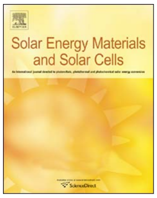
Solar Energy Materials and Solar Cells 176 (2018) 190–195

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat



Recovery of silver metallization from damaged silicon cells

Anna Kuczyńska-Łażewska[a], Ewa Klugmann-Radziemska[a,*], Zuzanna Sobczak[b], Tomasz Klimczuk[b]

[a] Gdansk University of Technology, Faculty of Chemistry, Poland
[b] Gdansk University of Technology, Faculty of Applied Physics and Mathematics, ul. Narutowicza 11/12, PL-80-233 Gdansk, Poland

ARTICLE INFO

Keywords:
Photovoltaic solar cells
Metallization
Silver recovery
Recycling

ABSTRACT

Metallization is one of the key process steps to fabricate solar cells with high performance in a cost-effective way. Majority of photovoltaic solar cell manufacturing uses thick film screen print metallization with Ag containing paste to produce solar cells.

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.

The proposed method of acidic and basic etching of contacts, presented in this article can be successfully applied to broken solar cells from the landfill without a specialist analysis procedure. The amount of silver that can be recovered from the etching solution is up to 1.6 kg/t of broken solar cells. The step-by-step procedure improves efficiency of silver recovery. The best and easiest method for general verification of the silver etching rate is classic titration with suitable concentrations of titrant solution.

1. Introduction

1.1. Contacts in photovoltaic modules manufacturing

Solar cells transmit electricity via contacts and metal bars printed on their front and back sides, positive on one side and negative on the other. While the back side of a solar cell can be fully covered by a metal layer, the front side typically has very thin metal bars, to make sure that shading of the solar cell is minimal.

The main contact function is to provide efficient charge transport in the solar cell structure.

It is very important for the front contact not to cover a large part of the surface of a solar cell and to have low contact resistance. Contact fingers have a width of about 0.1–0.2 mm and are 0.02 mm high. Fingers are perpendicular to the busbars with a pitch of typically 2 mm. Busbars, about 1.5–2.5 mm thick, run across the thin contact fingers. At all edges there typically is a 1.5 mm range which is not covered by contacts.

A standard H shaped silver front contact gives 8% of front side coverage of the solar cell [12].

The rear contact consists of pads in a mirror reflection of busbars from the front contact and a uniform layer of aluminium contact. Pads are made of silver with a small addition of aluminium and they make up 5% of the total rear contact surface. Their task is to collect the charge from the rear contact surface. Another important function is maintenance of low resistance on the contact surface and the side edge. The remaining area of the rear side consists of a multi-layer (0.005 mm), doped with an aluminium silicon surface, eutectic layer (0.01 mm) and on the top of its layer a layer of sintered aluminium paste with substantial in-diffuse of silicon [16].

Today, screen-printing of silver pastes is commonly used for front side metallization of silicon solar cells. Due to the high and momentary growing Ag price presented at Fig. 1 (http://uk.reuters.com/, 2017) [13], however, Ag pastes are one of the main cost drivers in industrial production.

Screen-printing allows to perform different shapes of the front contact grid [17].

Screen printing is performed on both the front and back sides of solar cells. Each of the screen printing processes can be divided into three major steps [10,31,8]:

1. Overprinting a collection of back contacts(Al/Ag) and drying,
2. Overprinting a front electrode (Ag) and drying,
3. Co-firing both front and back metal contacts.

Pastes mainly used include rear silver (Ag), rear aluminium (Al) and front silver (Ag) [21]. There are also other metals which can be expected in contacts such as titanium (Ti), palladium (Pd) ([20]) or

---

[*] Corresponding author.
E-mail address: ewa.klugmann-radziemska@pg.edu.pl (E. Klugmann-Radziemska).

https://doi.org/10.1016/j.solmat.2017.12.004
Received 26 May 2017; Received in revised form 31 October 2017; Accepted 5 December 2017
0927-0248/

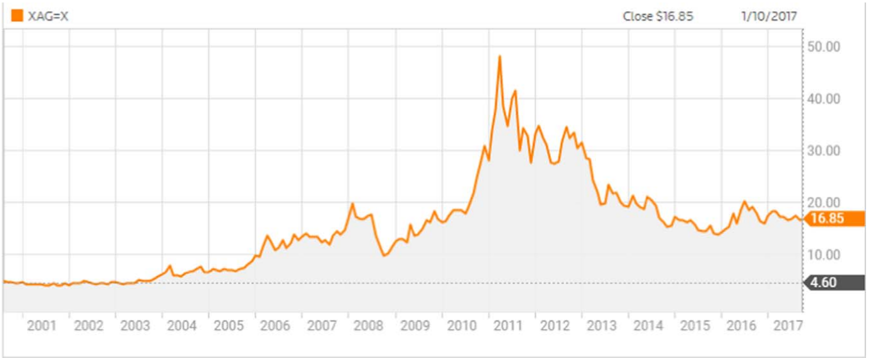


Fig. 1. Changes of silver prices since year 2000 (http://uk.reuters.com/, 2017) [13].

copper (Cu) and nickel (Ni) [22,26,29].

