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CHEMICAL TREATMENT OF CRYSTALLINE SILICON SOLAR CELLS AS A METHOD OF RECOVERING PURE SILICON FROM PHOTOVOLTAIC MODULES

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ABSTRACT

Photovoltaic technology is used worldwide to provide reliable and cost-effective electricity for industrial, commercial, residential and community applications. The average lifetime of PV modules can be expected to be more than 25 years. The disposal of PV systems will become a problem in view of the continually increasing production of PV modules. These can be recycled for about the same cost as their disposal.

Photovoltaic modules in crystalline silicon solar cells are made from the following elements, in order of mass: glass, aluminium frame, EVA copolymer transparent hermetising 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 construction material used.

Recovering pure silicon from damaged or end-of-life PV modules can lead to economic and environmental benefits. Because of the high quality requirement for the recovered silicon, chemical processing is the most important stage of the recycling process. The chemical treatment conditions need to be precisely adjusted in order to achieve the required purity level of the recovered silicon. For PV systems based on crystalline silicon, a series of etching processes was carried out as follows: etching of electric connectors, ARC and n-p junction. The chemistry of etching solutions was individually adjusted for the different silicon cell types. Efforts were made to formulate a universal composition for the etching solution. The principal task at this point was to optimise the etching temperature, time and alkali concentration in such a way that only as much silicon was removed as necessary.

Key words: *silicon, recycling, photovoltaic cells, etching, renewable energy sources*

INTRODUCTION

In recent years, photovoltaic systems have gained worldwide recognition and popularity as an environmentally friendly way of solving energy problems. However, the problem of recycling spent photovoltaic systems, the quantities of which will increase rapidly in the future, is yet to be solved. Establishing a technology for recycling and reusing spent photovoltaic panels is thus a necessity. Photovoltaic modules in crystalline silicon solar cells are made from the following elements, in order of increasing mass: glass, aluminium frame, EVA copolymer transparent hermetising 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 construction material used.

Crystalline silicon photovoltaic cells are produced in the form of silicon plates 200–500 μm thick with the following dimensions: 100x100 mm^2, 125x125 mm^2 or 150x150 mm^2. In the first step of PV cell manufacture, an n-p junction is formed on the front surface of these plates by the atomic diffusion of phosphorus, after which an anti-reflective coating (ARC) is applied to this layer. In the next step of the manufacturing process, two electrodes of aluminium and/or silver paste are formed on both the front and rear sides of the plate [1].

The PV module manufacturing process involves laminating single cells after the formation of the n-p junction connector layer and mounting them in an aluminium frame. The recycling process requires the modules to be disassembled according to the flow chart presented in Figure 1.

The recovered silicon could be utilised as a raw material in the photovoltaic industry, as an additive to alloy steel to alter its mechanical properties (hardness, tensile strength, impact strength), and as a material for ceramics, based on the manufacture of non-metal powders.

Figure 1. Thermal and chemical processes in PV crystalline cell and PV module recycling.

RECYCLING OF CRYSTALLINE SILICON PHOTOVOLTAIC CELLS AND MODULES

The PV module production process involves laminating single cells (after the formation of the n-p connector layer) and mounting them in aluminium frames. That is why the recycling

process requires the disassembly of the modules according to the flow chart shown in Figure 1.

A thermal process enabling the quick, simple and economically efficient disassembly of the module is the first stage in PV module recycling. Firstly, the EVA-laminated cells (EVA – Ethylene and Vinyl Acetate co-polymer) are separated. Tests have been conducted on chemical EVA layer removal: the results show that thermal separation is, from an economic and ecological point of view, the more favourable alternative when compared to chemical processes, which require the use of expensive and toxic reagents.

The second primary process carried out in PV module recycling is the chemical treatment of the solar cell.

In order to recover the silicon powder or plates for re-use in new photovoltaic cell production, the metal electrodes, AR coating and n-p connector layer have to be removed. These operations can be performed by dissolution in acidic or basic solutions.

A very important issue is the correct identification of the materials used in silicon PV cell production (Figure 2). Over 90% of all PV cells are silicon-based. Depending on the manufacturing technology, however, monocrystalline, polycrystalline and, occasionally, 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. The front-side electrodes are most commonly made from silver, while the ones located on the rear surface of the cell frequently have an additional thin coating of aluminium.

Figure 2. Types of materials used in PV cell production.

Because of the high light reflection index of silicon (33–54%), a layer decreasing that value needs to be incorporated – that is why the front surface of the cell is covered with an anti-reflective layer, which changes the colour of the cell (it usually turns 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.

Magnesium fluoride (MgF_2) is often used, since it is hard-wearing and is easily applied to substrates using physical vapour deposition. With such coatings, reflection as low as 1% can be achieved on ordinary glass, and even better results can be obtained on higher index media. Further reduction is possible by using multiple coatings, designed so that reflections from the surfaces undergo maximum destructive interference. By using two or more layers, broadband antireflective coatings for the visible range (400-700 nm) with maximum reflectivities of less than 0.5% are commonly achievable. Reflection in narrower wavelength bands can be as low as 0.1%. Alternatively, a series of layers with small differences in refractive index can be used to create a broadband antireflective coating by means of a refractive index gradient.

To enable the silicon base to be recycled from PV cells, a chemical process for removing different layers from the cell surface has been developed (Figure 3).

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

The main problems are choosing a suitable composition and concentration of the etching solution, as well as the optimal temperature range for the chemical reaction.

CHEMICAL ETCHING

The efficiency of the etching mixtures used in the chemical recovery of pure silicon from recycled PV modules depends largely on the amount and kind of contaminants and additives in the silicon. In the development of a general technology suitable for photovoltaic cells from different manufacturers, optimisation of the etching processes is therefore problematic.

The antireflective layer and n-p junction can be removed with a ternary mixture. In a number of selective etching steps these layers are removed consecutively with several mineral acids and acid mixtures. The etching recipes have to be adapted to the different cell technologies. A number of mixtures have been tested, based mainly on the following compounds:

- hydrofluoric acid - HF;
- hexafluorosilicic acid - H_2SiF_6;
- nitric acid - HNO_3;
- acetic acid - $C_2H_4O_2$;
- hydrogen peroxide - H_2O_2;
- distilled water - H_2O.

Experiments have also been conducted with solutions enriched with:

- potassium iodide – KI;
- silver nitrate - $AgNO_3$;
- copper nitrate - $Cu(NO_3)_2$;
- bromine - Br.

The specifications of some solutions used for silicon etching are given below:

- HNO_3(70%)/HF(48%) (2:1);
- HNO_3(70%)/HF(48%) (1:100);
- HNO_3(70%)/HF(48%)/$C_2H_4O_2$+Br_2(250:150:150:3);
- HNO_3(70%)/HF(48%)/$C_2H_4O_2$ (5:3:3), (5:1:2);
- H_2O_2(30%)/HF(48%)/H_2O (1:1:4);
- H_2SiF_6 /HNO_3/$C_2H_4O_2$ (1:1:1);
- HNO_3(70%)/HF(48%)/H_2O (1:2:2)+$AgNO_3$ (1 g).

