Separation of semiconductor layers from thin film solar panels using microwave radiation

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Abstract

Being the two most promising thin film solar cells, the production of Cadmium Telluride (CdTe)- and Copper Indium Gallium Diselenide (CIGS)-panels registered continuous growth in the last years. Although having a lower efficiency than conventional solar cells, the degree of automation during the production of thin film panels lead to their success on the market. These types of panels consist of light absorbing semi-conductors, which are deposited on a glass substrate using chemical bath (CBD) or chemical vapor deposition (CVD).

With rising production rates and the associated growing demand for Gallium, Indium and Tellurium for the semiconductor layers, the aspect of recycling becomes evident. Current recycling processes for the solar industry imply a hydrometallurgical treatment of the panels, which leads to consumption of different acids and chemicals. In this paper, a process for the separation of semiconductor layers based on microwave technology is presented, which is currently under investigation at IME, RWTH Aachen University in close cooperation with Accurec Recycling GmbH.

Introduction

With new laws promoting the development of renewable energy sources and new technologies for the energy sector, the global demand for technology materials is changing. Being one of the most promising renewable energy sources, the solar industry market experienced a strong growth over the last years. Beside silicon based photovoltaic modules (mono- and polycrystalline), Cadmium-Telluride (CdTe) and Copper-Indium-(Gallium)-Diselenide (CIS or CIGS, see Figure 1) based panels emerged as two popular technologies because of their relatively low manufacturing costs and acceptable yields.

With continuously rising production rates, the demand for critical materials like Tellurium, Indium and Gallium is growing. In addition to this, the life time cycle of a thin film solar panel does not exceed 20-30 years, which will lead to a strong increase of scrap amounts in the next decades. As a consequence, the European Union enhanced the WEEE directive committing the solar panel manufacturers to establish a Union wide recycling system. [1]

Glass	4000 µm
Encapsulation	700 µm
ZnO:Al	0,3 - 1 µm
i-ZnO	0,05 - 0,1 µm
CdS or ZnS	0,05 µm
CIGS [$Cu(In,Ga)Se_2$, $CuInS_2$]	1,5-2,5 µm
Mo	0,3 - 0,4 µm
Glass	3000 µm

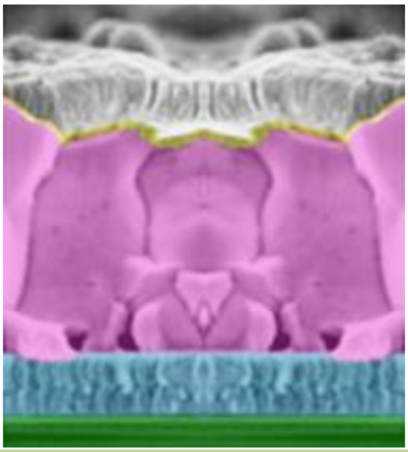

Figure 1: Exemplary composition of a CIGS thin film solar cell [2]

In the past years, several recycling processes for photovoltaic modules were developed, as presented in Table 1. Main challenge is to process this kind of material selectively, since the semiconductor layer thickness is in the range of 1 – 7 microns [2][3]. Thus, up to now, separation of thin film panel components (CdTe, CIS and CIGS) always implies one or more hydrometallurgical steps like leeching and subsequent precipitation of the semiconductor layers.

In this paper, a high temperature microwave assisted separation of the functional layers from the float glass is presented and discussed.

Table 1: Recycling processes for photovoltaic cells [2]

Company	**Sunicon**	**Solarcycle**	**First Solar**	**Loser Chemie**	**Saperatec**	**Lobbe**	**Reiling**
Module Types	Crystalline Si	Crystalline Si, CIS, CIGS	CdTe	CIS,CIGS, CdTe	CIS, CIGS, CdTe	Crystalline Si, CIS, CIGS, CdTe	Crystalline Si
Used Technology	Combination of thermic physical and chemical processing steps	Combination of thermic physical and chemical processing steps	Grinding, Combination of dry and wet processing	Delamination, chemical processing of semiconductor layers	Delamination and separation of semiconductor layers using tensides	Kombination aus Kälteschockversprödung und chem.-physik. Behandlung	Mechanical treatment and sorting

