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CHEMICAL TREATMENT OF CRYSTALLINE SILICON SOLAR CELLS AS A MAIN STAGE OF PV MODULES RECYCLING

OBRÓBKA CHEMICZNA KRZEMOWYCH OGNIW SŁONECZNYCH JAKO NAJWAŻNIEJSZY ETAP W RECYKLINGU MODUŁÓW FOTOWOLTAICZNYCH

Abstract: In recent years, photovoltaic systems have gained worldwide recognition and popularity as a environmentally friendly way of solving energetic problems. However, a problem of utilizing worn out photovoltaic systems, amount of which will rapidly increase in the future, is yet to be solved. Establishing a technology of recycling and reusing obsolete photovoltaic panels is a necessity. Photovoltaic modules of crystalline silicon solar cells are made of the following elements, in order of increasing mass: glass, aluminum frame, EVA copolymer transparent hermetizing layer, photovoltaic cells, installation box, Tedlar protective foil and assembly bolts. From an economic point of view, taking into account the price and supply level, pure silicon, which can be recycled from PV cells, is the most valuable building material used. A way of utilizing obsolete and out-of-use photovoltaic silicon cells has been presented. Because of a high quality requirement for silicon obtained, chemical processing is the most important stage of recycling process. Conditions for chemical treatment need to be precisely adjusted in order to achieve the required purity level of recycled silicon. For crystalline silicon based PV systems, a series of etching processes has been performed on, in order: electric connectors, ARC and *n-p* junction layer. The compositions of etching solutions were individually adjusted for different silicon cell types. Efforts were taken to formulate a universal etching solution composition, yet the results showed that a solution modification is required for different types of PV cells.

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

In recent years, photovoltaic systems have gained worldwide recognition and popularity as an environmentally friendly way of solving energetic problems. However, a problem of utilizing worn out photovoltaic systems, amount of which will rapidly increase in the future, is yet to be solved. Establishing a technology of recycling and reusing obsolete photovoltaic panels is a necessity. Photovoltaic modules in crystalline silicon solar cells are made of the following elements, in order of increasing mass: glass, aluminum frame, EVA copolymer transparent hermetizing layer, photovoltaic cells,

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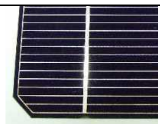
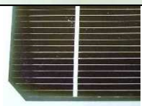
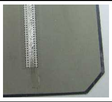
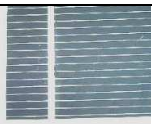
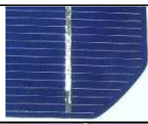
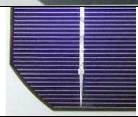
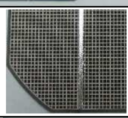
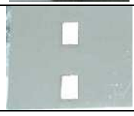
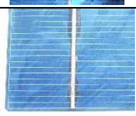
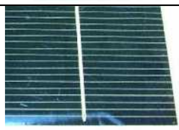
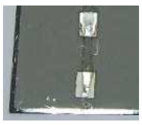
installation box, Tedlar protective foil and assembly bolts. From an economic point of view, taking into account the price and supply level, pure silicon, which can be recycled from PV cells, is the most valuable building material used. Several solar cells from different manufacturers were tested (Tab. 1).

Table 1

Tested silicon solar cells from different manufacturers

Sample	Cell Fragment		Cell Type	Thickness [μm]	Size a x b [mm]
	Front	Back			
1			Monocrystalline	345	125x125
2			Monocrystalline	295	125x125
3			Monocrystalline	545	125x125
4			Monocrystalline	235	125x125
5			Monocrystalline	340	125x125
6			Monocrystalline	275	125x125
7			Polycrystalline	356	125x125
8			Polycrystalline	395	125x125
9			Polycrystalline	250	125x125
10			Polycrystalline	300	105x105

Crystalline silicon photovoltaic cells are produced as plates of 200÷500 μm thickness and in sizes: 100 x 100 mm^2, 125 x 125 mm^2 or 150 x 150 mm^2. On the frontal surface of these plates, through the process of atomic diffusion of phosphorus, an *n-p* semiconductor layer is created, on which an anti-reflective coating (ARC) is applied. In the next phase of the production process, two electrodes made of aluminum and/or silver paste are created on the plate front and back side [1].