Röver et al. [2] have reported some results of texture etching with the use of HF/HNO_3/H_2O solution. The chemical etching of semiconductors with HF/HNO_3/H_2O solution is divided into two steps: oxidation and reduction, followed by dissolution of the oxidation products to form a soluble ion complex.

The causative role of oxidant is usually played by nitric acid (HNO_3), but the faster for the formation of soluble salts is mostly hydrofluoric acid (HF). Both of these reactions take place in almost the same time, and they result in a uniform etching; but in the case of n-p junction etching (as in the case of silicon recovered from recycled PV modules) the oxidation and reduction reaction rates should be markedly different. During silicon etching, hexafluorosilicic acid (H_2SiF_6) is produced. It is formed in a formalised two-step-process

during the dissolution of silicon in the HF/HNO_3 mixture. In the first step silicon is formally oxidised by HNO_3 to SiO_2. In the second, the oxide reacts with HF to yield SiF_4, i.e. it is complexed in excess HF as SiF_6^{2-}. The overall reaction is written as follows [4]:

$$3Si + 4HNO_3 + 18HF \rightarrow 3H_2SiF_6 + 4NO + 8H_2O. \quad (1)$$

The degree of selectivity and the etching rate are functions of the crystallographic orientation, surface and volumetric structural defects in the silicon and the temperature of the etching mixture (Figure 4), as well as the hydrodynamics of the boundary layer between the mixture and semiconductor. The temperature affects the etching rate, the dependence being exponential. The etching process can be limited by the chemical reaction rate or by the diffusion rate of the etching mixture through the surface layer of semiconductor.

Stirring of the etching mixture accelerates etching and promotes uniform dissolution.

Most etching mixtures contain hydrofluoric acid (HF) as the oxidation product solvent and nitric acid (HNO_3) as the oxidising agent.

Two processes accompany the etching of the semiconductor surface:

- transport of the etching mixture reaction products to and from the etched module surface,
- chemical reaction on the semiconductor surface.

Figure 4. Etching rate as a function of the etching solution composition [5].

Etching should be continued until the relevant layers have been removed, although it is essential to avoid too great a loss of silicon. For the silicon base to be suitable for incorporation in new cells, it must not be too thin – a loss of mechanical strength may cause the base to break during the technological processes performed on its surface.

EXPERIMENTAL RESULTS. REMOVING THE METAL COATING

The metal coating is removed by a sequence of etching. The rear-side metal coating of older solar cells often contains silver. During this step, the silver is dissolved; it can be recovered from the waste acids by electrolysis. The yields of silver recycled with different metal concentrations in the acid and silver prices were analysed by Müller et al. [3].

An aqueous solution of KOH and NaOH was used to remove the Al layer from the cell's rear surface (Figure 5). A Teflon bath containing the etching mixture was immersed in a water bath with heating elements embedded in its walls and base. The process was carried out over a temperature range of 20–80°C. Etching rates were measured isothermally using mono- and polycrystalline silicon wafers.

Figure 5. Temperature and concentration dependence of the removal rate of the rear-side Al metal coating.

Because the etching rate for the rear-side metal coating depends strongly on temperature, it is beneficial to use a low-concentration solution and a bath temperature of 60–80°C, which reduces the process time. Maximum etching rates were achieved with 30% KOH; the efficiency was optimal for 30% aq KOH at 80°C (Figure 6).

Figure 6. Efficiency of removal of the rear-side Al metal coating .

It is possible to dissolve the Ag metal coating with aq HNO_3. Figure 7 shows the etching rate vs. concentration of nitric acid and bath temperature.

During the test carried out with 10% aq HNO_3 at 20°C there were no observable effects of etching after 40 min, whereas during the test at 80°C with 40% aq HNO_3 the entire metal coating was removed within 15 min.

Figure 7. Temperature and concentration dependence of the removal rate of the Ag metal coating with HNO_3.

EXPERIMENTAL RESULTS. REMOVING THE AR COATING AND THE n-p JUNCTION

Two types of mixture – $H_2SiF_6/HNO_3/C_2H_4O_2$ and $H_2SiF_6/HNO_3/H_2O$ – have been tested for removing the ARC and n-p junction. A thorough rinse in deionised water is required after etching has been completed.

Figure 8. Temperature dependence of the ARC and n-p junction/metal coating removal rate.

The antireflective coating and n-p junction can be removed using a $HF/C_2H_4O_2/HNO_3$ (1:2:5) mixture. Figure 9 illustrates the change in the etching rate of the successive layers as a function of temperature for two mixtures ($H_2SiF_6/HNO_3/H_2O$ and $H_2SiF_6/HNO_3/C_2H_4O_2$) in comparison with the results obtained by Wolf [5].

Figure 9. Temperature dependence of the etching rate.

Mixtures containing added hydrogen peroxide were also tested: the results are comparable to those obtained with $HF/C_2H_4O_2/HNO_3$ solution (see Figure 10).

Figure 10. Composition of the etching mixture in the $HF/H_2O_2/HNO_3$, $H_2SiF_6/H_2O_2/HNO_3$ and $HF/C_2H_4O_2/HNO_3$ systems.

The temperature dependence of the n-p junction etching rate for the following mixtures is presented in Figure 11:

- HF/H_2O_2 $/H_2O$;
- $HNO_3/C_2H_4O_2/HF+KJ$;
- H_2SiF_6 $/HNO_3/C_2H_4O_2$;
- $HNO_3/HF/H_2O+Cu(NO_3)_2$;
- $HNO_3/HF(40\%)/H_2O+AgNO_3$;
- $HNO_3/HF/C_2H_4O_2$;
- $HNO_3/HF/C_2H_4O_2+Br_2$.

Figure 11. Temperature dependence of n-p junction etching rate for different mixtures.

EXAMINATION OF THE ETCHED CELLS

A change in the surface structure of the wafers could be observed in all the different baths after a certain number of etching runs. The etched cells were examined under a metallographic microscope (Leica Reichert MEF4M) with a dual reflex module, a beam splitter prism and a TV CCD camera for digital image acquisition and computer image analysis (MultiScan Software®) (Figures 12, 13, 14). This optical microscope is an inverted wide field Metallograph with a high degree of automation and is equipped with IMIX (Integrated Microanalyser for Images and X-rays) software for image analysis and offers versatility in the following techniques: Bright Field Imaging, Differential Interference Contrast, Digital Image Acquisition, Field Imaging, Interferometry, Polarised Light and Polarisation Contrast.

Figure 12. Microscopic view of the rear side of the PV cell after etching in KOH.

Figure 13. Microscopic view of the etched cell: front and rear side of the PV cell.

Figure 14. Polycrystalline structure of PV cells after etching: a – front (magnification 25×), b – rear (magnification 100×).

In the next step the recycled wafers were characterised by a non-contacting resistivity measurement and determination of thickness.

Removal of the n-p semiconductor junction continued until the diffusion layer dissolved, with simultaneous control of the sheet resistance R_s [Ω/□] (ohms per square) using a four-point probe. The resistivity of a semiconducting material, a direct function of dopant concentration, is one of the basic parameters characterising silicon PV cell bases, allowing the dopant concentration in the base, the homogeneity of the dopant surface concentration, the depth of the n-p junction, and the distribution of dopant concentration in different layers to be determined.