Fundamentals

Microwaves (MW) are electromagnetic waves which cover frequencies from 300 MHz to 300 GHz with corresponding wavelengths from λ =1 mm to 1 m. Since Microwaves follow the laws of optics, they can be transmitted, absorbed or reflected by matter. [3] Although developed for military use (radar, communication), MWs find a broad band of application as heating technology in different industries.
In principle, the heating effect is based on the interaction of the electric and magnetic field with the material to be heated. The electric field causes a polarization effect, i.e. an interfacial or dipolar polarization. [4] These dipoles, however, are "unable" to meet the rapidly changing electric field and generate heat. The magnetic field has been given no contribution to the warming in the past. However, this is contradicted by recent studies. In fact, metals can be heated and even melted by microwave radiation. Unlike in dielectrics, the penetration depth of the microwave in most metals is only a few microns, which can be explained by the skin effect. The magnetic field causes eddy currents, which lead to a joule heating of the material. [4]. These interactions between microwaves and metals were confirmed by several studies. [6][7][8][9]

Experimental

Goal of the presented work in this paper is to study the influence of MW radiation on the removal of the semiconductor layers from CIGS solar panels. As stated before, thin film solar modules consist of thin functional metal and semiconductor layers which are deposited on glass. Since glass is transparent for microwaves, most of the absorbed energy will be dissipated as heat in the thin layers.
The experimental work took place in a controlled atmosphere microwave unit (constructed by Fricke und Mallah Microwave Technology GmbH), which allows to run processes under high-vacuum or inert gases. The test chamber of 650 mm diameter has the capability to handle batches in kilogram-scale. The microwave unit is equipped with eight radial positioned magnetrons (microwave generators) of 6 kW each to provide on-line adjustable power of max. 48 kW. The process is observed by in situ video camera, temperature measures are monitored by an lR-camera placed on the top of the furnace. This allows the study of heat distribution across the complete surface of the charged material. The microwave unit is controlled by a custom designed LabVIEW Software. As input material, CIGS panel fragments were used, which were detached from adhering organics (encapsulation material), since they would otherwise interfere with the process. Batches of approximately 5 kg were charged into a calcium silicate container, which is transparent for microwaves and heat resistant up to 1200 °C (Figure 2). The conducted trials were performed using different power levels and times. During the experiments, local hotspots on the samples’ surface were measured. Furthermore, flashes of light were noticed both on the surface of the samples and in the reaction chamber which are caused be exceeding the breakdown voltage of the present gas and subsequent plasma formation.

Figure 3 shows an exemplary result of a microwave treatment after 120 sec under atmospheric conditions, which reveals clear changes in the surface color.

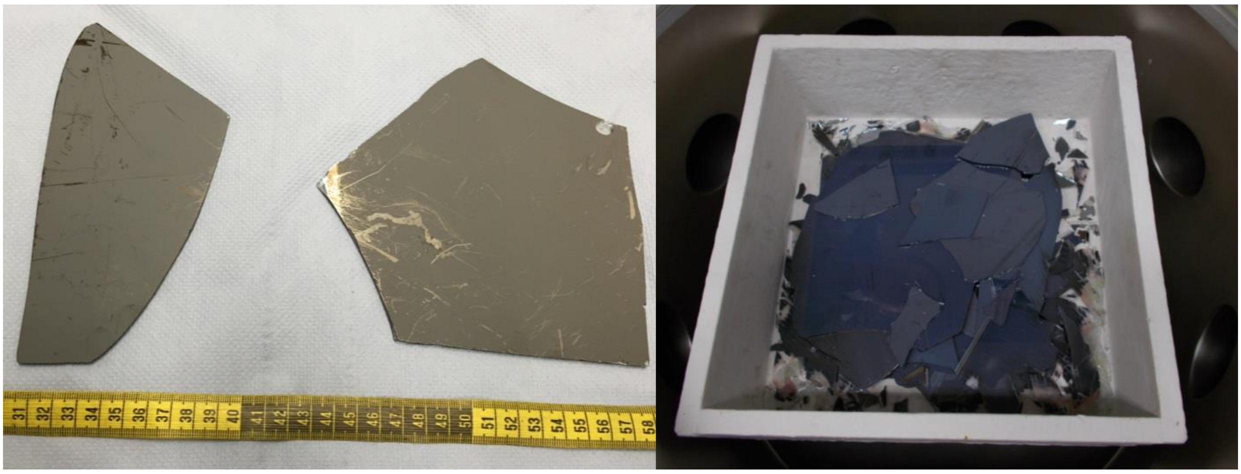

Figure 2: Used CIGS Panel fragments (left), charge in calcium silicate container (right)

