes to produce completely lead-free PV modules that can compete with their lead-containing counterparts in terms of sustainability and costs (LCOE). The work also suggests focus on cell metallization pastes, driven by future market demand, to develop lead-free pastes that can achieve better fine line printing capabilities to allow greater flexibility when converting an existing production line to produce lead-free PV modules.

Keywords: Sustainable, Ribbons, LCA, Lead-free, Lead, Bismuth, Cell interconnection, Metallization

1. INTRODUCTION

For c-Si photovoltaic (PV) modules, lead is a common material contained in cell metallization pastes and as solder material in cell connectors: Our estimations yield that a conventional PV module typically contains around 8-10 g/m² of lead. Although PV modules are currently exempt from the European “Restriction of Hazardous Substances Directive” (RoHS[1]), a restriction of the use of lead is currently discussed on different regulatory levels, e.g., as part of the EU-ecodesign guidelines.

Although the approach to replace lead with alternative materials while retaining conventional industry processes is not completely new, few sources for a study on the feasibility and sensibility, as well as the resulting environmental effects are available. It is, however, crucial for policy makers and module manufacturers alike to evaluate the current situation and determine, how easy a lead-free PV module production is realizable and which steps are necessary to react on a respective regulation in the future.

The herein chosen approach of the research project was to adapt the “state-of-the-art” module and cell manufacturing processes do make them lead-free. For this, the lead-containing materials in the screen printing and soldering process were replaced with lead-free alternatives to develop a “green” RoHS-compliant solar module. To ease the transition and minimize costs, solutions compatible with established industrial production lines are investigated

For this, 4500 pre-processed silicon wafers underwent cell production tests in the backend line of Fraunhofer ISE PV-TEC in which the screen printing properties of lead-free silver-based front side metallization pastes and the electrical properties of the resulting cells were investigated and compared to conventional lead-containing pastes. Subsequently, the produced cells underwent soldering tests on an industrial stringer, using lead-free ribbons. The applicable temperature window for soldering was determined as well as the mechanical stability of the joints.

Subsequently, the produced PV modules were tested and compared in terms of electrical performance and

reliability by power measurements at STC and accelerated aging tests, respectively.

Furthermore, sustainability and economic aspects of lead-free materials were investigated in life-cycle-assessment (LCA) and a cost analysis, respectively. The LCA particularly focused on a comparison of the environmental impact of the lead-free materials and the different allocation methods for the co-products lead and bismuth. The LCA was supported by leaching experiments, which determined the heavy metal concentration leaching out of PV modules in a simulated worst-case end-of-life scenario.

2. METHODS

2.1. Cell Metallization

Throughout the project, around 4500 passivated emitter and rear solar cells (PERC) were processed in the backend line of Fraunhofer ISE PV-TEC. We used two types of industrially pre-fabricated p-type Czochralski-grown silicon (Cz-Si) PERC precursors with rear side passivation and SiN_x anti-reflection coating on the front side and a n-type emitter with a nominal sheet resistance of $R_{sh1} \approx 100 \Omega/\text{sq}$ (type 1) and $R_{sh2} \approx 120 \Omega/\text{sq}$ (type 2). The rear side was metallized with silver (Ag) pads and surrounding full area aluminum (Al) metallization on the fully automatic Asys XH-2 screen printing lines at Fraunhofer ISE PV-TEC. On the front side, an H-pattern grid consisting of 100 fingers and 5 busbars was applied, using commercially available lead-free and lead-containing Ag paste as a reference. Throughout the project, 9 different lead-containing and lead-free Ag and Al pastes for front and rear side metallization were tested.

2.2. Cell Interconnection and Reliability

For cell interconnection, an industrial stringer was used to operate at comparable condition with respect to an industrial cell production. The stringer used was the TT1800 of *teamtechnik* that uses IR light as primary heat source for the soldering process. We compared three different lead-free solder alloys with one lead-containing reference. The solder alloys were used as coatings of 0.9 mm × 0.22 mm copper ribbons, to interconnect solar cells

with five busbars.

