

# PRODUCTION OF PHOTOCATALYST FROM SILICON RECOVERED FROM END-OF-LIFE PHOTOVOLTAIC PANEL

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## Abstract

Lifecycle impacts of photovoltaic panels (PVP) have been highly explored scientifically in the recent years. However, the end-of-life (EoL) PVP waste is growing exponentially and it is expected that its disposal will become a relevant environmental and economic issue in the next decades. Today, most of the EoL PVP waste ends up in a landfill.

This work addresses the need to develop a novel alternative pathway of reusing recovered silicon from EoL (c-Si) photovoltaic panels (PVP). Recovering silicon from EoL PVP modules can lead to economic and environmental benefits. Because of the high quality requirement for the recovered Si from EoL PVP, a combination of mechanical, thermal and chemical processes is deployed to obtain pure Si. A simple chemical treatment that can be scaled up to process large volumes of EoL PVP waste is used to convert recovered Si to a potential photocatalyst. A series of etching steps were carried out on thermal pretreated flakes.

EoL Silicon (c-Si) PVP's were initially mechanically and thermally pretreated (550 °C for 30 min), in order to remove the polymer sheets. A mixture of glass, silicon, electrodes and ash were recovered and separated in a trommel. The fraction containing silicon flakes was washed with water, acetone, HNO<sub>3</sub>, and HF in order to obtain pure Si. Recovered silicon was then etched through an Ag Assisted Chemical Etching (ACE) process and doped with Ag and Cu. Doping was performed in aqueous HF solutions containing metal salts, AgNO<sub>3</sub> and CuSO<sub>4</sub> respectively. The structure of the photocatalyst was examined through SEM and XRD. The photocatalytic activity was tested in a photocatalytic batch reactor irradiated by a 150W Xenon arc lamp. Photocatalytic degradation of methylene blue was examined as a model compound in order to evaluate the photocatalyst. SEM images after the recovery and cleaning processes indicated that high purity Silicon can be obtained. However due to the high initial Ag content, some residues could be observed. Initial photocatalytic experiments have exhibited a pollutant reduction of 29.4-36.6% for the samples prepared using chemical etching and doping, in comparison with direct photolysis which led to a 10% reduction.

## **Keywords**

Photocatalyst; Silicon; Photovoltaic panel; Recovery; Metal doping; Metal assisted chemical etching.

## **1. INTRODUCTION**

During the last decades the world has turned towards green energy production. Due to the rapid development of photovoltaic panels (PVP's) industry, the recycling and reuse of PVP waste is becoming a highly critical and global challenge. The life cycle of photovoltaic panels (PVP) is estimated to be 20 to 30 years. According to the prediction of the International Renewable Energy Agency (IRENA), the amount of PVP waste will increase to 20 million tons by 2050 (IRENA, 2016; Komoto et al., 2018).

However, as c-Si PVP installed are approaching their end of life, the need for a sustainable recovery and a recycling plan becomes more imperative, in order to avoid discarding of useful materials. Photovoltaic companies and researchers have begun addressing this issue, looking for ways to recover valuable materials from end of life PVP (Report IEA-PVPS), but in many cases, like Greece, there is no current application of such a plan.

First generation panels use monocrystalline or polycrystalline Silicon as semi-conductor and contain metals like Ag and Cu in the form of electrodes. Reports already show that recovery of those valuable materials is achievable through thermal and hydrometallurgical processes (Huang W.H. et al, 2017). Silicon's ability to absorb solar light alongside other properties of its nanostructures render it a potential catalyst for solar driven applications (Liu D. et al, 2017). Reports indicate that nanostructured surfaces like Si nano-wires display promising solar photocatalytic activity in pollutant degradation (Ghosh R. et al, 2018; Megouda et al, 2011, 2013, 2016). Those reports mainly use commercial wafers of specific crystallinity, but it would be of great importance to examine the possibility to reuse Si retrieved from end-of-life PVP in such applications (Shin et al., 2017).