Recycling of crystalline silicon photovoltaic cells and modules

The PV module production process involves laminating single cells (after the creation of *n-p* connector layer) and mounting in aluminum frames. That is why the recycling process requires disassembling the modules according to the flow chart shown in Figure 1.

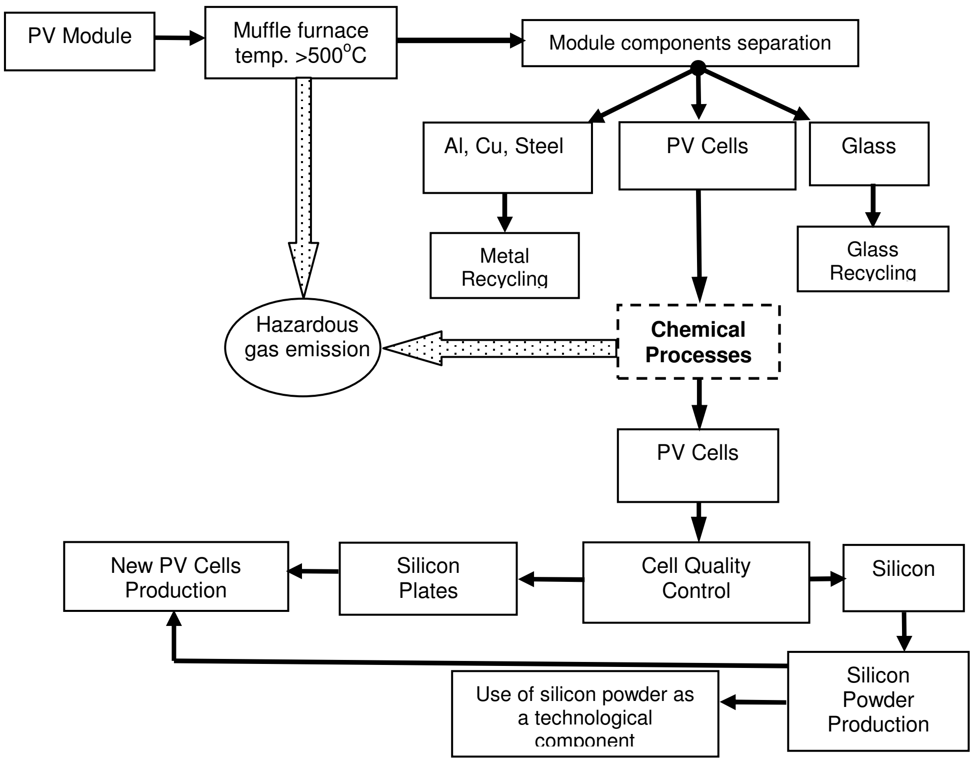


Fig. 1. Thermal and chemical processes involved in crystalline cell and module recycling

A thermal process allowing fast, simple and economically efficient module part disassembling is the first stage of PV module recycling. Firstly, the EVA-laminated cells (EVA - Ethylene-Vinyl Acetate copolymer) are separated. Tests with chemical EVA layer removal have been conducted. Results of these tests show that thermal separation is, from an economical and ecological point of view, a more favorable alternative, when compared with chemical processes, requiring the use of expensive and toxic agents.

The second primary process carried out in PV module recycling is the solar cell chemical treatment. In order to reacquire the silicon powder or plates, available for use in new photovoltaic cell production, the removal of metal electrodes, AR coating and *n-p* connector layer is required. These operations may be performed through dissolving in acid or base solutions. Röver's team research experience on cell texturization with $HF/HNO_3/H_2O$ mixture [2] has been acknowledged in this research.

Identification of materials used in silicon PV cell production

Over 90% of all PV cells are silicon-based. Depending on the manufacturing technology - monocrystalline, polycrystalline and, rarely, amorphous cells are produced.

Several types of PV cells manufactured by different producers and distinguished by the type of ARC and electric contact material applied, are available on the market. Frontal electrodes are most commonly made out of silver, while the ones placed on the cell's back surface are frequently additionally covered with an aluminum thin layer.