The herein presented solar cells with a lead containing cell metallization and a lead-free cell metallization were used (s. Section 2.1), as well as commercially available solar cells.

To find an optimal process window for interconnection of each solder alloy, the temperatures within the stringing process (IR radiation & hotplates) were varied. For each solder alloy, three adapted temperature profiles were used. Additionally, a fourth temperature profile, representing the standard soldering process for Sn60Pb40, was tested.

For each parameter set, 90° peel tests of the solder joints were performed on a peel testing machine of *Zwick Roell*. Due to the tapered busbar design of the front side, the measured values at the soldering pads were evaluated. Same for the rear side, only the maximum achieved peel force for each solder pad was used as value for the analysis.

In addition, 3-cell-strings were made to build small-scale modules to perform the temperature cycling test. A further cell was used to investigate the solder alloys in terms of optical behavior (effective width measurement), and microscopic examinations namely cross sections and imaging as well as SEM/EDX measurement to investigate the solder joint in detail. For the best interconnection parameters, full size modules (1700 mm × 1000 mm, 60 full cells each) were manufactured for accelerated aging tests according to IEC 61215-2:2016.

2.3. Sustainability and Cost Assessment

The study was modelled in the LCA software Umberto LCA+. For the life cycle inventory data, it was ensured that corresponding data from upstream processes are available in the Ecoinvent database. The scope of investigation was defined according to ISO 14040: The product system under investigation was an industrially manufactured lead-free Cz PERC module. The functional unit was –in accordance with PEFCE and PVPS– 1 kWh of electrical energy. The lifetime for a standard module was assumed to be 30 years with an annual power degradation of 0.7 %.

A cradle-to-grave analysis was performed to map the environmental impacts of the module from production through use to end-of-life. The focus of the actual analysis was primarily on the toxicity-related impact categories such as human toxicity, acidification and eutrophication. It has to be mentioned that especially the results from toxicity-related impact categories showed a higher uncertainty than for example the CO₂ footprint. The USEtox model in particular is considered to be particularly reliable and was therefore selected for the analysis. For the LCA three different leaching scenarios were considered: a) groundwater contamination, b) agricultural soil contamination and c) contamination of soils used for other purposes.

The cost analysis was carried out using the Total Cost of Ownership (TCO) model developed at Fraunhofer ISE [2] and extended for the lead-free PERC modules to be developed in this work. Cross-cutting cost analyses were carried out across the value-added stages of cell, module and system. A monofacial p-type Cz M6 wafer 60-cell PERC module (reference) was compared with a lead-free PERC module (reference). with a lead-free PERC module.

3. RESULTS AND DISCUSSION

3.1. Cell Metallization

During several printing pre-tests, it was found that the selected lead-free paste did not perform equally well as the conventional lead-containing paste with respect to the printability of fine lines. While the lead-containing paste was able to print contact fingers down to a nominal finger width of $w_n = 33 \mu\text{m}$, the lead-free paste was limited to $w_n = 40 \mu\text{m}$ (status 2019). Furthermore, depending on the fine line printing capability and contacting behavior of the metallization paste, the efficiency of the lead-free cells could be up to 0.3 %_{abs.} lower compared with the lead-containing reference.

It is assumed that the fine line printing performance of lead-containing silver pastes is generally on a higher level due to a substantially higher market demand and thus R&D activities for the optimization of lead-containing pastes. An increasing market demand regarding lead-free pastes will probably enable further paste development activities in order to achieve a comparable fine line printing capability of lead-free pastes.

After several pre-tests, an optimal configuration regarding pastes, screens and printing/firing process was selected to metallize the required large number of solar cells for interconnection and module integration.

3.2. Cell Interconnection and Reliability

A cross comparison of lead-free and lead-containing cell metallization with lead-free and lead-containing solder alloys was carried out at Fraunhofer ISE Module-TEC. We compared three different lead-free solder alloys (thus three different melting temperatures), namely Sn42Bi58, Sn60Bi40 and Ecosol, with the leaded reference Sn60Pb40.