The sheet resistance is a measure of the resistance of thin films with a uniform thickness. It is commonly used to evaluate the outcome of semiconductor doping, metal deposition and resistive paste printing. The utility of sheet resistance, as opposed to resistance or resistivity, is that it is measured directly using a four-point probe measurement. Sheet resistance is measured in ohms/square, and is applicable to two-dimensional systems where the thin film is considered to be a two-dimensional entity. It is equivalent to resistivity as used in three-dimensional systems. When the term 'sheet resistance' is used, the current must be flowing along the plane of the sheet, not perpendicular to it. In a regular three-dimensional conductor, the resistance can be expressed as [6]:

$$R = \rho \frac{L}{A} = \rho \frac{L}{Wd} = R_s \frac{L}{W}. \tag{2}$$

Because it is multiplied by a dimensionless quantity, the units are ohms. 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 condition that $d/s < 0.5$ with an accuracy of measurement = ±0.26%).

The results of sheet resistance measurements with a four-point probe are given in Figure 15 and Table 1. The parameters of the etching processes were established on the basis of these results.

Figure 15. Time dependence of the sheet resistance R_s.

Table 1 Sheet resistance and etching depth as a function of etching time

Next, the conductivity type of the semiconductor was determined using a thermal probe. The measuring procedure was as follows: in an n-type semiconductor, the hot edge becomes positively charged as a result of electron loss. As a consequence, the cold edge, towards which the electrons have diffused, is then negatively charged. Conversely, for the p-type semiconductor, the hot edge becomes negatively charged and the cold edge positively charged.

The results of silicon plate thickness measurements with respect to the temperature of the etching solutions are given in Figure 16. Measurements were carried out with an accuracy of ±1 μm. At temperatures > 40°C, the thickness decreased to < 280 μm because of the rapid increase in the etching rate in that temperature range. That is why precise control of the reaction time is required for the plate's immersion in the etching solution at the desired temperature.

Figure 16. Temperature dependence of silicon plate thickness.

THE QUALITY OF NEWLY PRODUCED CELLS

The closed cycle of recycling leads to the production of new cells on the basis of wafers obtained as a result of the chemical processes.

The cell manufacturing sequence involves the following main steps: texturisation, emitter formation, parasitic junction removal, passivation, antireflective coating deposition, front and rear contact formation.

The most important step in the manufacturing process of solar cells is n-p junction formation. Emitter diffusion can be generated in a diffusion furnace in an open or closed system. The phosphorus concentration depends on the diffusion time and temperature. Another type of n-p junction formation is the diffusion technique with the use of phosphorus-doped silica paste. Initially screen-printed on silicon wafers, the paste is then dried and placed in an IR furnace, where the temperature reaches 900°C. After parasitic junction removal, surface passivation is

achieved and the antireflective layer is deposited. Thereafter, the front and rear contacts are applied by screen-printing and co-fired in the IR furnace.

The quality of the cells obtained will be inspected by analysis of the current-voltage characteristics obtained under Standard Test Conditions (1000W/m^2, 25°C). A typical configuration of the circuit for cell examination is shown in Figure 17.

Figure 17. Electric circuit for cell examination.

CONCLUSIONS

Crystalline silicon-type PV modules consist, in order of mass, of glass, an aluminium frame, an EVA coating, solar cells, a terminal box, back film and tapping screws. From the economic point of view, pure silicon, recoverable from spent cells, is the most important material owing to its cost and shortage. For crystalline, silicon-based PV cells, the following chemical treatments were performed: removal of the metal coating, followed by the removal of ARC and n-p junction by etching.

The standard acid etching mixtures contain high amounts of toxic nitrogen oxides, fluorides and different silicon species, which require costly disposal measures. Moreover, autocatalysing reactivity effects complicate the controllability of these processes, which leads to losses of silicon and increased costs.

The compositions of etching solutions were adjusted individually for different silicon cell types. Despite the efforts made to formulate a universal etching solution composition, the results showed that solutions need to be modified in accordance with the type of PV cells to be recycled.

One way of recycling silicon-based PV cells from spent or damaged PV modules is discussed in this article. Bearing in mind the objective of recovering high-purity materials from the recycling process, chemical treatment is the most important stage of this method.

For crystalline silicon-based PV cells, the following chemical treatments were applied: removal of the metal coating, and etching of the ARC and n-p junction.

Recycling of the most valuable materials can be applied at the production stage to the c. 5% of manufactured cells that do not meet quality requirements, as well as to spent cells or cells damaged as a result of unsuitable transport conditions, faulty assembly or misuse.

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Acknowledgements

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Figure

Figure 1. Thermal and chemical processes in PV crystalline cell and PV module recycling.

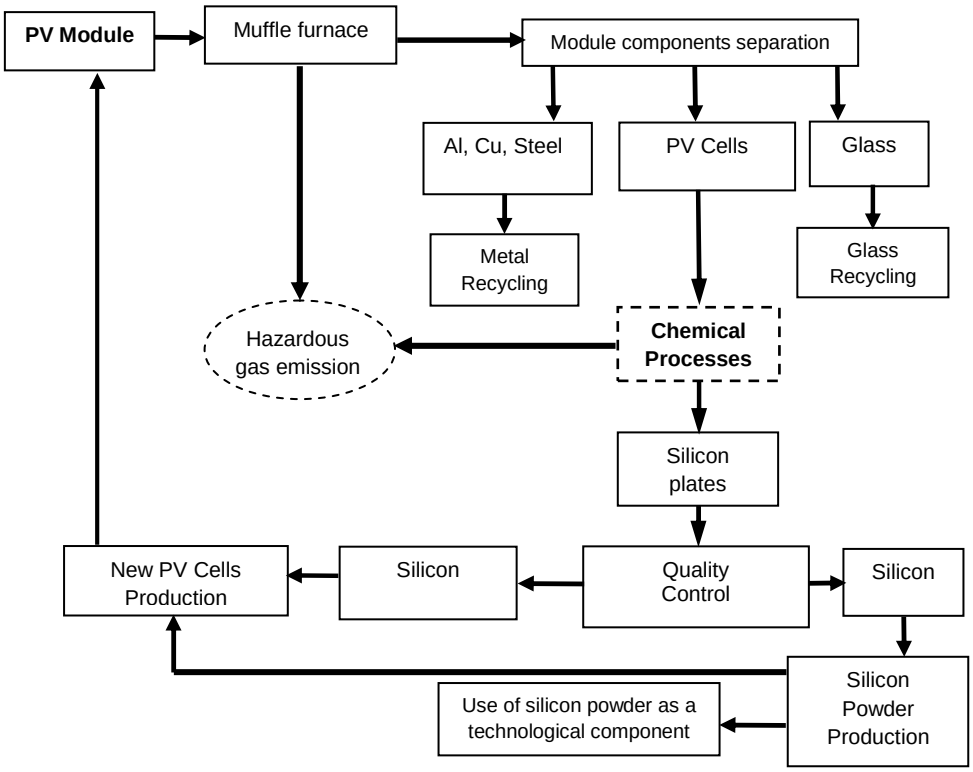


Figure 2. Types of materials used in PV cell production.