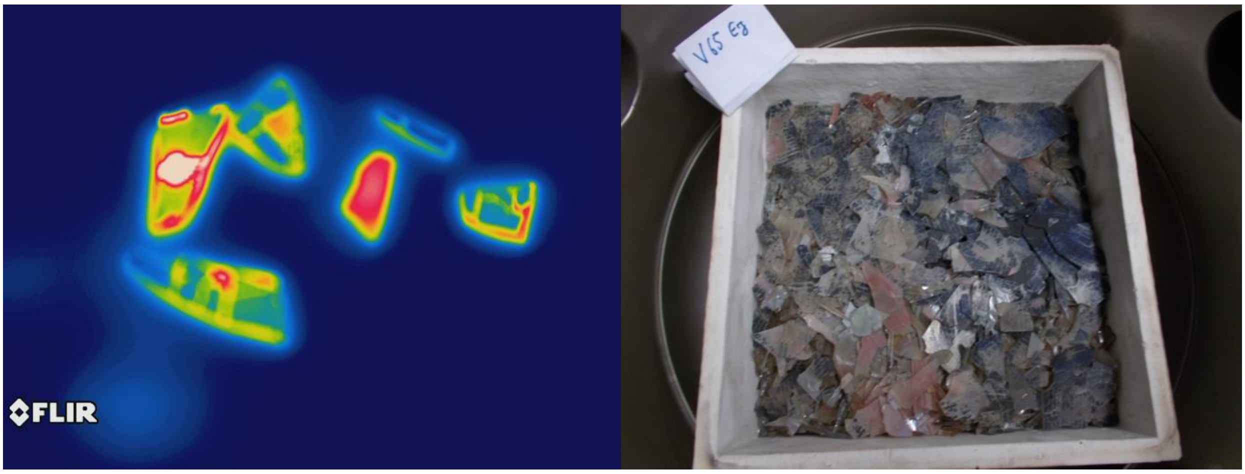

Figure 3: Thermal image of CIGS panel fragments (left), whole batch (right) directly after microwave treatment

The obtained samples were ground using a planetary ball mill to powder with a grain size of less than 90 microns and analyzed by XRF for their chemical composition. Additional SEM/EDX was performed on selected samples for detailed investigation of the semiconductor layers.

Results and Discussion

The conducted experiments show a large scatter in terms of the removal of semiconductor layers, which is mainly due to the inhomogeneous temperature distribution in the reactor. While maximum surface temperatures of 350 °C depending on the power were measured in the center, panel fragments were melted in the edges of the batch. Figure 4 shows different CIGS panel fragments from the same batch after microwave treatment. Some sample parts seem unaffected by microwave radiation, whereas the sample in the bottom left of Figure 4 became transparent. The needed high temperatures for the melting of the glass were achieved by plasma arcing on the sample surface. This plasma arcing also caused a removal of the surface layers in the so called laser scribes of the panels. Laser scribes are grooves on the panel surface, which are cut during the production process of solar panels. This effect can be seen in the center top sample in Figure 4.
In all trials microwave treatment lead to shattering of the samples, most probably due to local hotspots as displayed in Figure 3. A complete removal of the surface layers was not achieved. In general, higher MW-generator powers and longer process times lead, obviously, to a faster change in the surface nature with a higher proportion of transparent panel fragments.

Figure 4: Selected CIGS Panels after microwave treatment

Table 2 shows the results of the XRF analysis. Since the samples inevitably have to be processed with the float glass, the concentrations of the surface layer materials are displayed as trace elements. In comparison to the input material, three sample types after microwave treatment were analyzed, which exhibited different color modifications on the surface. While most elements remain unaffected, the concentrations of Cu and Se are lower, the more transparent the sample is.