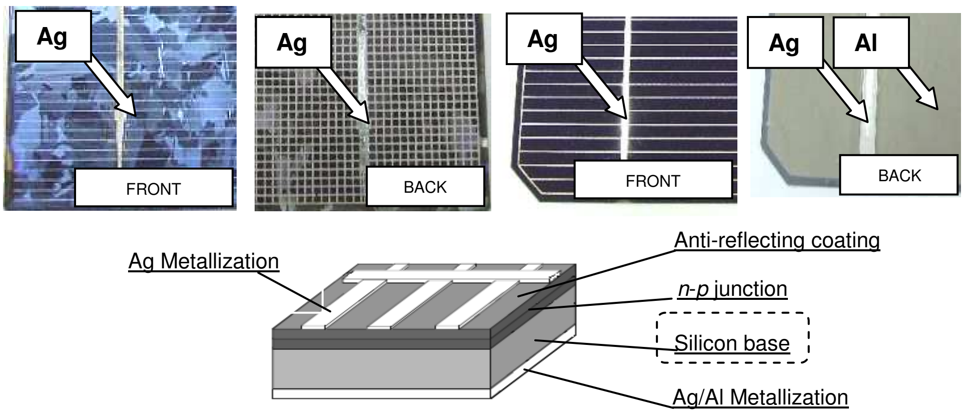


Fig. 2. Types of materials used in the production of PV cells process

Because of the high value of light reflection index for silicon (33÷54%), a layer decreasing that value needs to be adopted - that is why the frontal surface of the cell is covered with an anti-reflection layer, which changes the color of the cell (usually it becomes blue). AR coatings are made from substances such as:

- Ta_2O_5 - tantalum pentoxide;
- TiO_2 - titanium dioxide;
- SiO - silicon monoxide;
- SiO_2 - silicon dioxide;
- Si_3N_4 - silicon nitride;
- Al_2O_3 - aluminium oxide;
- ITO (*Indium-Tin-Oxide*) - Tin doped In_2O_3.

The best results are achieved when multiple coatings are applied, eg a combination of zinc sulfide (ZnS) and magnesium fluoride (MgF_2). Furthermore, trace amounts of soldering alloys (Sn/Pb) are present.

Recycling of silicon base from spent or damaged PV cells

To allow the recycling of the silicon base from PV cells, a chemical process for removing different layers from the cell's surface has been developed (Fig. 3).

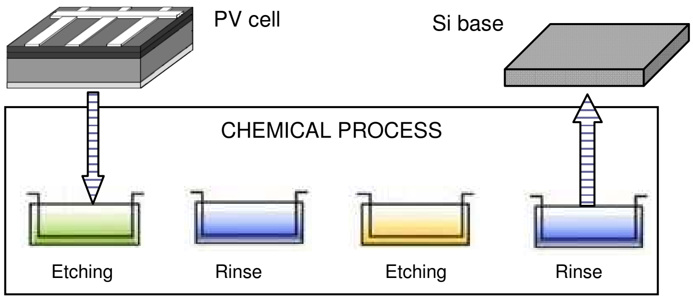


Fig. 3. Recovery of the silicon base from the silicon PV cells

The main problem is choosing the suitable composition and concentration of the etching solution as well as the optimal temperature range for the chemical reaction.

Base solution etching - removing the Al metallization

In order to remove the Al layer from the cell's back surface, an aqueous solution of KOH has been utilized (Fig. 4).

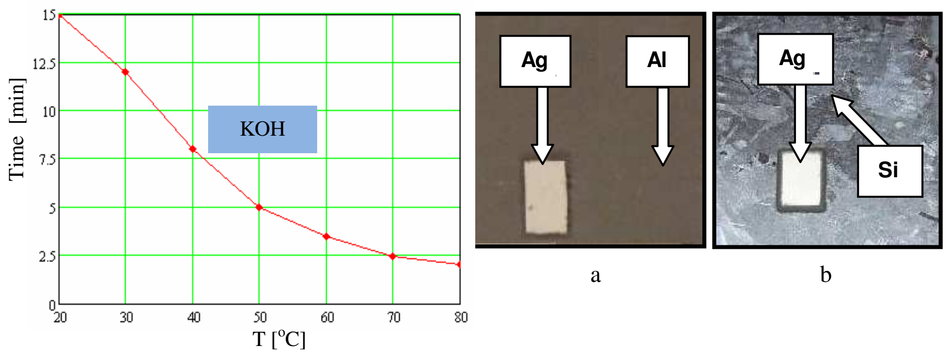


Fig. 4. Temperature dependence of the back metallization removing rate and picture of the solar cell before (a) and after (b) removal of the back metallization with potassium hydroxide