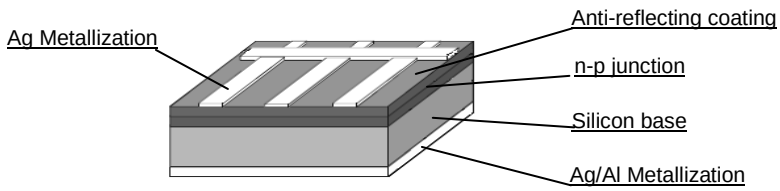


Figure 3. Recovery of the silicon base from silicon PV cells.

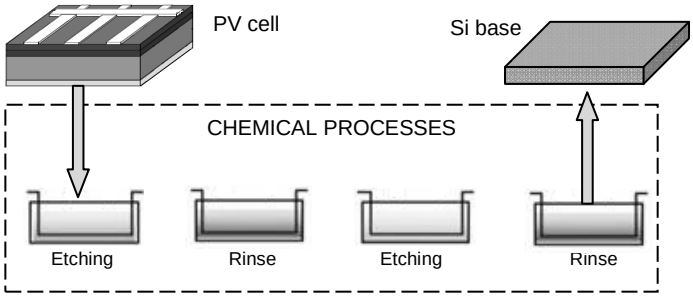


Figure 4. Etching rate as a function of the etching solution composition [5].

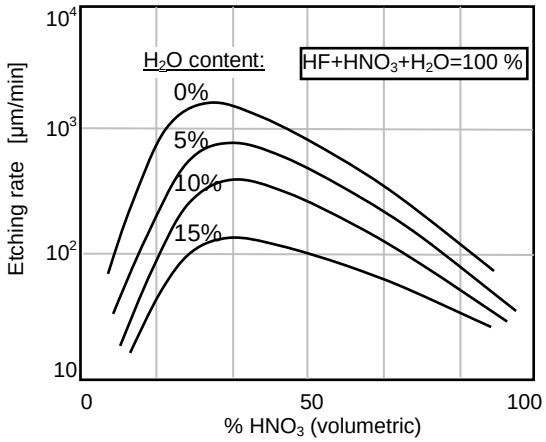


Figure 5. Temperature and concentration dependence of the removal rate of the rear-side Al metal coating.

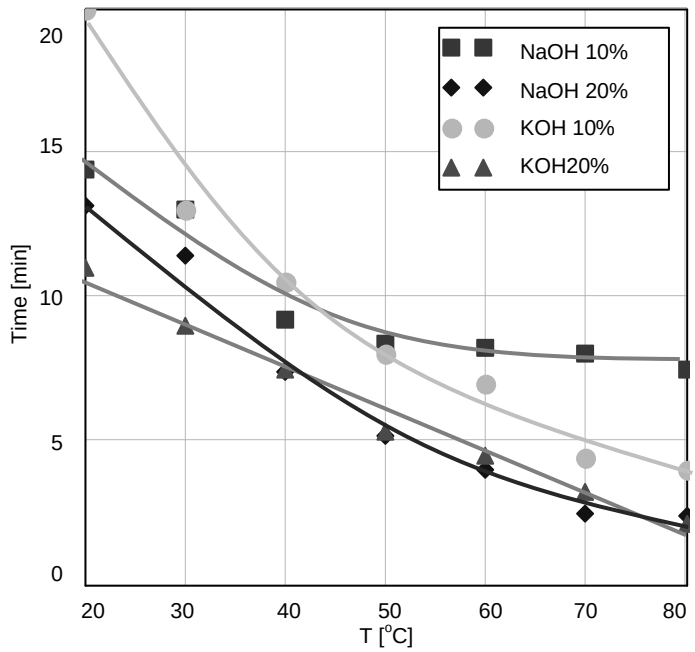


Figure 6. Efficiency of removal of the rear-side Al metal coating .

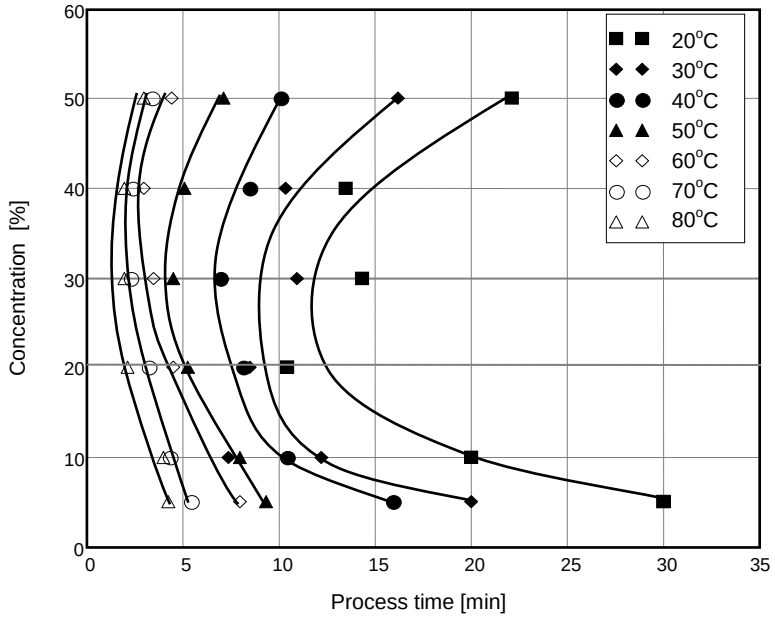


Figure 7. Temperature and concentration dependence of the removal rate of the Ag metal coating with HNO_3.

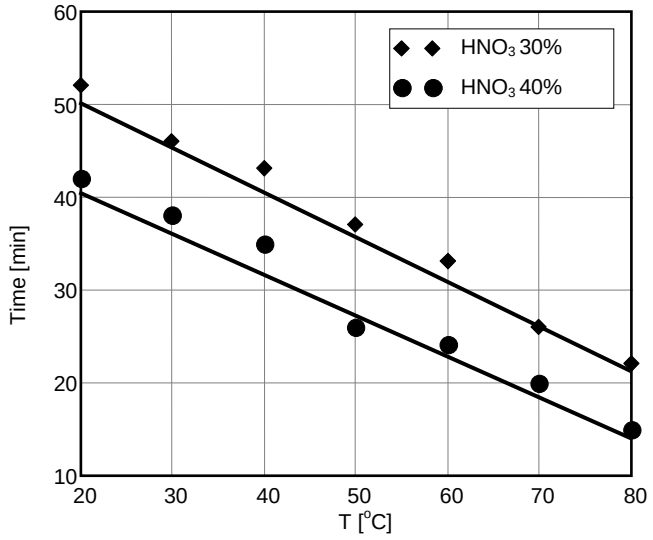


Figure 8. Temperature dependence of the ARC and n-p junction/metal coating removal rate.