Thus, the purpose of present work is to investigate the potential of elaborating Si nanostructures using Si recovered by end-of-life, first generation (c-Si) PVP samples, modified by metals that exist in those panels, in order to be used as a potential photocatalyst in solar driven photo degradation of Methylene Blue (MB) dye.

## **2. MATERIALS AND METHODS**

### **2.1 Materials**

Polycrystalline Si End-of-life PVP were provided by POLYECO S.A. Silicon (100) p-type wafers were obtained by Sigma-Aldrich. Copper (II) sulfate 5-hydrate (99%), hydrogen fluoride (48%), oxygen peroxide (30%), nitrates of silver (99.8%) and acetone (99.5%) were obtained from Panreac

– AppliChem. Nitric acid (65%) was obtained from Honeywell - Fluka. Methylene blue powder with a purity of 95% was used without further purification.

## 2.2 Silicon Recovery

The PVP was cut into pieces and placed in a furnace in porcelain crucibles at 550 °C for 30 min to remove polymer sheets, ethylene vinyl acetate (EVA). The resulting mixture of Si flakes, glass, electrodes and ash was separated in a trommel screen (Figure 1). The fraction containing Si flakes was washed with deionized water and acetone to remove ash and residues, followed by 4N HNO<sub>3</sub> treatment shaken at 200 rpm for 24h in order to obtain metals in solution (Si) flakes from metals. The samples were also treated with 10% w/w HF aquatic solution for 3h to remove Anti-Reflective Coating (ARC), Al coating and oxides from their surface. Both acid treatments were performed at a 5% w/v solution: 5g of Si flakes. Finally, the flakes were dried and ground.



**Figure 1.** Silicon flakes, glass and electrodes separated after thermal treatment

## 2.3 Modifications on recovered Silicon

The first process is a two-step Ag assisted chemical etching, which aims to create high surface area NanoWire structures on Si. In the first step Si powder was immersed into a 4.6 M HF aquatic solution containing 0.03M AgNO<sub>3</sub> for 3 minutes at 50 °C in order to deposit Ag on the surface of the sample. The second step involved etching in a 4.6M HF containing 0.5M H<sub>2</sub>O<sub>2</sub> at 50 °C for 3 min. After the etching Ag particles and Si oxides were removed from the sample's surface using 30% w/w HNO<sub>3</sub> and 10% w/w HF aqueous solutions for 5 min and 1 min respectively. Finally, the samples were rinsed with deionized water and dried at 105 °C for 24h. Adding metals on the semiconductor's surface creates a Schottky barrier that acts as an electron trap. This barrier inhibits the recombination of photo-generated electron-hole pairs assisting the photocatalytic mechanism. Thus, the second process, metal doping, is a simple chemical deposition in HF solutions that contain metal salts. Specifically, the deposition of Ag and Cu on the etched Si surface was carried out in 1.4M HF aquatic solutions for 2 min at room temperature containing 0.02M AgNO<sub>3</sub> and 0.14M CuSO<sub>4</sub>·5H<sub>2</sub>O respectively.

## 2.4 Photocatalytic experiment

The MB solution with initial concentration of 10<sup>-5</sup>M was prepared by dissolving MB powder in deionized water under magnetic stirring at room temperature for 10 min. The photocatalytic degradation was carried out by dispersing the photocatalyst's powder into a 500mL aqueous

solution of MB under stirring. Dispersed photocatalyst was allowed 30 min prior irradiation to achieve equilibrium. At  $t = 0$  min, the concentration was measured in order to determine the adsorption on the catalyst surface and the new value was considered as the initial concentration  $C_0$ . The solution was then irradiated with simulated solar light from a 150W Xenon arc lamp (KARL-BRIEDEN) immersed in the reactor (Figure 2) using an immersion tube for 90 min. The photocatalytic performance was measured by the decay of the characteristic absorption peak of MB at 665 nm every 10 min.