The evaluation of the 90° peel tests showed that the weakest interface of the leaded cell group was always the interface between metallization paste and silicon wafer. The metallization stuck to the ribbon and was separated from the solar cell (s. Figure 1 a). This result correlates well to previous findings, published by other researcher [3–5], highlighting the necessity to optimize metallization and interconnection hand-in-hand. In comparison, for the commercial reference cell, a cohesive fracture within the metallization was observed. The lead-free cell metallization showed a mixed fracture pattern (s. Figure 1 b): cohesive within the metallization paste as well as adhesive between busbar and wafer, or even rupture of silicon pieces from the wafer.

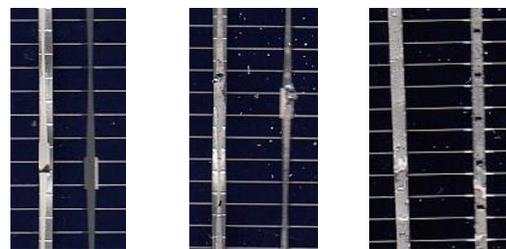


Figure 1: Top view images of the fracture pattern of leaded cell metallization (left), lead-free cell metallization (middle) and commercial reference cell (right).

These findings cannot be generalized for all combinations of metallization pastes and solder alloys, since only two different metallization pastes in combination with one type of precursor was tested. However, the most important finding is that lead-free metallization pastes can be contacted by soldering, resulting in a joint that is comparably stable as for

established lead-containing materials.

The peel forces measured on commercial solar cells in combination with the different solder alloys are presented in Figure 2. Our results show that lead-free solder alloys have the potential to perform at the same level as a lead-containing solder alloy or even above. Regarding mechanical stability directly after soldering, lead-free solder alloys can easily replace lead-containing solder alloys. The achieved peel forces reached > 1 N/mm for a broad range of process parameters and remained the same as for a common lead-containing alloy.

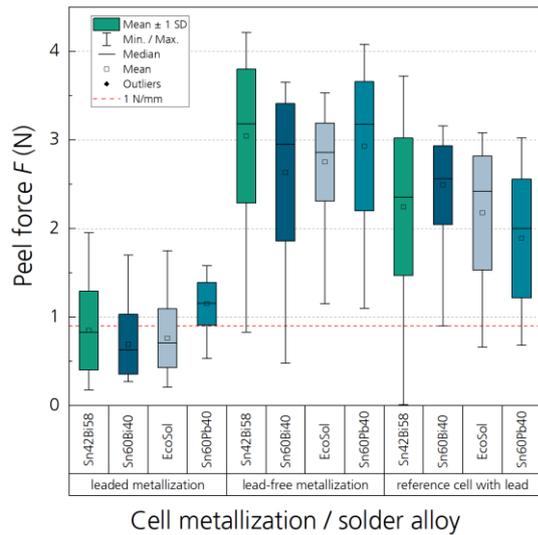


Figure 2: Measured 90° peel forces of the cell front side after soldering. For the group with lead-containing paste, the achieved peel forces were limited by the weak cell/metallization interface. The results show that lead-free pastes (middle) can operate on a comparable or even higher level to lead-containing pastes.

Some of the soldered strings were used to prepare metallographic cross sections for microscopy analysis. With SEM and EDX characterization, an intermetallic Ag_3Sn phase was observed (s. Figure 3 right), confirming a successful solder joint formation with SnBi solder.

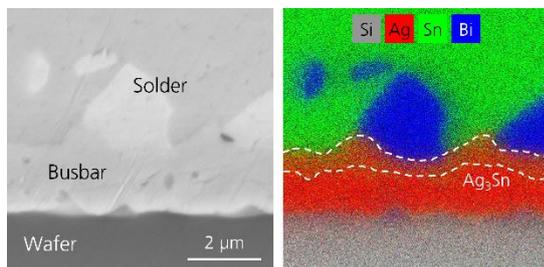


Figure 3: SEM and EDX images of a cross section of a lead-free solder joint. An Ag_3Sn phase is formed at the interface between solder and Ag metallization.