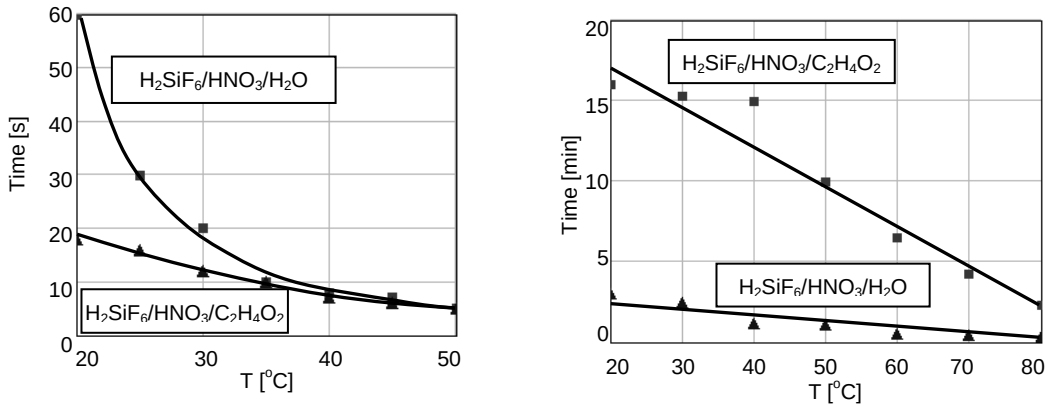


Figure 9. Temperature dependence of the etching rate.

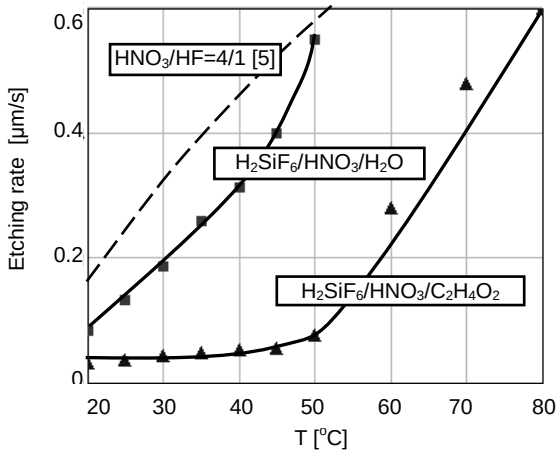


Figure 10. Composition of the etching mixture in the $HF/H_2O_2/HNO_3$, $H_2SiF_6/H_2O_2/HNO_3$ and $HF/C_2H_4O_2/HNO_3$ systems.

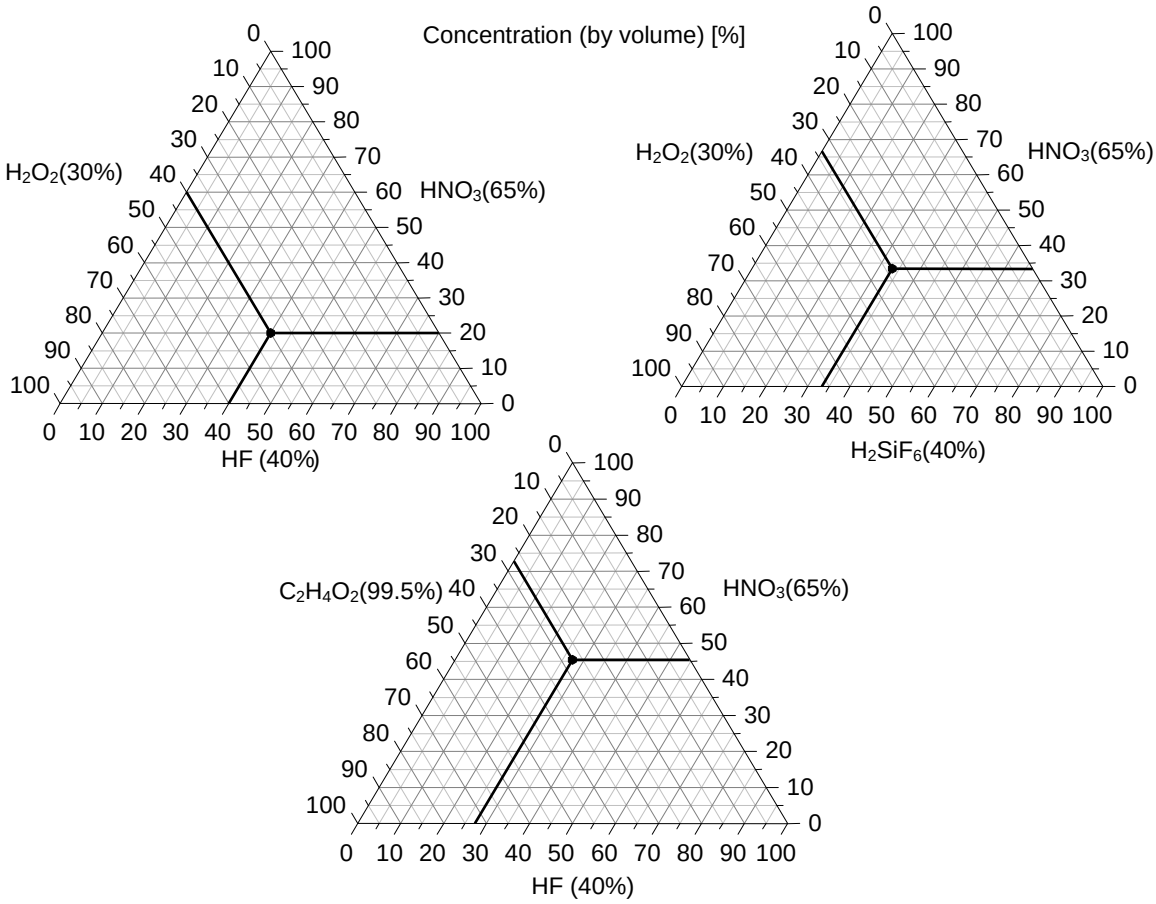
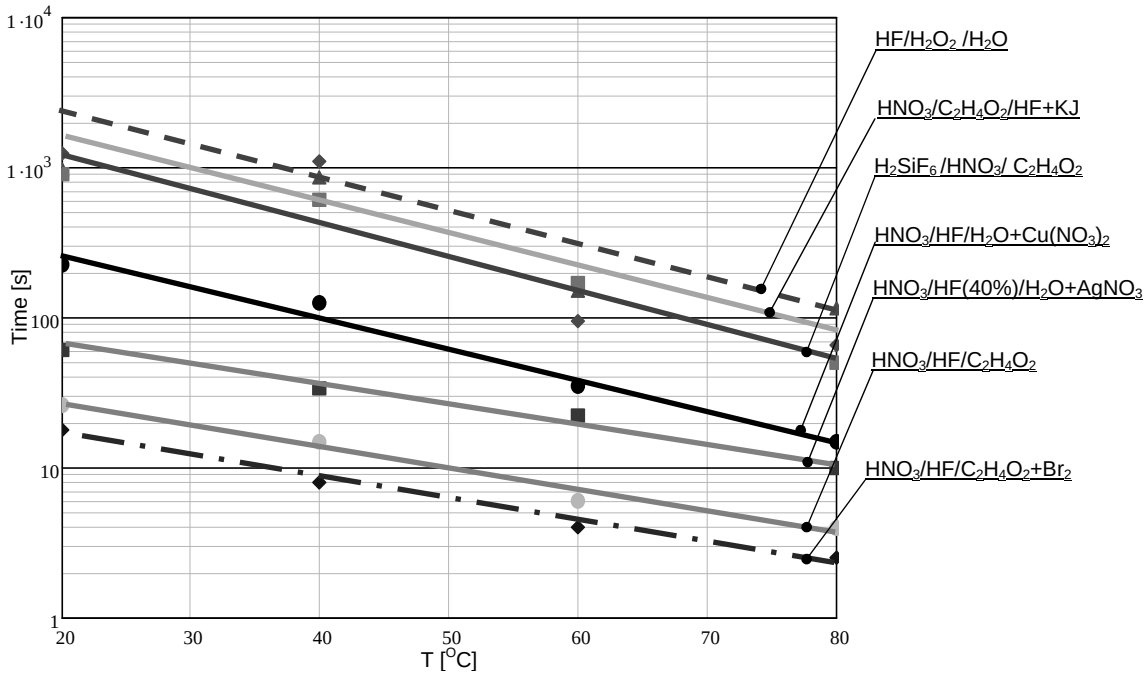


