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CHEMICAL, THERMAL AND LASER PROCESSES IN RECYCLING OF PHOTOVOLTAIC SILICON SOLAR CELLS AND MODULES

OBRÓBKA CHEMICZNA, TERMICZNA ORAZ LASEROWA W RECYKLINGU OGNIW I MODUŁÓW FOTOWOLTAICZNYCH Z KRYSTALICZNEGO KRZEMU

Abstract: In recent years, photovoltaic power generation systems have been gaining unprecedented attention as an environmentally beneficial method to solve the energy problem. From the economic point of view the pure silicon, which can be recapture from the used cells, is the most important material due to its cost and shortage. In the paper selected methods of used or damaged module and cells recycling and experimental results are presented. Advantages and disadvantages of these techniques are described, what could be helpful during the optimization of the method. The recycling process of PV module consists of two main steps: separation of cells and its refining. During the first step cells are separated due to the thermal or chemical methods usage. Next, the separated cells are refining. During this process useless layers are removed: antireflection, metallization and p-n junction layer, for silicon base - ready to the next use - gaining. This refining step was realized with the use of chemical and laser treatment as well.

Keywords: recycling, solar energy, silicon, photovoltaic solar cells, renewable energy

Production of photovoltaic modules on a commercial scale dates back to 1980's. PV module manufacturers provide a work warranty of 20-30 years, so modules produced back in the 1980's should be put out of commission and recycled during this decade, while modules manufactured in 2000 should be recycled by 2030. A particularly difficult task is developing an optimal technology of recycling and covering its high investment costs. This question is especially interesting because of the market's demand on silicon for PV cell production and - consequently - the need for its recycling.

This paper covers selected methods of recycling used or destroyed PV modules and photovoltaic cells and practical experiments results with chemical, thermal and laser

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recycling methods. Advantages and disadvantages of these methods, helpful in optimizing the recycling process for commercial use, were described.

PV recycling process requires two main stages:

- ***PV solar cell separation***. In this process, cells that are part of the commercial PV modules have been separated as a result of thermal or chemical processes;
- ***cleaning the surface of PV solar cells***. In this process, silicon solar cells separated from the PV modules underwent a process of purification, in which unwanted layers were removed (antireflection layer, metallization and a p-n semiconductor) - it was possible to recover the silicon substrate suitable for reuse. Stage surface cleaning of silicon PV cells was carried out using chemical and laser techniques.

Separation of silicon solar cells from damaged or used PV modules

In PV module production process, a predetermined number of silicon cells is hermetized with the use of such materials as EVA copolymer, Tedlar®, glass. The PV cell hermetization aims to secure it from harmful effects of atmospheric conditions or from mechanical damaging. EVA copolymer hermetiziation is done through covering both sides of cells with the polymer, while Tedlar® is used only on the bottom surface. Additionally, the front of a PV module is covered with glass (Fig. 1).

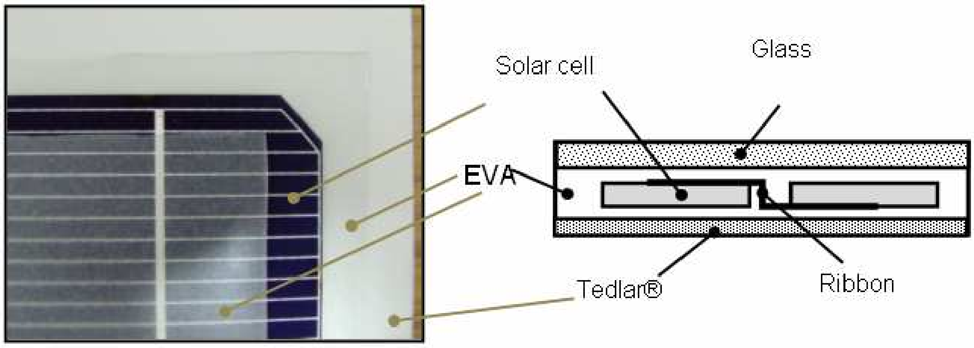

Fig. 1. Encapsulation of PV cells

In order to recycle silicon cells from damaged PV modules, it is required to introduce the delamination process [1]. In this process, the EVA is removed and materials such as glass, Tedlar, aluminum frame, steel, copper, and plastics are separated. Properties of the EVA copolymer have been thoroughly analyzed in paper [2]. The delamination process was conducted through two methods:

- Chemical treatment;
- Thermal treatment.

Chemical treatment in PV module recycling

As a result of the conducted chemical delamination with tetrahydrofurane (THF) (Fig. 2) it was possible to separate the materials from a damaged PV module.

