

Use of $\text{SnO}_x\text{:F}$ in the Recycling of Silicon Solar Cells

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Amongst the many parts of a silicon cells photovoltaic module, silicon is the most important and expensive constituent. Thus, research on silicon recycling from damaged cells can lead to economic and environmental benefits. In this work, the broken silicon cells were tailored to function along with the fluorine-doped tin oxide as the transparent electric conductors. The broken silicon cells were analyzed by the current density versus voltage plots, together with the Mott-Schottky, X-rays diffraction and fluorescence analysis. Under light, the damaged cells sandwiched between the two transparent electric conductors presented photovoltaic effect. However, such effect was not obtained after the removal of the antireflection layer due to the destruction of the n-type layer as demonstrated by the Mott-Schottky analysis. The X-rays diffraction revealed samples rich on silicon atoms and the presence of aluminum atoms as impurity.

Keywords: *Silicon cells, Recycling, Photovoltaic.*

1. Introduction

The conversion of solar energy into electricity by photovoltaic cells is an alternative to produce energy, besides being a cleaner path to energy production, when faced with the fossil fuels option. Amongst the photovoltaic technologies, the silicon semiconductor has dominance on the market; however, its limited lifetime means that silicon photovoltaic modules will become electronic waste ¹.

The recycling of photovoltaic modules is important for the recovery of materials, reduction of costs and environmental impacts. Yet, the recycling is not economically advantageous without government incentives ². For this reason, many damaged modules have been rejected into the environment without any recycling process, causing environmental negative effects ³. In opposition to others types of industrial waste, the photovoltaic waste is unique because there is a longer time between production and discard, approximately 20 years ^{4,5}.

The silicon is the more important constituent in photovoltaic modules and is responsible for about 60% of the modules total cost ³. The recovery of the silicon when the modules suffer damage or after the end of its useful life has both environmental and economic benefits ^{4,5}. Beyond the silicon, the modules can contain toxic materials such as Pb, Cd, Cr and Bi, which are harmful to humankind ³. The chemical treatment is the commonly used process in the recycling or removal of impurities and silicon recovery ⁴.

As an alternative to the silicon technology, other types of materials, generally called transparent conductor oxides (TCOs), have been investigated in the assembly of silicon

free photovoltaic cells ⁶⁻⁸. Thus, the aim of this work was to establish a relationship between TCOs and silicon cells for the studying of the photovoltaic behavior of the system TCO / SAMPLE / TCO. The system was constructed using fractions of damaged silicon cells as SAMPLES and TCOs of fluorine-doped tin oxide ($\text{SnO}_x\text{:F}$). Experiments of electrical behavior nature, X-rays diffraction, X-rays fluorescence and Mott-Schottky analysis were carried out with the purpose of understanding the system.

2. Materials and Methods

Silicon photovoltaic cells that were damaged during the assembly of didactic photovoltaic modules to be used in the practice classes of the Renewable Energy Engineering course at Federal University of Ceará were used as raw material. The blades with conductors films of $\text{SnO}_x\text{:F}$ produced in the Laboratory of Thin Films and Renewable Energy ^{9,10} were used as transparent electric conductors substrates.

Initially, the assembly of the system TCO/SAMPLE/TCO was made in a sandwich configuration by the cells fractions (SAMPLE) between two TCOs, using a clip to keep the materials together. Afterwards, an optimization in the assembly was made adding solid electrolyte, from a solution of chitosan/0.05g LiClO_4 , between the TCOs conductor surfaces and the SAMPLE photoactive area.

From the system TCO/SAMPLE/TCO (1.0cm x 0.7cm SAMPLE dimensions), fotokit (Metrohm) equipped with white light LED connected to Potentiostat/Galvanostat PGSTAT302N (Metrohm), using the program NOVA 1.10

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(Metrohm), provided the distribution profiles of current density *versus* voltage. The system was under the white light with intensities of about 0.025, 0.050, 0.075 and 0.100 W/cm².

Fractions of damaged cells (SAMPLE) were submitted to manual removal by sandpaper 1200. After this process, an electrochemical cell with three electrodes (work electrode: SAMPLE without antireflection layer and area of 0.50 cm²; counter electrode: platinum plate and area of 6.00 cm²; reference electrode: Ag/AgCl), immersed in aqueous solution of 1M KCl, was used for Mott-Schottky analysis with experimental conditions such as scanning frequency range of 100mHz to 0.1 MHz and potential range of - 0.9 V to + 0.9 V.