Having in mind that the electric contacts in a majority of produced PV cells are made of Ag, it is possible to dissolve those elements in nitric acid.

Acid etching - removing the AR coating and the n-p junction

Two types of mixtures: $H_2SiF_6/HNO_3/CH_3COOH$ and $H_2SiF_6/HNO_3/H_2O$ have been tested for ARC and *n-p* junction removal.

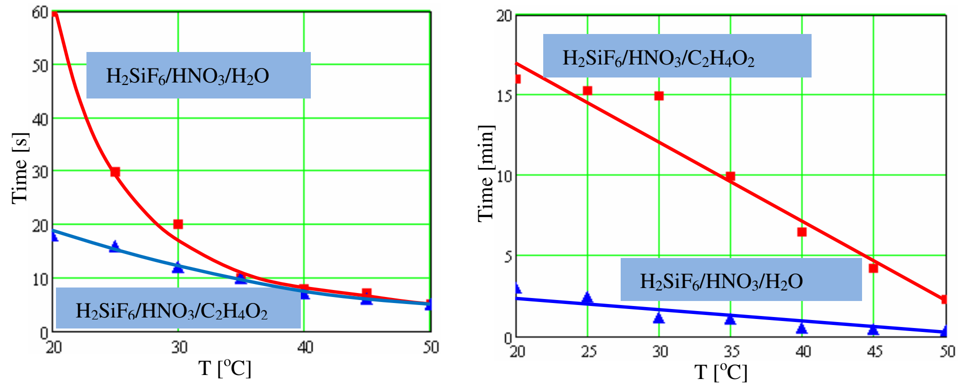


Fig. 5. Temperature dependence of the ARC and n-p junction/metallization removing rate

The process of removing the *n-p* semiconductor junction was carried out until the dissolution of diffusion layer occurred, with simultaneous control of sheet resistance R_s [Ω/□] (Ohm by square) with a four-point probe (Fig. 6). The term ohms/square is used because it gives the resistance in ohms of current passing from one side of a square region to the opposite side, regardless of the size of the square (on the condition: $d/s < 0.5$ with reached accuracy of the measurement: ±0.26%).

Resistivity of a semiconducting material, a direct function of dopant concentration, is one of the basic parameters characterizing silicon PV cell bases, allowing the determination of:

- doping agent's concentration in the base,
- homogeneity of dopant's surface concentration,
- depth of the *n-p* junction and distribution of dopant concentration in different layers.

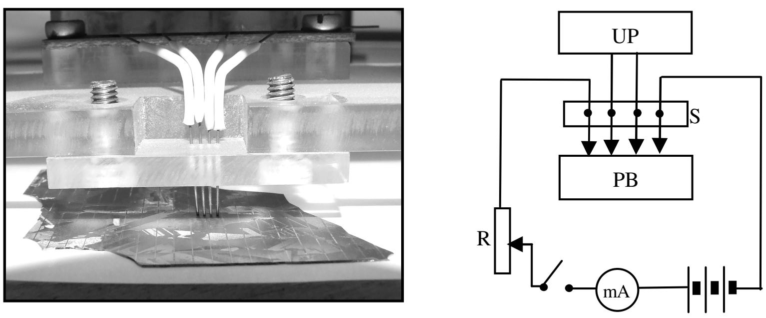


Fig. 6. Measurement of the sheet resistance with the use of four-point probe: UP - voltage meter circuit, S - four-point probe, PB - tested sample

Results of sheet resistance measurements with a four-point probe have been shown in Figure 7. Based upon these results, the etching processes' parameters have been set - 2 minutes for the frontal surface in a mixture of acids and 33 minutes for the back surface in an aqueous KOH solution.