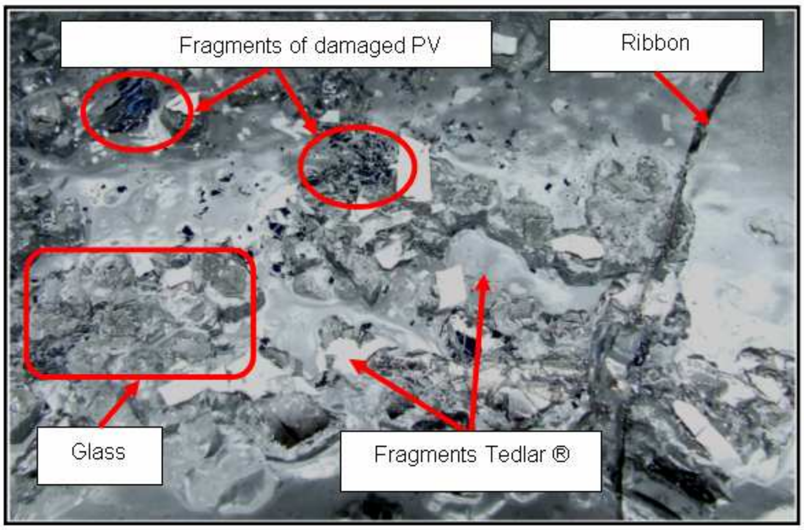

Fig. 2. The process of the removing of PV cell encapsulation using THF

The efficiency of the used method of chemical treatment was insufficient. Too long period of time needed for achieving satisfying results, in conjunction with a fairly high price of the solvent used, does not justify the use of this method for commercial PV cell and module recycling purposes. That is why, thermal treatment was proposed and investigated.

Thermal treatment in PV module recycling

In order to separate silicon photovoltaic cells from a damaged PV module, the module was placed in a SiO_2 bed which then was heated, to increase its temperature in time (Fig. 3).

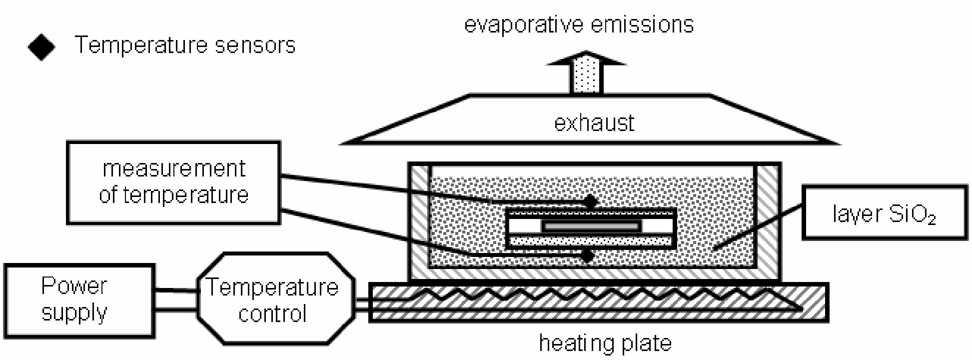

Fig. 3. The stand-up for the photovoltaic module lamination removing

In comparison to chemical treatment, the duriaton of the process is significantly shorter, also the problem of spent solvent does not occur. However, a disadvantage of thermal treatment is the emission of gas during EVA copolymer thermal degradation.

Nevertheless, this method, taking into account its simplicity and high efficiency, may be used in commercial PV recycling installations.