To further evaluate the technologies, reliability tests with the focus on thermal cycling were carried out on small-scale modules with a wide range of soldering conditions and material combinations, including lead-free and -containing metallization and solder, respectively, with a focus on resistance against thermomechanical stress (not shown). Based on these experiments 60-cell modules were produced, characterized in terms of I - V -parameters and electroluminescence imaging. The group achieving the best average value in terms of P_{MPP} was a lead-free

group.

The reliability of the produced modules was demonstrated in accelerated aging tests according to IEC 61215. Full-size lead-free modules passed the criteria for damp heat, thermal cycling and combined UV/TC/HF tests with a good margin to the pass-fail criterion of -5% relative P_{MPP} loss, which is typical for state of the art modules [6].

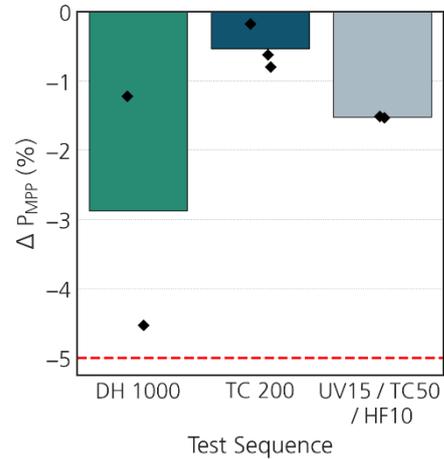


Figure 4: Power loss of lead-free modules after reliability tests according to IEC 61215-2:2016. The modules pass the tests with a good margin to the pass-fail criterion (-5%).

3.3. Sustainability and Cost Assessment

A comparative LCA was performed for both module variants. For the analysis of the lead-free module, the lead, was replaced by bismuth in a mass ratio of one-to-one. Since no production or emission data for bismuth is available in the common LCA databases (e.g. GaBi or ecoinvent), it was modelled as a co-product of lead production according to literature [7, 8]. Different approaches for allocation (economic, physical) were used in a sensitivity analysis. The life cycle impact results for the indicators climate change, toxicity, eutrophication, acidification, ozone depletion and photochemical oxidation show a difference of $< 1\%$ for cell as well as module production in all impact categories. Furthermore, literature suggests that the life cycle impact of bismuth may be worse in some categories than that of lead, since additional processing steps can be required for both production and recycling [7]. Since bismuth is often a by-product of lead mining, increased demand for bismuth could additionally increase the amount of lead mined.

However, our analysis also shows the toxicity of possible lead leaching into different soils, which may well be possible due to improper end-of-life storage in countries without a proper end-of-life treatment scheme in place [9]. Experimental leaching tests, into different solutions like simulated ground water or acidic rain, in simulated end-of-life scenarios were performed during the project, which showed a lower tendency of bismuth to leach out compared to lead. Additionally, less leaching was observed for modules after aging. Bismuth is also considered a critical, possibly rare resource for terawatt-scale PV expansion [10].

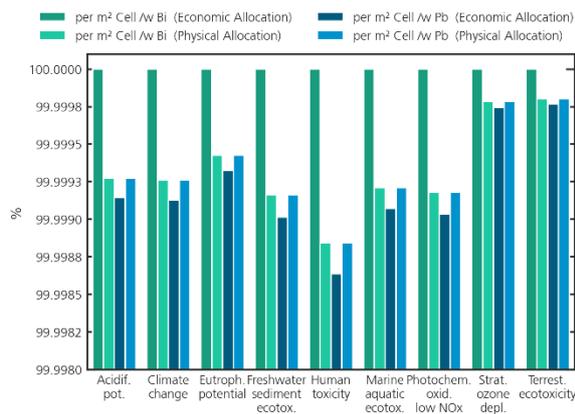


Figure 5: Life-cycle assessment of lead-containing and lead-free solar cells across different categories.

In conclusion, bismuth does not necessarily perform better as an alternative to lead in PV production, when considering the whole value chain. Nevertheless, lead, in contrast to Bismuth, has been shown to be toxic to humans and the environment when released into the environment.