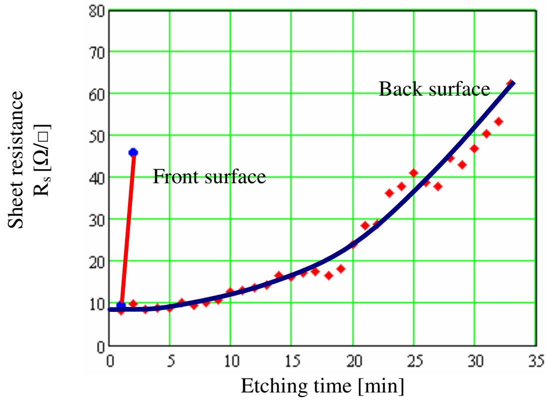


Fig. 7. Time dependence of the sheet resistance R_s

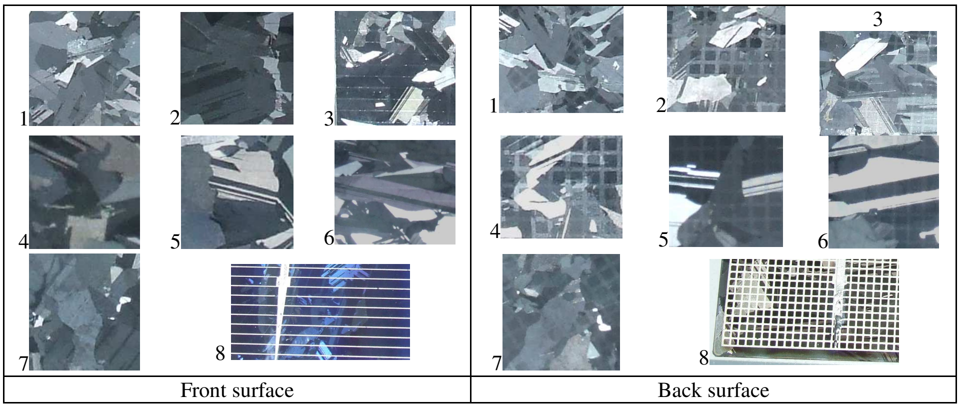


Fig. 8. View of front and back surfaces after etching in $H_2SiF_6/HNO_3/H_2O$ solution - samples 1÷7, 8 - sample before etching

Figure 9 shows a change in etching rate of consecutive layers in the function of temperature for two mixtures: $H_2SiF_6/HNO_3/H_2O$ and $H_2SiF_6/HNO_3/CH_3COOH$.

Etching processes should only be conducted until the removal of desired layers, whereas it is essential to avoid too great loss of silicon. For the silicon base to be proper for production of new cells, its thickness must not be too small - a loss of strength may cause that the base breaks during the series of technological processes carried out on its surface.

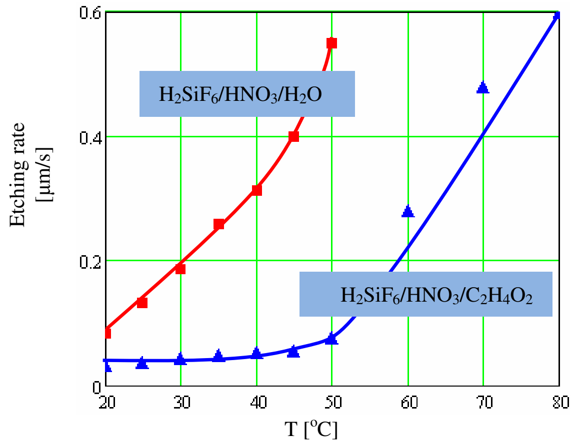


Fig. 9. Temperature dependence of etching rate

Results of silicon plate thickness measurements in dependence on temperature of the applied etching solutions have been shown on Figure 10. Measurements were carried out with ±1 µm accuracy. For temperatures above 40°C, thickness has decreased below 280 µm because of a rapid increase of the etching rate in that temperature range (Fig. 10). That is way a precise time control is required for the plate's immersion in the etching solution in desired temperature.