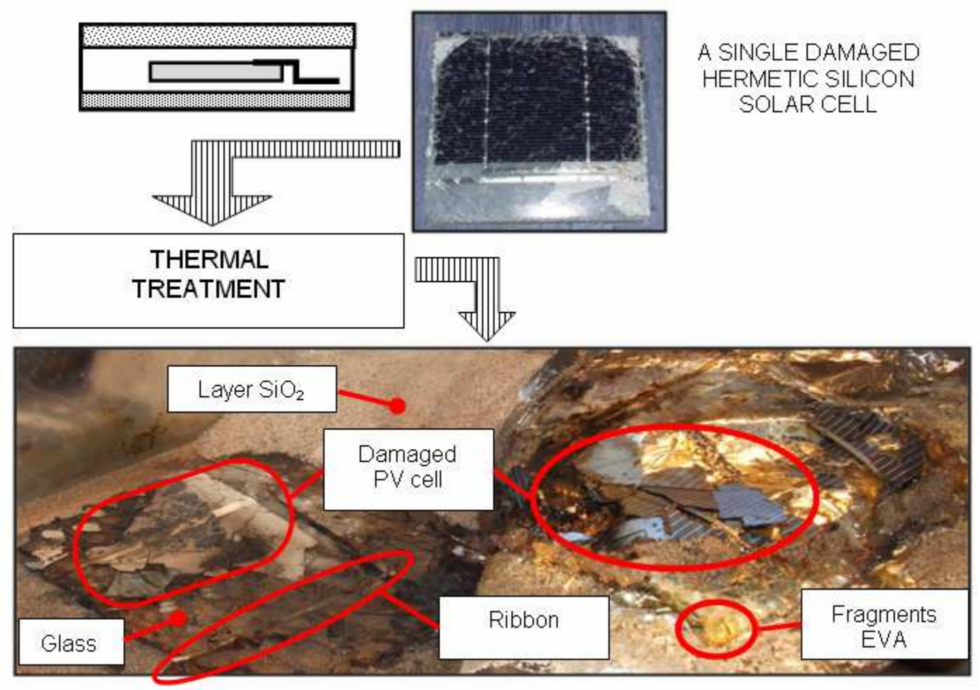

Fig. 4. The process of thermal removing of PV module encapsulation

When comparing chemical treatment with thermal treatment, it was found that for the delamination process, thermal treatment is a far more convenient method to use. With a moderate energetic cost, it is possible to obtain better process effectiveness. On the other hand, chemical treatment effectiveness is fairly low, the process lasts for a longer period of time, which additionally decreases effectiveness. The price of chemical compounds used, because of their type as well as their quantities, is high. Additional costs of waste solution disposal must also be taken into account in case of chemical treatment.

Surface purification of PV modules

Another stage of PV cell and module recycling - after cell separation - is the recovery of pure silicon. In order to extract the silicon base from exploited, obsolete or damaged PV cells, two methods were introduced: chemical treatment and laser surface cleaning.

Chemical treatment of silicon-based PV cells

After separating the cells from PV modules, in order to recover pure silicon, different layers of material, put on in the production process, must be removed in specific order: frontal metallization, bottom metallization, antireflective coating and n-p junction connector. A chemical process of removing different layer, needed for recovering the silicon bed, was designed (Fig. 5).

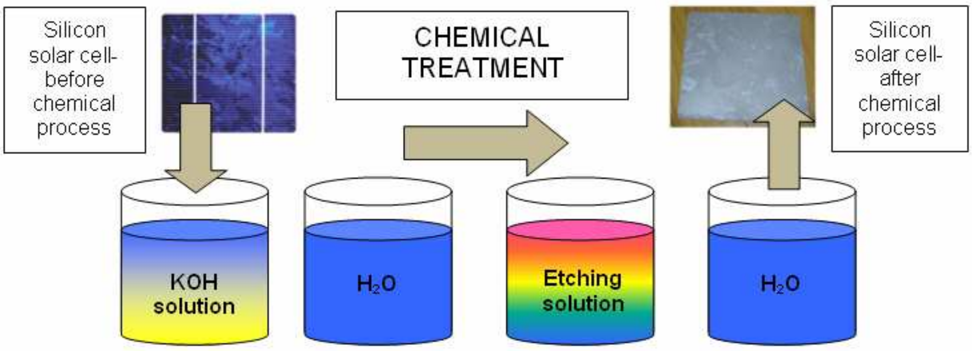

Fig. 5. Recovery of silicon base from the damaged PV cells

The main problem is choosing the proper composition of etching solutions, its concentration and optimal process temperature.

The application of laser technique for PV cell surface purification

Two types of PV cells were chosen for experiments - the samples for unnecessary layer removal originated from mono- and polycrystalline photovoltaic cells (Fig. 6).

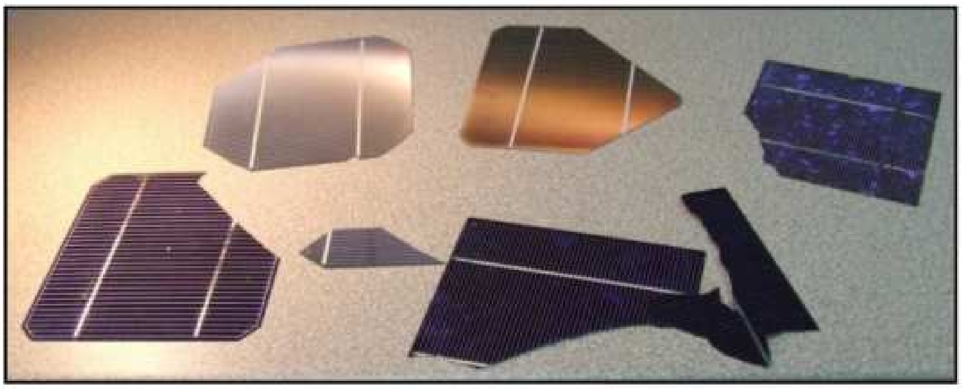

Fig. 6. Selected samples for the surface cleaning with the use of laser

The experiments were carried out with the use of neodymium impulse laser (wavelength λ = 1064 nm) Nd:YAG (*Yttrium-Aluminum-Garnet*), frequency up to 120 Hz, beam energy of 300 mJ per impulse, with 10 ns long impulses. It was possible to remove the aluminum bottom metallization and the antireflective coating from the PV cells. (Figs 7 and 8).