**Figure 2.** Photoreactor set up by Peschl Ultraviolet GmbH, Mainz -Germany.

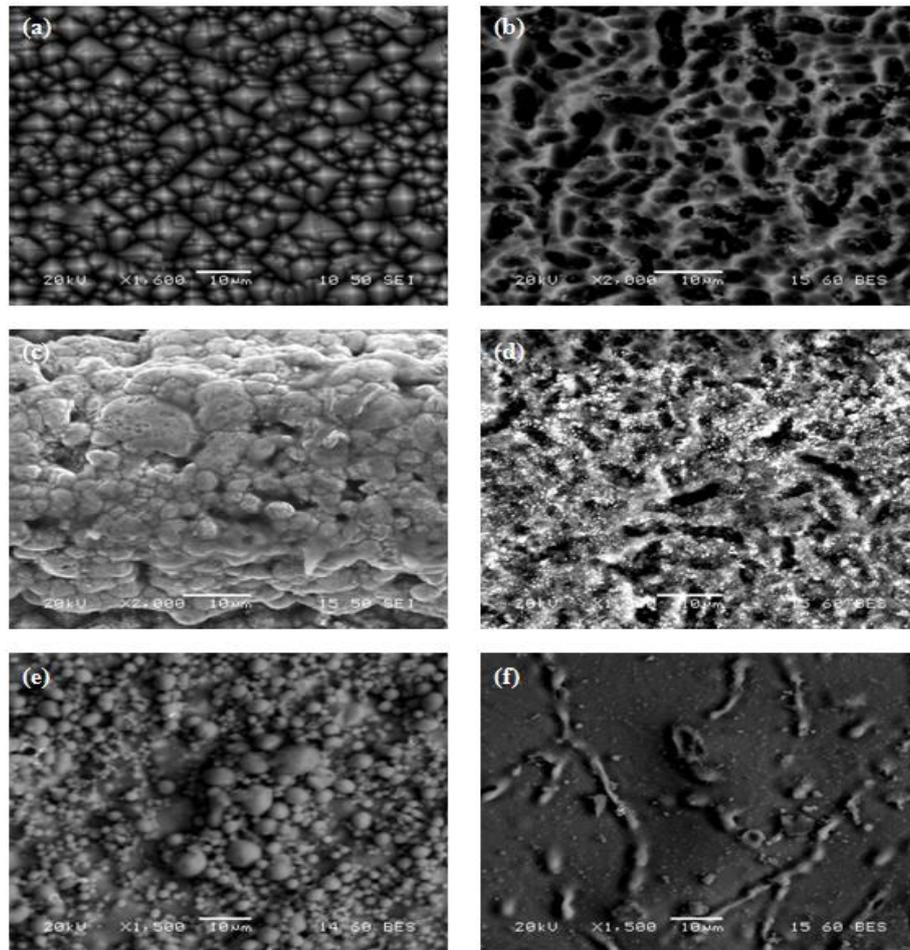
## 2.5 Characterization

The morphology of the samples was examined by SEM using a Jeol 6380 L V Scanning Electron Microscope. Experimental conditions involved 20 kV accelerating voltage, using both backscattered and secondary electron detectors. Spot chemical analysis of the sample particles was carried out by an Oxford INCA Energy Dispersive Spectrometer (EDS) (not shown) connected to SEM. X-ray diffraction spectra were obtained by a BRUKER D8 ADVANCE diffractometer in a powder sample. Resulting diffraction peaks were identified through the software database. The absorption spectra of MB solutions were measured using a HACH LANGE DR6000 UV-vis spectrophotometer.

## 3. RESULTS AND DISCUSSION

### 3.1 Morphology after cleaning

In Figure 3 SEM images of recovered Silicon flakes before and after the cleaning process are presented. Comparison of Figures 3a, 3b and 3e, 3f indicates that HF treatment efficiently removed both the ARC from the front side and the Al coating from the back side of the Si flake. In figures 3c, 3d it can be observed that HNO<sub>3</sub> removed Ag electrode from the front side, although few residues still existed. Figures 3b and 3d show that pores were formed in the front side after the etching of ARC and this might affect the direction of the following Ag assisted chemical etching process.



**Figure 3.** SEM images of recovered polycrystalline Si flakes before cleaning (a, c - front, e - back) and after cleaning (b, d - front, f - back).