In the Total Cost of Ownership (TCO) analysis, cross-cutting cost analyses were carried out across the value-added stages of cell, module, and system. Overall, the lead-free variant and the lead-containing reference differ only slightly, *i.e.*, < 0.5 % for absolute module production costs and < 1 % for electricity production costs at Freiburg, even if the module efficiency of the lead-free variant is assumed < 0.3 %_{abs.} lower than the leaded reference.

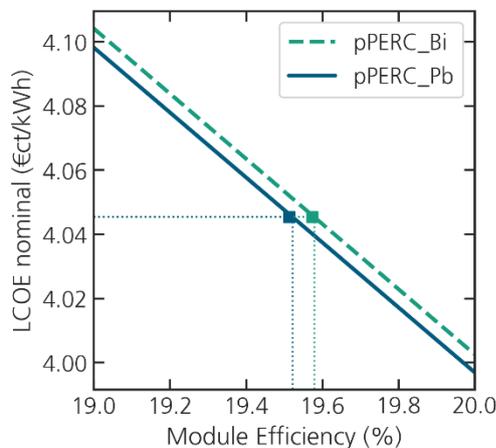


Figure 6: Sensitivity analysis of the influence of module efficiency on the LCOE at the Freiburg site

4. CONCLUSION AND OUTLOOK

This project investigated and evaluated the feasibility of producing lead-free PV modules using state-of-the-art production techniques such as screen printing and solder interconnection. To this end, nine different lead-containing and lead-free Ag and Al pastes for front and rear side metallization as well as four different solder alloys for cell interconnection were tested.

On cell level, the processability and printing properties of the lead-free metallization pastes required a relatively large finger thickness and showed slightly reduced efficiencies in some cases. An increasing market demand regarding lead-free pastes will probably enable further paste development activities in order to achieve a

comparable fine line printing capability of lead-free pastes.

Concerning the cell interconnection, peel tests demonstrated that lead-free solder alloys can replace conventional alloys. Furthermore, they allow variations in soldering temperatures which can be beneficial for temperature-sensitive next-generation cell technologies like heterojunction [11, 12] or perovskite-Si-tandem [13].

As demonstrated on 60-cell PV modules, the power and reliability of lead-free modules was comparable and the modules passed critical accelerated aging tests.

The LCA showed that using bismuth is not necessarily better than lead in terms of environmental impacts. Further studies need to be done due to the availability of other lead-free soldering methods, which also do not contain bismuth. It is important to identify other soldering metals regarding the environmental aspect which can be than test in modules.

Besides the investigated technologies, there are already PV module products on the market, that are intrinsically lead-free, *e.g.* based on silicon heterojunction [14, 15] or IBC cells.

Furthermore, there exist new alternative metallization and interconnection concepts, *e.g.* plating [16] and conductive adhesives [17] respectively. These approaches are more complex to implement into an existing production line but are under continuous development and can be a viable alternative to achieve lead-free and sustainable PV modules. An in-depth comparison of different technological options is under development.

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5. REFERENCES

- [1] *Restriction of the use of certain hazardous substances, Directive 2011/65/EU: RoHS*, 2011. [Online]. Available: <http://data.europa.eu/eli/dir/2011/65/oj>
- [2] S. Nold, Fraunhofer-Institut für Solare Energiesysteme -ISE-, Freiburg, Albert-Ludwigs-Universität Freiburg, Technische Fakultät, E. R. Weber, and S. W. Glunz, “Techno-ökonomische Bewertung neuer Produktionstechnologien entlang der Photovoltaik-Wertschöpfungskette. Modell zur Analyse der Total Cost of Ownership von Photovoltaik-Technologien,” Stuttgart: Fraunhofer Verlag, Stuttgart.
- [3] A. De Rose, D. Erath, T. Geipel, A. Kraft, and U. Eitner, “Low-temperature soldering for the interconnection of silicon heterojunction solar cells,” in *Proceedings of the 33rd European Photovoltaic Solar Energy Conference and Exhibition (EU PVSEC)*, Amsterdam, Netherlands, 2017, pp. 710–714.
- [4] D. Güldali and A. De Rose, “Material Joint Analysis of Lead-Free Interconnection Technologies for Silicon Photovoltaics,” in *45th International Spring Seminar on Electronics Technology (ISSE)*, 2022. [Online]. Available: <https://ieeexplore.ieee.org/document/9812798>
- [5] T. Geipel, D. Eberlein, and A. Kraft, “Lead-free solders for ribbon interconnection of crystalline silicon PERC solar cells with infrared soldering,”