Fig. 7. Removing the ARC layer from PV cells using laser technology

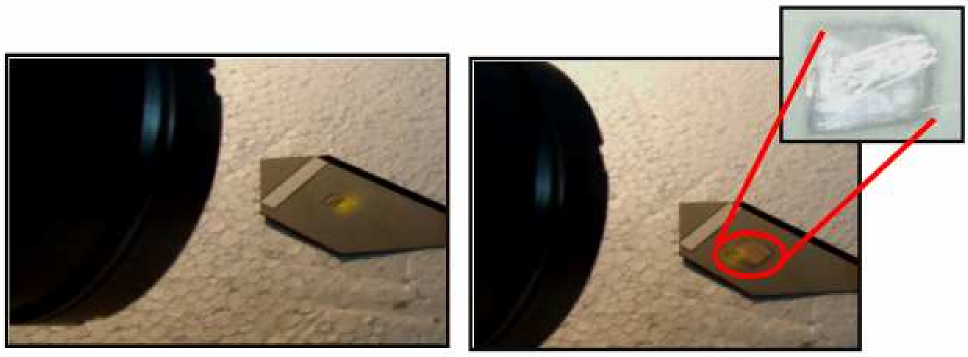

Fig. 8. Removing the back metallization from the PV cells, using laser technology

When comparing the methods used, it was determined that chemical treatment is far more advantageous. Because of the laser method's high price and low effectiveness, it is essential to further improve and optimize chemical methods of removing unwanted layers from PV cells. An estimated time of removing layers with the use of laser method is about 1 min/cm^2.

When utilizing chemical treatment, it is possible to purify the whole cell's surface during that time. For chemical purification, the following etching solutions may be applied: $HF/HNO_3/H_2O$, $H_2SiF_6/HNO_3/H_2O$ or $H_2SiF_6/HNO_3/C_2H_4O_2$ [3-5].

Conclusion

The reason for conducting experimental work described in this paper was the effort to solve a more and more important problem of recycling obsolete, damaged or exploited PV devices with a minimal impact on the environment and with acquiring ecologically as well as economically worthy results.

The results of PV cell separation processes and unwanted layer removal processes, in order to recover pure silicon, show that recycling of PV modules is possible.

Separation of cells from damaged PV modules through chemical treatment is not economically worthwhile, a far more better solution is to use thermal treatment. Also, the implementation of laser techniques in unwanted layer removal stage, in comparison with chemical treatment, is also disadvantageous. An optimal solution is to use thermal treatment for cell separation and chemical treatment for removing the metallization, contacts, antireflective coating and the n-p junction.

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Abstrakt: W ostatnich latach systemy fotowoltaiczne stają się bardzo popularne na całym świecie jako korzystne dla środowiska rozwiązanie problemów energetycznych. Zagadnienie zagospodarowania zużytych elementów systemów fotowoltaicznych, których ilość w przyszłości może być znaczna, nie zostało do tej pory opracowane. Konieczne jest znalezienie optymalnej metody recyklingu i ponownego wykorzystania wycofanych z użycia elementów składowych systemów PV. W artykule przedstawiono wybrane sposoby prowadzenia recyklingu zużytych lub uszkodzonych modułów i ogniw fotowoltaicznych oraz praktyczne wyniki prac eksperymentalnych z wykorzystaniem metod: chemicznych, termicznych oraz techniki laserowej. Opisano wady i zalety stosowanych technik, pomocne przy optymalizowaniu metody recyklingu dla zastosowań komercyjnych. Proces recyklingu modułów PV wymaga zastosowania dwóch zasadniczych etapów: separacji ogniw PV i oczyszczania ich powierzchni. W procesie separacji ogniwa - wchodzące w skład modułu PV - zostają rozdzielone w efekcie zastosowania procesów termicznych lub chemicznych. W następnej fazie ogniwa poddaje się procesowi, w którym usuwa się niepożądane warstwy: antyrefleksyjną, metalizację oraz złącze n-p, aby uzyskać podłoże krzemowe, nadające się do powtórnego zastosowania. Etap oczyszczania powierzchni krzemowych ogniw PV realizowano z zastosowaniem obróbki chemicznej oraz techniki laserowej.

Słowa kluczowe: ogniwa fotowoltaiczne, krzem, recykling, energia słoneczna, odnawialne źródła energii