Copper can be a promising material for substituting silver as metallization on solar cells. Also, a combination of silver and nickel can enhance efficiency at low cost [12].

Selective Laser Sintering (SLS) is a modern manufacturing technique, which uses a high power CO_2laser to melt or sinter metal powder particles into a mass that has a desired three-dimensional shape in precisely defined areas. The whole process is controlled by software that is used for micro-processing [9].

1.2. Silver recovery in photovoltaic modules recycling

Most of the recycling pathways are focused on recovering silicon, glass and aluminium. Removing silver contacts is mainly a side effect but different methods of contacts removing were worked out (Table 1).

The mainly used method for silver recovery from solar cells is etching in acidic solution based on nitric acid (HNO_3). The efficiency of this reaction is low – 86% [29] but with a high purity, even up to 99.999% [29]. Sequence etching and fluidal bed usage can enhance the efficiency but is cost and energy consuming. Many techniques used do not include silver recovery. Removing contacts is only one of the steps to prepare the silicon wafer for reuse.

Ecological value of silicon is high according to the fact that metallurgical process of silicon purification have high energy demands because of submerged arc and induction furnaces usage, also some toxic compounds can be emitted [3]. Adding pure silicon from the recycling process decrease high cost of solar grade silicon production and limit unfavourable influence to the environment. Despite that silicon is the most important material recoverable from the classic crystalline silicon (c-Si) solar cells [15], the value of silver increases profitability of the recycling process [29]. Basing on literature data [6,23] contribution of silver in the solar module can be calculated. From 1 m^2 of a solar module 7 g of silver can be recovered, from 1 kg of separated solar cells over 14 g can be restored, but 1 t gives 0.5 kg of pure silver. According to the purity of the obtained silver the price varies but for hallmarks 925 the price is 17.96 $/ozs (0.578 $/g) (http://uk.reuters.com/, 2017) [13].

The main focus of this work is to prepare technique that is easy to obtain and does not require big investment at low environmental cost. Presented research are based on the assumption if there is need to use highly corrosive substances such as hydrofluoric acid [11,15], strong oxidising agents [18,24] or temperatures above 60 °C [11,29] only to remove metallization from the solar cells surface. Experiments were made on the raw material from the landfill to prepare universal treatment for all kinds of solar cells because most works presented above use at the experiments solar cells from only one company.

1.3. Silver recovery techniques

Main silver recovery techniques are presented in the context of x-ray film or photographic waste (Table 2) Electrolysis is most popular because of the high purity of the final product (even 98% [19]), but it can be applied only with solutions with high silver concentration. The solution after the process is still rich in silver and the concentration is below 100 mg/l [19] which is still too high for environmental limits. This drawback can be overcome by post treatment for example precipitation with chloride ions [2]. The main disadvantage of this method is that it requires electric energy at a rate of 3.81 kWh per kg of silver production [4].

The process of metallic replacement, also called the cementation process, is more complex. This method is based on a simple metallic replacement reaction where the more active metal (exp. Zn [1], Fe) passes into the solution while the less active (exp. Ag) is transferred into the solid state. Despite the simple theory, the silver sludge received after the process demands a very complex and expensive remediation procedure [19].

Chemical precipitation is a simple and widely used method. Silver can be precipitated by sulphide even at concentrations as low as

Table 1
Summary of experimental work on silver recovery from recycled solar modules.

Author	Leaching conditions	Scale
Tao and Yu [29]	● Sequence of 40% HNO_3 at 40 °C and 30% KOH at 80 °C	● Academic studies
Frisson et al. [11]	● Sequence of 15% HF, 4:1 H_2SO_4: H_2O_2 at 80 °C, 40% HNO_3 at 80 °C	● Pilot plant
Klugmann-Radziemska and Ostrowski [15]	● Removing Al with 30% KOH ● Etching with mixture of 40% HF, 65% HNO_3, 99.5% CH_3COOH and Br_2	● Academic studies
Kang et al. [14]	● Etching solution with surfactants	● Academic studies
Wang et al. [32]	● Etching with acid	● Academic studies
Müller et al. [23]	● Etching with acid ● Electrolysis	● Academic studies
Palitzsch and Loser [25]	● Aluminium backside removed by aluminium chloride ● Silver at the front removed by nitric acid	● Pilot plant
Nieland et al. [24]	● Etching of silver by using hydrogen peroxide with organic and nonorganic catalysts ● Alkaline bath for removing the aluminium contact	● Pilot plant
Loser and Palitzsch [18]	● Etching with sulfonic acid ($R-SO_2-OH$) in the presence of oxidising agent	● Pilot plant