### 3.2 Modifications on recovered Silicon

The method employed to elaborate the recovered Silicon into a potential photocatalyst is a two-step Ag assisted electroless chemical etching (Brahiti N. et al, 2012; Chartier C., 2008; Chiou A. et al, 2013). The process proved to be efficient in commercial (100) monocrystalline Si wafers producing Si Nano-Wires and in this work, it is tested if it is possible to function on recovered polycrystalline Si powder from end-of-life PVP. In addition, a comparison is made with commercial (100) p-Si wafers that are ground and have undergone the same treatment.

During the first step of the process, Ag particles are deposited on Si surface in the HF / AgNO<sub>3</sub> solution. These particles are reduced by electrons from neighboring Si atoms, producing SiO<sub>2</sub>, which is dissolved by HF; this way the surface is etched beneath the deposited Ag, as described by equations (1) - (4).



In the second step, the sample is immersed in an HF / H<sub>2</sub>O<sub>2</sub> oxidizing solution. The etching rate is relatively slow during the first step, but in the presence of H<sub>2</sub>O<sub>2</sub>, Ag particles are oxidized, improving the etching rate according to Equations (4) and (5), (Chiou A. et al, 2013).

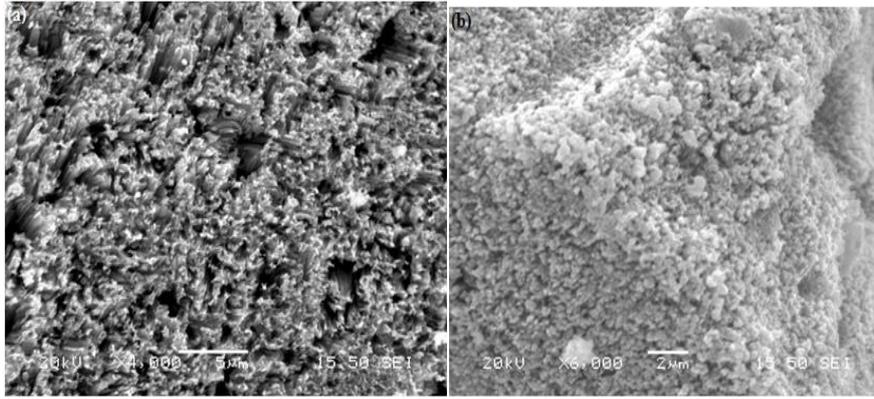


The photocatalytic efficiency of Si Nano-Wires has been proved to be improved by deposition of precious metals on their surface (Brahiti N. et al, 2015). Reports indicate that Cu and its oxides can also improve their photocatalytic activity (Naama S. et al, 2016). Since Ag and Cu are metals that exist in crystalline Si PVP in the form of electrodes that can be recovered through hydrometallurgical processes, it is examined if they can be used to improve the modified Si photocatalyst in the context of a cyclical process. Equations (6) and (7) describe the cathodic reactions that take place in the HF / AgNO<sub>3</sub> and HF / CuSO<sub>4</sub> solutions respectively (Naama S. et al, 2016).