Figure 11. Temperature dependence of n-p junction etching rate for different mixtures.



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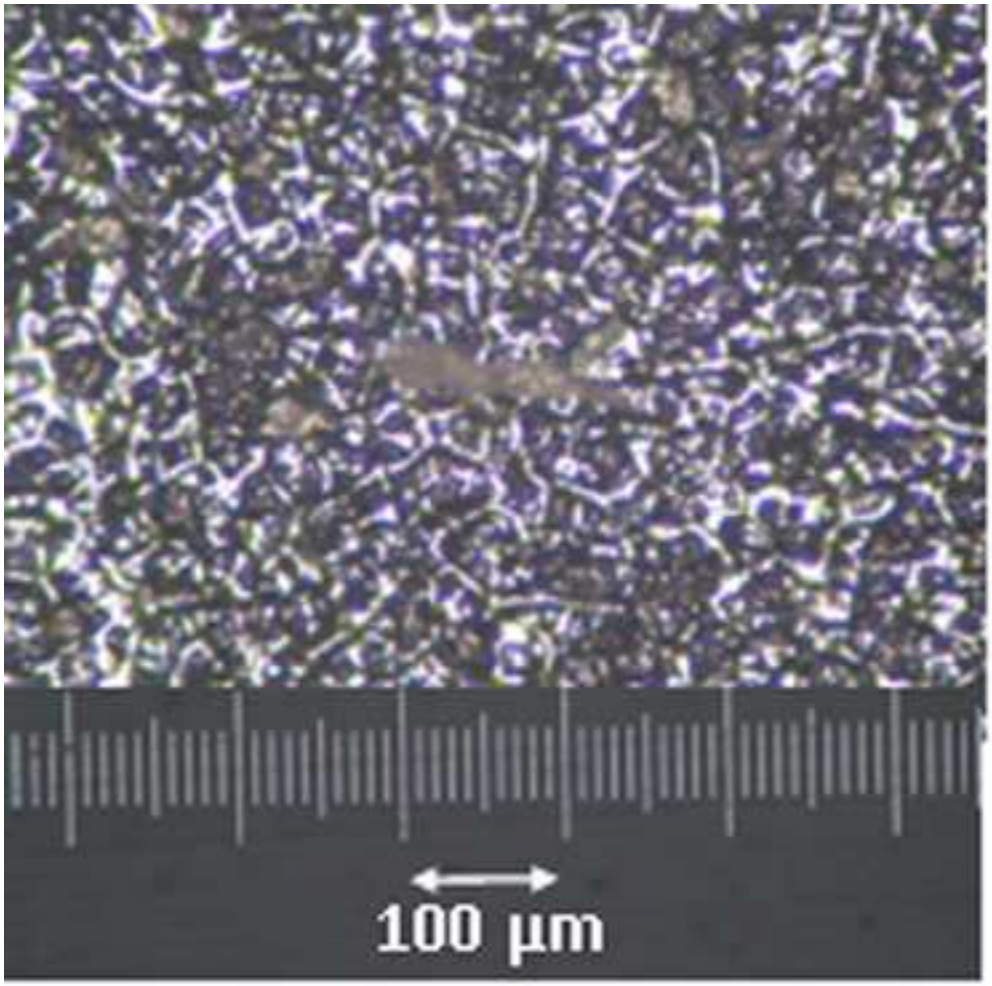