- in *AIP Conference Proceedings 2156*, Konstanz, 2019, p. 20015.
- [6] P. Gebhardt, G. Mühlhofer, A. Roth, and D. Philipp, "Statistical analysis of 12 years of standardized accelerated aging in photovoltaic-module certification tests," *Prog. Photovolt: Res. Appl.*, 2021, doi: 10.1002/pip.3450.
- [7] Umweltbundesamt, *ProBas Datensatz Wismut*. Projektorientierte Basisdaten für Umweltmanagement-Instrumente. [Online]. Available: <http://www.probas.umweltbundesamt.de/php/prozessdetails.php?id={7FB2B6A5-43ED-4A2F-8866-F2E6A8126C68}>
- [8] T. Ibn-Mohammed *et al.*, "Life cycle assessment and environmental profile evaluation of lead-free piezoelectrics in comparison with lead zirconate titanate," *Journal of the European Ceramic Society*, vol. 38, no. 15, pp. 4922–4938, 2018, doi: 10.1016/j.jeurceramsoc.2018.06.044.
- [9] P. Sinha and A. Wade, "Comment on "Long-term leaching of photovoltaic modules"," *Jpn. J. Appl. Phys.*, vol. 57, no. 1, p. 19101, 2018, doi: 10.7567/JJAP.57.019101.
- [10] L. Bongartz, S. Shammugam, E. Gervais, and T. Schlegl, "Multidimensional criticality assessment of metal requirements for lithium-ion batteries in electric vehicles and stationary storage applications in Germany by 2050," *Journal of Cleaner Production*, vol. 292, p. 126056, 2021, doi: 10.1016/j.jclepro.2021.126056.
- [11] B. A. Korevaar, J. A. Fronheiser, X. Zhang, L. M. Fedor, and T. R. Tolliver, "Influence of annealing on performance for hetero-junction a-Si/c-Si devices," in *Proceedings of the 23rd European Photovoltaic Solar Energy Conference and Exhibition*, Valencia, Spain, 2008, pp. 1859–1862.
- [12] S. De Wolf, A. Descoedres, Z. C. Holman, and C. Ballif, "High-efficiency Silicon Heterojunction Solar Cells: A Review," *Green*, vol. 2, no. 1, pp. 7–24, 2012, doi: 10.1515/green-2011-0018.
- [13] M. de Bastiani, M. Babics, E. Aydin, A. S. Subbiah, L. Xu, and S. de Wolf, "All Set for Efficient and Reliable Perovskite/Silicon Tandem Photovoltaic Modules?," *Solar RRL*, vol. 6, no. 3, p. 2100493, 2022, doi: 10.1002/solr.202100493.
- [14] A. Schneider, *Meyer Burger opens high tech module factory in Freiberg, Germany*, 2021. Accessed: Sep. 7 2022. [Online]. Available: <https://www.meyerburger.com/de/newsroom/artikel/meyer-burger-eroeffnet-hightech-solarmodulfabrik-in-freiberg>
- [15] A. Schulze, *Another green check for the lead-free REC Alpha Pure: Certified as a Low Carbon Footprint solar panel*. Munich, 2022. [Online]. Available: <https://www.recgroup.com/en/news/another-green-check-lead-free1-rec-alpha-pure-certified-low-carbon-footprint-solar-panel>
- [16] B. Grübel *et al.*, "Progress of plated metallization for industrial bifacial TOPCon silicon solar cells," *Prog. Photovolt: Res. Appl.*, 2021, doi: 10.1002/pip.3528.
- [17] L. P. Bauermann *et al.*, "Qualification of conductive adhesives for photovoltaic application - accelerated ageing tests," *Enrgy Proced.*, vol. 124, pp. 554–559, 2017, doi: 10.1016/j.egypro.2017.09.266.