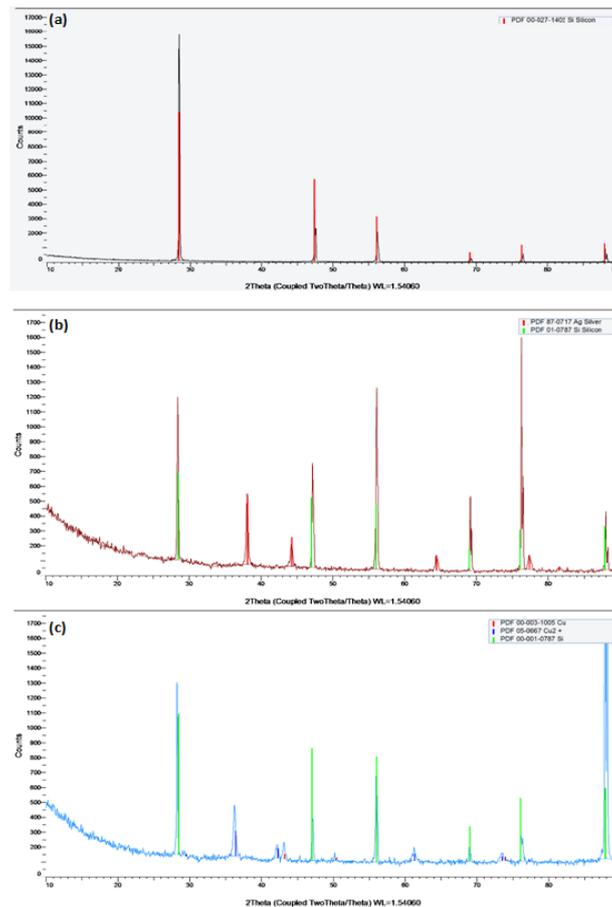
### 3.3 Morphology after modification

SEM images of modified Silicon powder using Ag assisted chemical etching and doping with Ag and Cu are presented in **Figure 4**. Examining Figure 4a, pits and wire bundles can be observed. The agglomeration of the wire tips observed is attributed to Van Der Waal forces (Chiou A. et al, 2013; Naama S. et al, 2016). Etching has not been homogeneous and vertical due to the various crystallographic orientations of the polycrystalline powder. Etching appears limited because it is oriented preferably in (100) plane, since Si atoms on (100) planes have two covalent bonds connected to the substrate while (111) and (110) planes are much denser with more than two bonds (Brahiti N. et al, 2018; Wu S. L. et al, 2012). Those dense planes are dominant in recovered polycrystalline Si according to the XRD scan of Figure 5a, leading to slow etching rates. An Ag film was partially formed on the etched surface, Figure 4a and a thin layer of Cu totally covered the etched Silicon's surface, (Figure 4b). The latter might prohibit irradiation to reach the photocatalyst's surface, potentially lowering its effectiveness.



**Figure 4.** SEM images of recovered polycrystalline Si after etching and doping with (a) Ag, (b) Cu.

Figure 5 displays XRD scans of PV Polycrystalline recovered Silicon. In Figure 5a the characteristic peaks of polycrystalline silicon at  $28.4^\circ$  (111),  $47.3^\circ$  (220),  $56.1^\circ$  (311),  $69.1^\circ$  (400),  $76.4^\circ$  (331) and  $88^\circ$  (422) (National Bureau of Standards, 1976) after cleaning indicate, as aforementioned, that (111) and (110) are the dominant crystallographic planes of the sample. Comparing distribution of planes in Figures 5a - 5c there is a notable decrease of the initially dominant planes' ((111) and (110)) intensity after etching and doping. Specifically, in the case of Ag doping only (311) plane has a slight increase whereas in the case of Cu doping there is a slight increase in (422). Cu cations observed in Figure 5 are attributed to Copper oxides possibly created during drying of the sample, since copper can be oxidized by air.



**Figure 5.** XRD scans of recovered polycrystalline Si (a) after cleaning, after etching and doping with (b) Ag, (c) Cu.