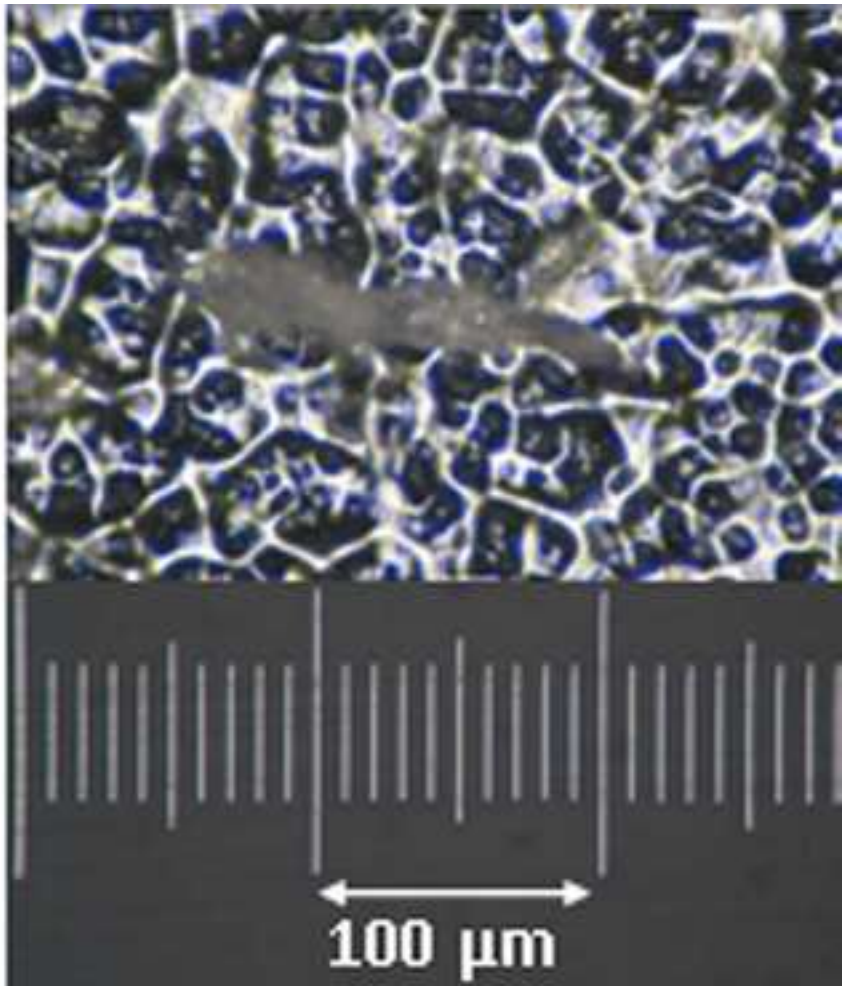

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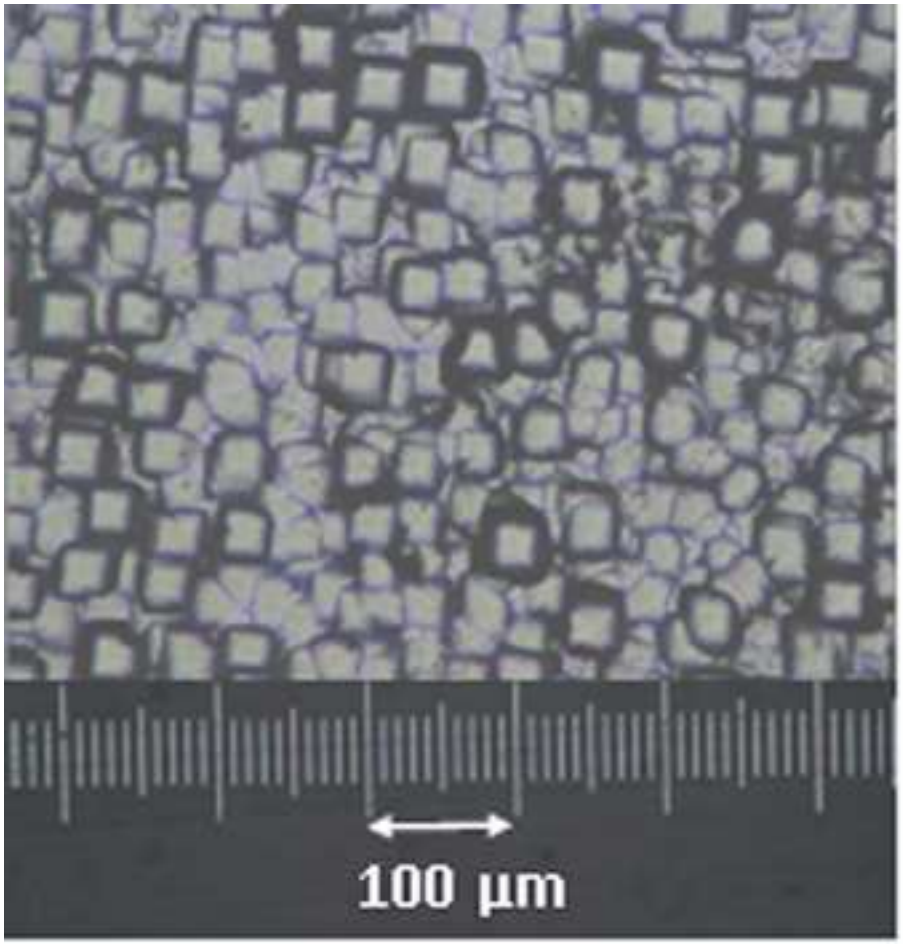