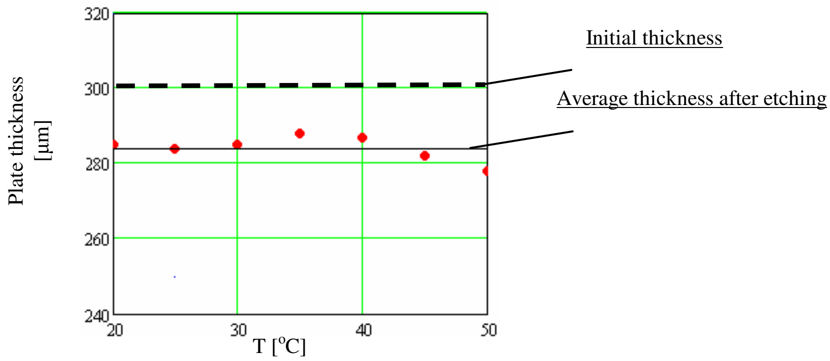


Fig. 10. Temperature dependence of obtained silicon plates thicknesses

Conclusion

A way of utilizing silicon based PV cells from obsolete or damaged PV modules has been presented. Having in mind the objective of reacquiring high purity materials from the recycling process, the chemical treatment is the most important stage of this method.

For crystalline silicon-based PV cells, the following chemical treatment processes have been conducted: removal of metallization, removal of ARC and *n-p* junction removal through etching. To develop a universal etching solution, modifications of mixture compositions are required, depending on PV cell's production technology.

Recycling of the most valuable materials may be applied on the production stage, for an average 5% of manufactured cells, which do not meet the quality requirements, as well as for cells spent or damaged cells through improper transport, assembly or use.

References

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[2] Röver, I., Wambach, K., Weinreich, W., Roewer, G. and Bohmhammel K.: *Process Controlling of the Etching System HF/HNO$_3$/H$_2$O*, 20th European Photovoltaic Solar Energy Conference 2005, Barcelona, Spain

OBRÓBKA CHEMICZNA KRZEMOWYCH OGNIW SŁONECZNYCH JAKO NAJWAŻNIEJSZY ETAP W RECYKLINGU MODUŁÓW FOTOWOLTAICZNYCH

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Abstrakt: W ostatnich latach systemy fotowoltaiczne stają się niezwykle popularne na całym świecie jako korzystne dla środowiska rozwiązanie problemów energetycznych. Problem, jak zagospodarować zużyte elementy systemów fotowoltaicznych, których ilość w przyszłości może być znaczna, nie został do tej pory rozwiązany. Konieczne jest opracowanie metody recyklingu i ponownego wykorzystania wycofanych z użycia elementów składowych systemów PV. Moduły fotowoltaiczne wykonane w technologii krystalicznego krzemu składają się (w kolejności według masy) z następujących elementów: szkła, aluminiowej ramy, przeźroczystej warstwy hermetyzującej z kopolimeru EVA, ogniw fotowoltaicznych, puszki przyłączeniowej, warstwy folii ochronnej (Tedlar) i śrub. Z ekonomicznego punktu widzenia oraz z uwagi na jego cenę i ograniczoną podaż najcenniejszym materiałem, który może być odzyskany z ogniw PV, jest czysty krzem. W artykule przedstawiono sposób zagospodarowania krzemowych ogniw PV, pochodzących z wycofanych z użycia modułów. Z punktu widzenia wymaganej wysokiej jakości odzyskiwanych materiałów najważniejszym etapem proponowanej metody recyklingu są procesy chemiczne. Warunki prowadzenia procesu muszą być opracowane w taki sposób, aby uzyskać wysoką jakość krzemu z uwzględnieniem jego parametrów elektrycznych. Dla ogniw wykonanych z krystalicznego krzemu prowadzono następujące po sobie procesy usuwania poprzez wytrawianie kontaktów elektrycznych, warstwy antyrefleksyjnej oraz złącza n-p. Składy roztworów trawiących były dostosowywane do różnych rodzajów ogniw krzemowych. Podjęto próby opracowania składu uniwersalnej kąpieli trawiącej, przy czym konieczne okazało się wprowadzanie modyfikacji składu roztworu w zależności od rodzaju ogniw PV.

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