Table 2: Trace elements concentration of CIGS material before and after microwave treatment

	Cu ppm	Ga ppm	In ppm	Se ppm	Mo ppm	Sn ppm	Zn ppm
CIGS (input)	**311**	**62**	**250**	**364**	**288**	**36**	**10**
CIGS (brown)	**320**	**46**	**190**	**144**	**282**	**39**	**12**
CIGS (red)	**218**	**68**	**240**	**8**	**269**	**39**	**10**
CIGS (transparent)	**152**	**49**	**160**	**8**	**285**	**37**	**10**

Figures 5 to 8 show SEM images and corresponding EDX analyses of a panel sample before and after microwave treatment (latter corresponds to a CIGS red sample in the table above). While the original panel consists of clearly separated layers with Cu, In, Ga and Se as main elements in the top layer, the surface morphology changes after microwave irradiation. Copper, Selenium and Gallium are not detectable, the major elements on the surface are Molybdenum and Indium.

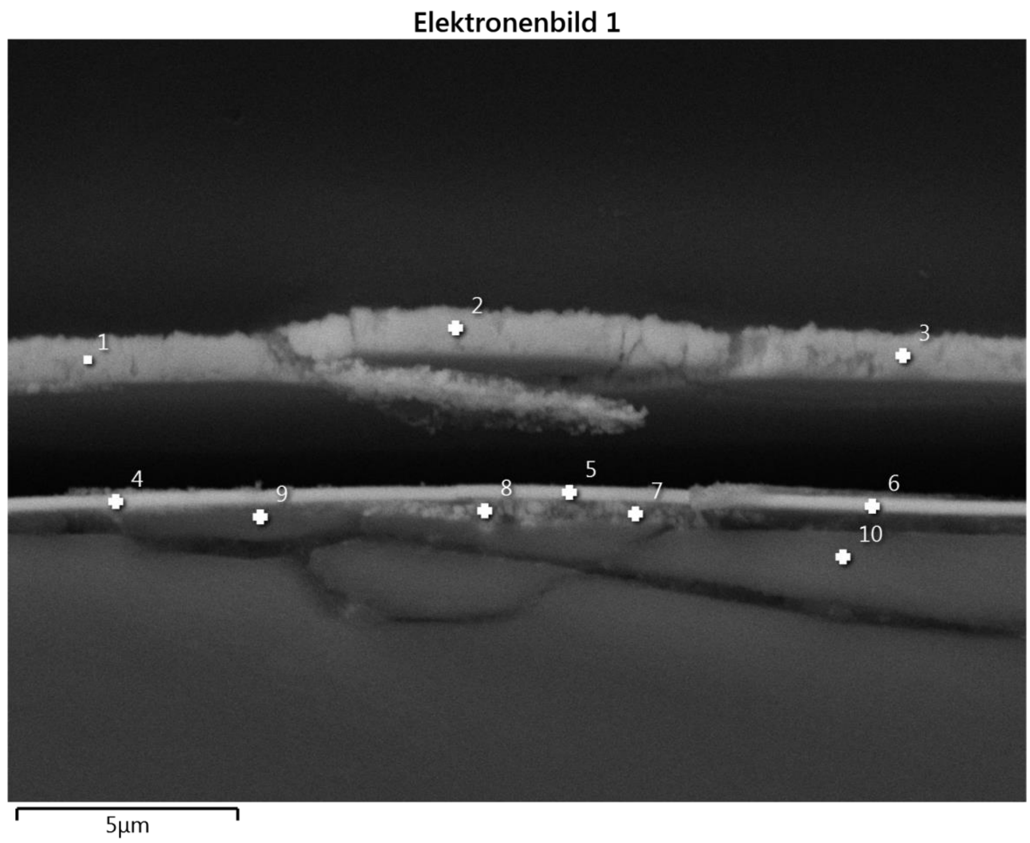

Figure 5: SEM image of a CIGS panel before microwave irradiation

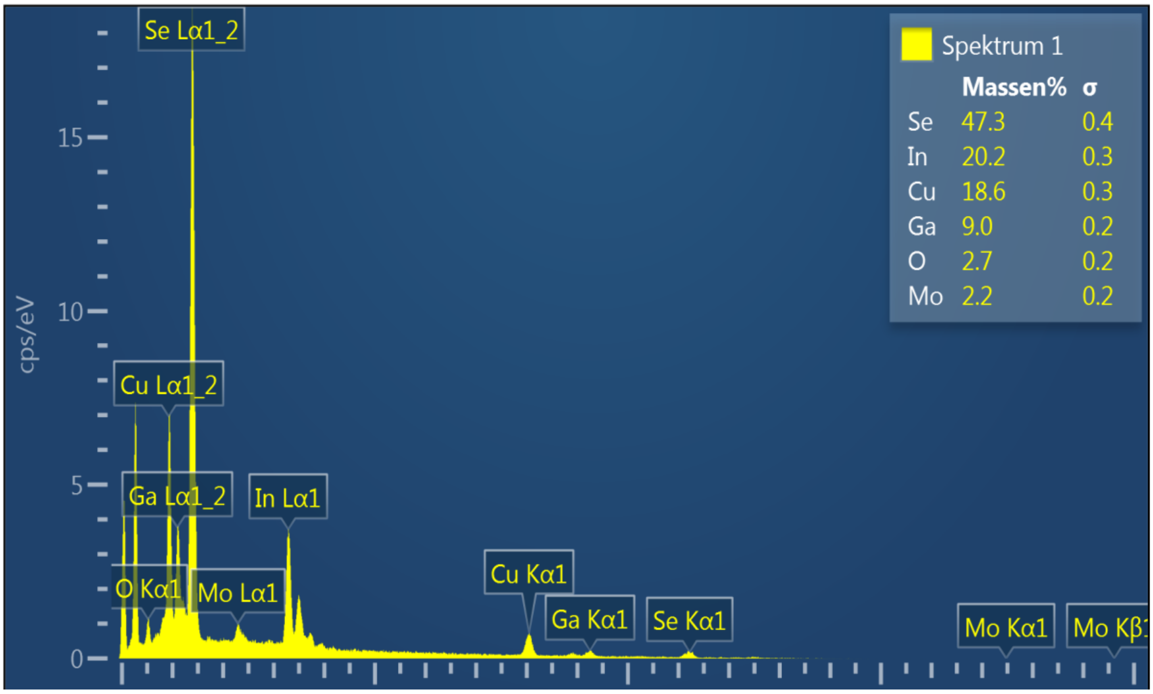

Figure 6: EDX analysis of a CIGS panel before microwave irradiation

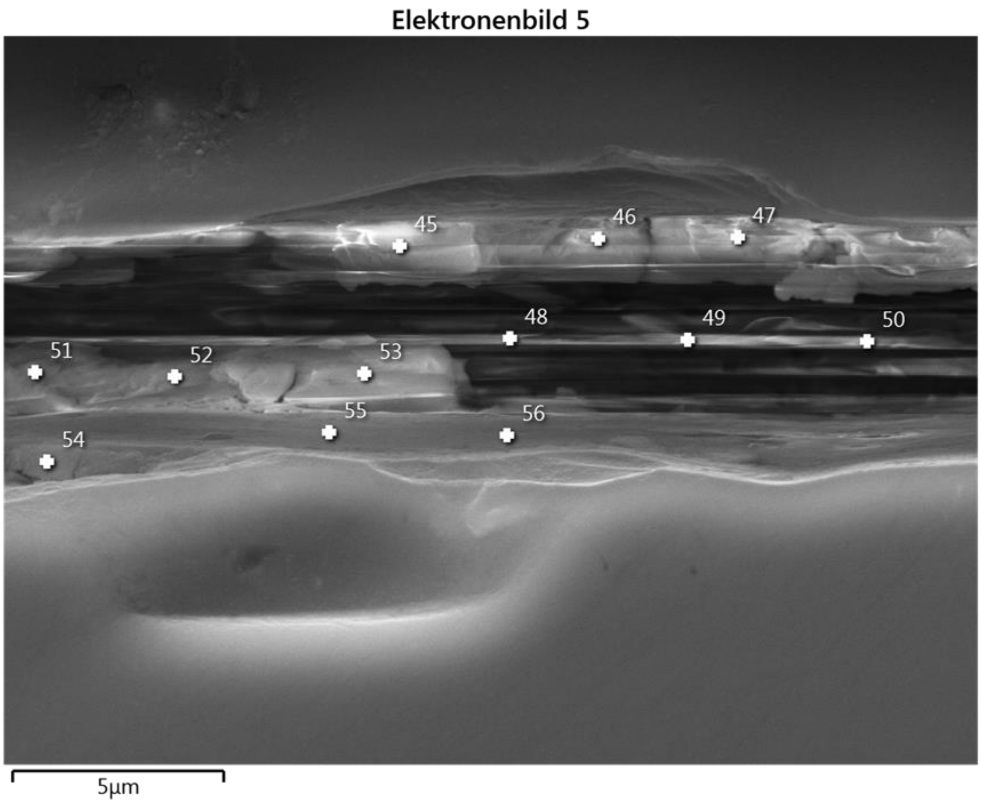

Figure 7: SEM image of a CIGS panel after microwave irradiation

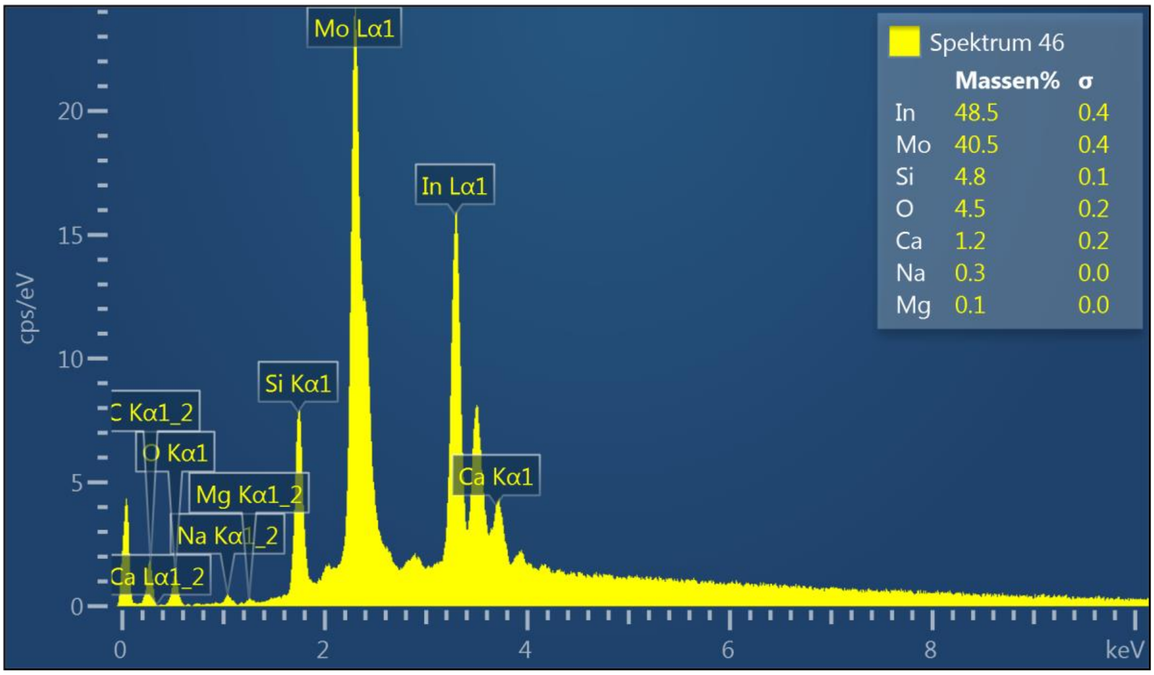

Figure 8: EDX analysis of a CIGS panel after microwave irradiation

Conclusions

In the present study, the influence of microwave irradiation on the separation of semiconductor layers from CIGS (copper indium gallium diselenide) thin film solar panels was investigated. Experiments show, that the microwave-material interactions are strongly dependent on the field distribution in the reactor chamber. In general, the removal of semiconductor layers can be lead back mainly on plasma formation and the corresponding high temperatures on the sample surface. Both XRF and EDX analyses show, that the Copper and Selenium contents in the surface layers are significantly lower or in the case of EDX not detectable. This has to be proofed in additional trials. A full removal of the layers could not be achieved.

In further studies, trials under vacuum will be conducted in order to eliminate the plasma formation and to study the direct influence of microwave irradiation on the material.

Acknowledgements

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