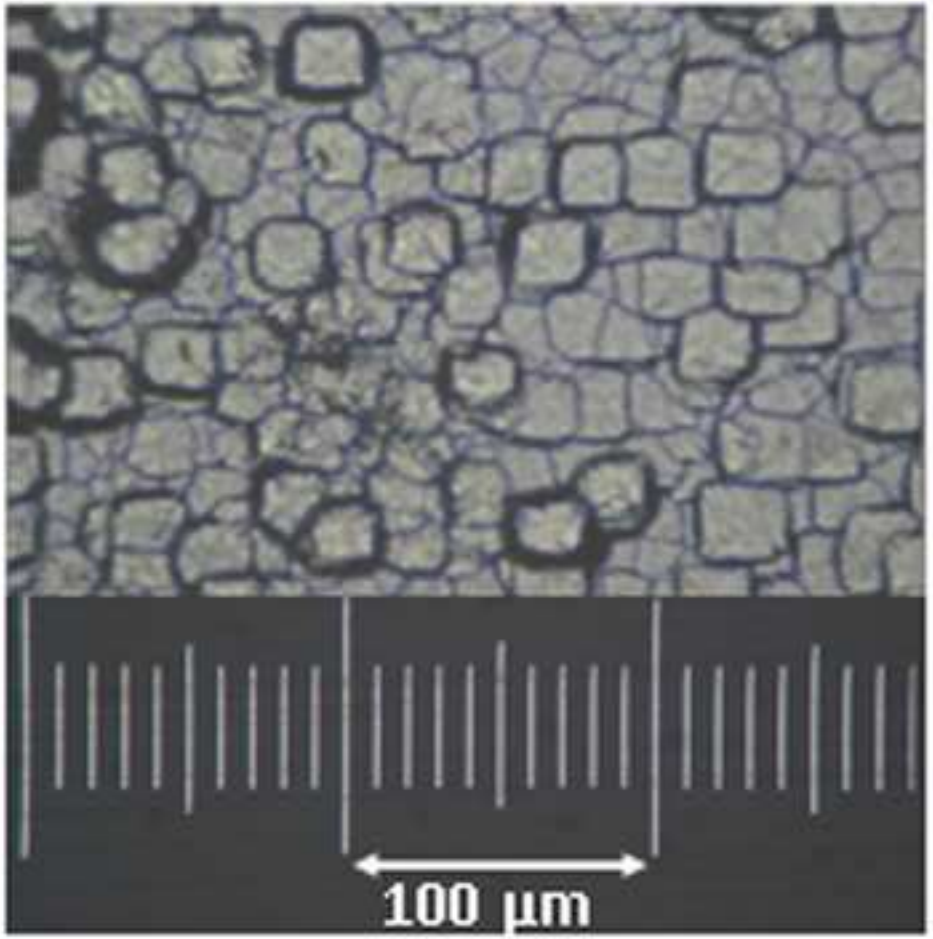

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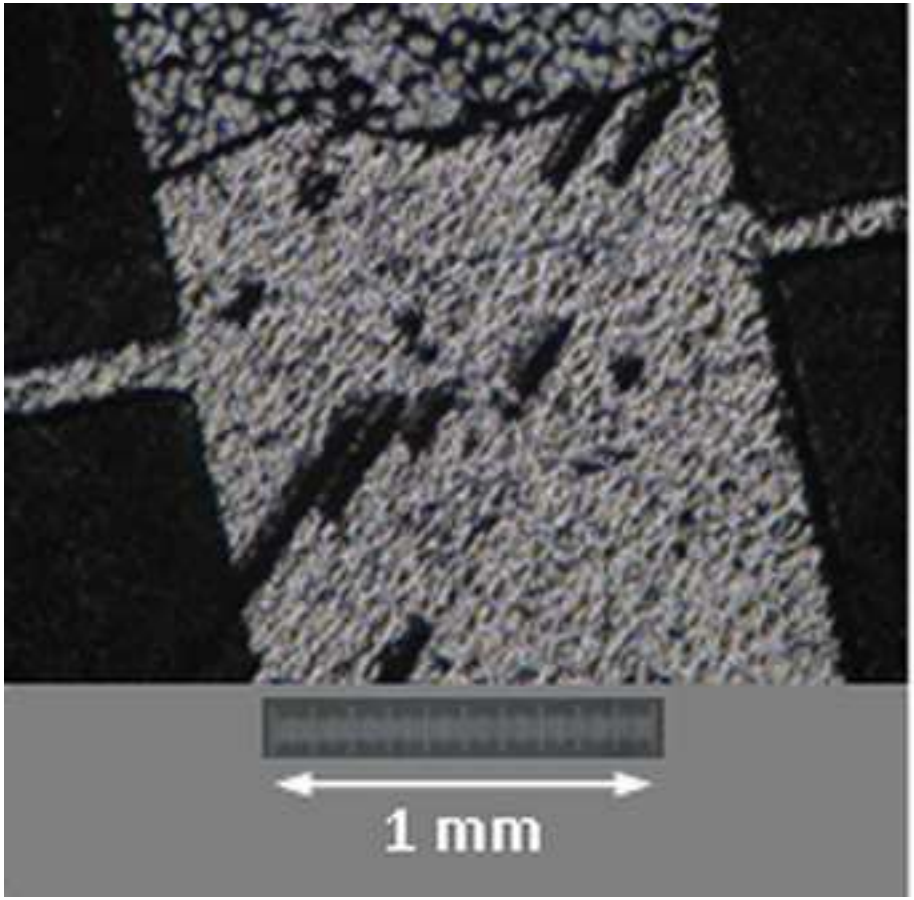
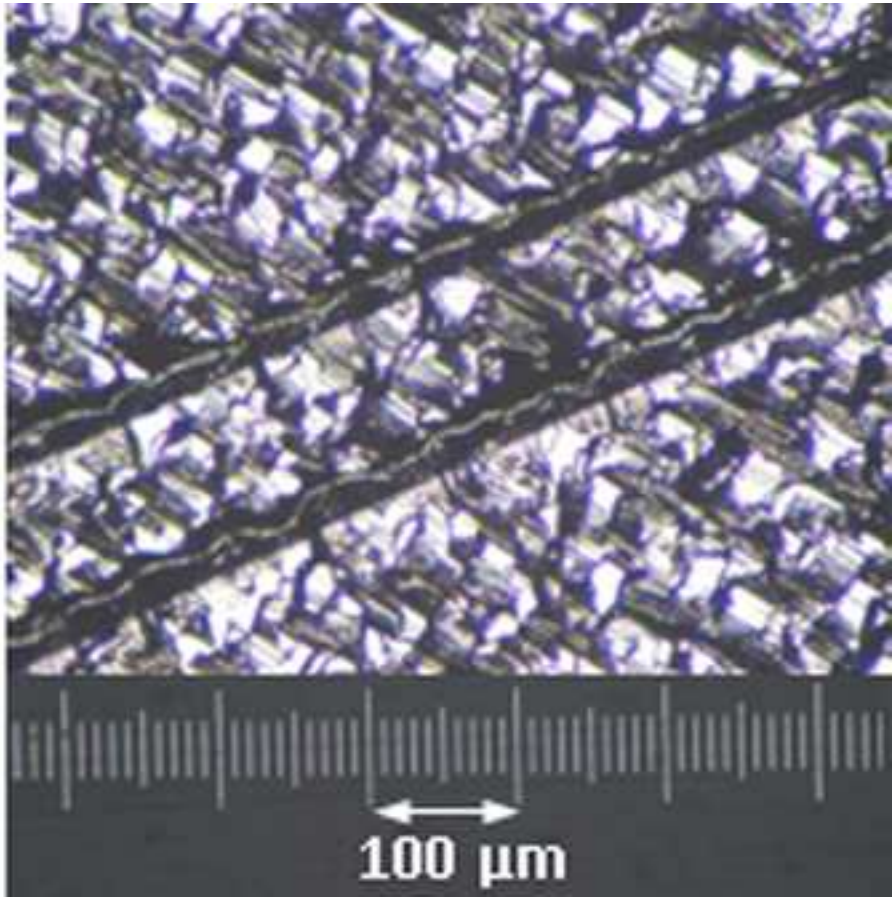




Figure

Figure 15. Time dependence of the sheet resistance R_s.

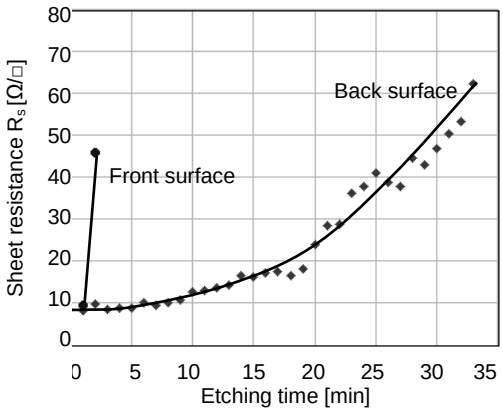


Figure 16. Temperature dependence of silicon plate thickness.

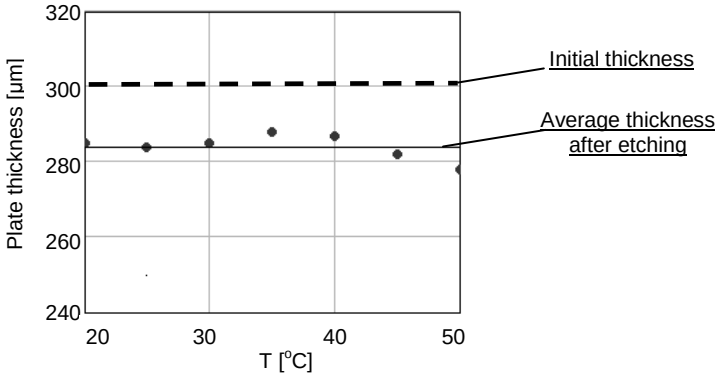
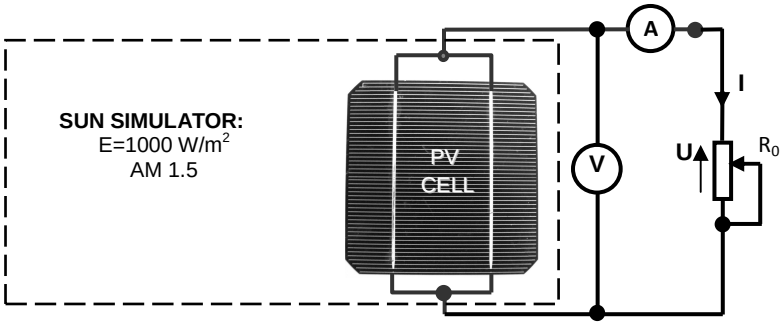


Figure 17. Electric circuit for cell examination.



Table

Table 1 Sheet resistance and etching depth as a function of etching time

Etchant: KOH		Type of a cell/ conductivity	Sheet resistance front-emitter	Etchant: $HF:C_2H_4O_2:HNO_3$		Etching depth
time [min]	temp.[^oC]		R_s [Ω/□]	time [min]	temp.[^oC]	[μm]
15	80	mono - p	32	6	20	19
15	80	poli - p	51	3	20	7
15	80	poli – p	46	33	20	55
15	80	mono – p	40	24	20	59
15	80	mono - p	-	18	20	15