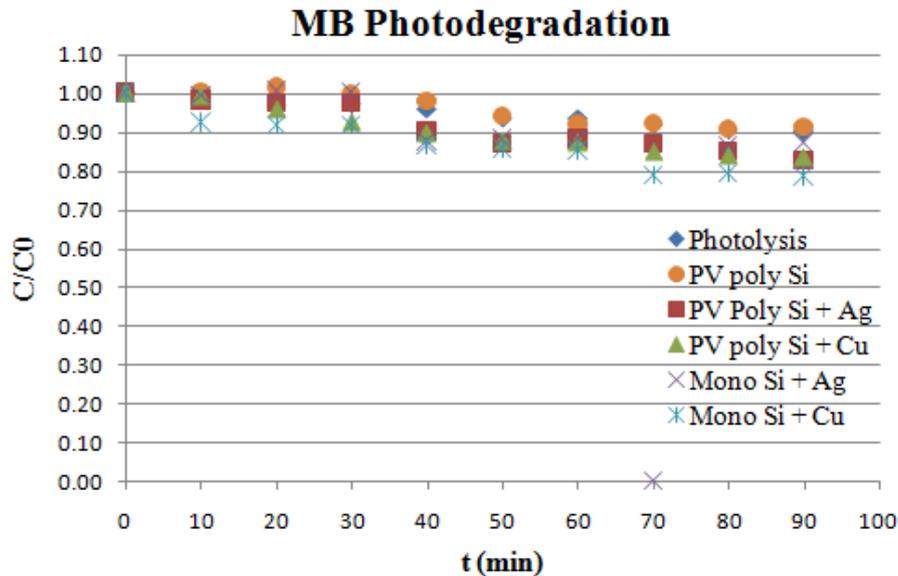
### 3.4 Photocatalysis

Catalytic activity of EoL PVP recovered polycrystalline Si powder modified by Ag assisted chemical etching and metal doping was examined and compared to that of a commercial (100) monocrystalline Si wafer subjected to the same modifications. The ratio of the concentration (C) to initial concentration ( $C_0$ ) after 90 min of solar light simulated irradiation using the prepared photocatalyst is displayed in Figure 6 and the corresponding results are reported in Table 1. Degradation by 10% is observed in the absence of a photocatalyst, whereas all the prepared samples exhibit only a slight increase in photocatalytic activity, up to 21.4% for monocrystalline Si doped with Cu. In the case of the etched sample with no metal doping there is no enhancement of photocatalytic activity. Grinding of the (100) wafer before etching has affected significantly the crystallographic orientation in which the etching occurred leading to a behavior similar to that of the aforementioned recovered polycrystalline sample, explaining in turn their similar photocatalytic behavior.

It is worth noting in Table 1 that the samples during the 30 min that are dispersed in the absence of irradiation adsorbed 15.7 - 23.8% of the MB, contributing more than photocatalytic degradation to the total reduction of 29.4 - 36.6%, with exception of non-doped, etched, polycrystalline Si, which displayed poor performance. Results indicate the pollutant is adsorbed in the catalyst's surface but the degradation rate is quite slow. Despite metal doping being necessary to achieve increased photocatalytic performance, overloading semiconductor surface with metals, as discussed in Figure 4, could limit photo-excitation of photocatalyst's electrons. Values obtained by end-of-life PVP recovered Si are very close to those of the purchased wafer, indicating that field aging does not seem to affect the photocatalytic capacity of the recycled semiconductor, instead the processes deployed to clean and modify it as well as their parameters seem to greatly affect the final product.

**Table 1.** Percentage of: adsorption before irradiation, photo degradation and total pollutant reduction.

<b>Sample</b>	<b>Adsorption %</b>	<b>Degradation %</b>	<b>Total Reduction %</b>
<b>Photolysis</b>	-	10.0	10.0
<b>PV poly Si</b>	5.5	8.8	13.8
<b>PV poly Si + Ag</b>	20.4	17.2	34.1
<b>PV poly Si + Cu</b>	15.7	16.3	29.4
<b>mono Si + Ag</b>	23.8	12.8	33.6
<b>mono Si + Cu</b>	19.3	21.4	36.6



**Figure 6.** MB concentration degradation under solar light irradiation as a function of time without catalyst and with heterogeneous Si photocatalysts.

#### 4. CONCLUSION

High purity Si was obtained from end-of-life c-Si PVP by the proposed process which was etched and metal doped through simple, electroless, chemical methods. The resulting material was tested in heterogeneous photocatalysis of MB photodegradation under simulated solar light irradiation. Structural analysis through SEM and XRD alongside with photocatalytic results indicate that the polycrystalline structure of the ground material decelerates the etching procedure causing limited nanowire development. Enhancement with Ag or Cu doping was required to achieve a slight increase in photocatalytic capacity under solar irradiation. Field aging of Si in PVP did not seem to affect the process. Based on the results obtained in this work, Si and metals like Ag and Cu recovered from end-of-life PVP can be reused to fabricate a photocatalyst for solar light applications, although it is necessary to improve the properties of the material or its photocatalytic capacity. In order to minimize the environmental impact, less aggressive recovery and treatment practices should be investigated to make the process more sustainable overall.

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