Before the characterization by X-rays diffraction and fluorescence, the SAMPLES (with and without antireflection layer) were converted to powder by a mortar. The cleaning of the mortar was made before and after each process. The cleaning was carried out crushing pieces of glass inside the mortar with the aid of a pistil. Experimental conditions were: Diffractometer (Model Xpert Pro MPD - Panalytical): Co-K α , $\lambda = 1.789\text{\AA}$, 40kV, 40 mA, hole of 1/2 and scanning 2 θ between 10 $^\circ$ and 100 $^\circ$. The ZSX Mini II - Rigaku equipment was used for quantification of elements from fluorine until uranium by X-rays fluorescence.

3. Results and Discussion

The photovoltaic cells electrical behavior was investigated under light and employed as a tool to analyze the quality of the cells¹¹⁻¹⁶. The efficiency of light intensity conversion into electricity is the key parameter in the photovoltaic cells characterization. A general criterion to analyze the efficiency (η) is the use of graphs describing the current density versus voltage, where the values of the open circuit voltage (V_{oc}), fill factor (FF) and short circuit current density (J_{sc}) can be extracted. Figure 1 has the profile of the TCO/SAMPLE/TCO system without the addition of Chitosan/ LiClO₄ electrolyte (system I).

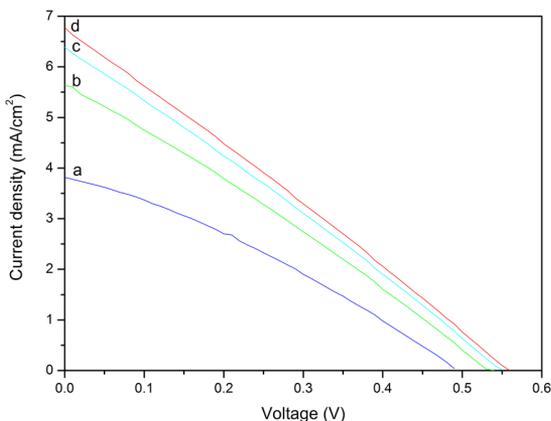


Figure 1. Current density *versus* voltage of system I: a) 0.025 W/cm², b) 0.050 W/cm², c) 0.075 W/cm² and d) 0.100 W/cm².

A standard curve of a photovoltaic cell has an "elbow" format. The loss of the "elbow" can be caused by high ohmic resistance or high charge recombination¹⁵. The loss of the "elbow" format (system I) was probably due to a combination of two factors: i) a greater surface area with higher gaps of air between conductive surfaces of TCOs and the photoactive surface of the SAMPLE, increasing the contact resistance and ii) charges recombination due to the imperfect contact between surfaces and the air gaps. Those facts had direct influence in the low FF, which decreased the efficiency of the system (Table 1).

A solid electrolyte film of Chitosan/LiClO₄ was added, between the conductive surface of TCO and photoactive area of SAMPLE (system II), to mitigate the previously mentioned effects. The open circuit voltage (V_{oc}), factor form (FF), short circuit current density (J_{sc}) and efficiency (η) for both systems are shown in Table 1. In Figure 2, it is exposed the obtained profiles for system II. Analyzing the current density *versus* voltage profiles, only for the radiation about 0.025W/cm² there is a tendency to form a similar curve to the one found in a standard photovoltaic cell.

The loss of the "elbow" format (Figure 2), as the radiation increased, was caused probably by the solid electrolyte electrical saturation or the chitosan degradation, or both. The low value of the current density can be due to a short photoactive area of the SAMPLE or to the damage of the SAMPLE during the assembly of the systems. However, as it is inferred by the data in Tables 1, the photovoltaic parameters are still dependent on the light intensity, since the TCO of the SnO_x:F allows the light to reach the photoactive area.

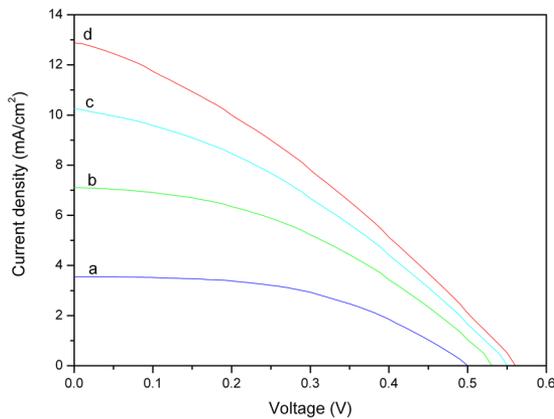
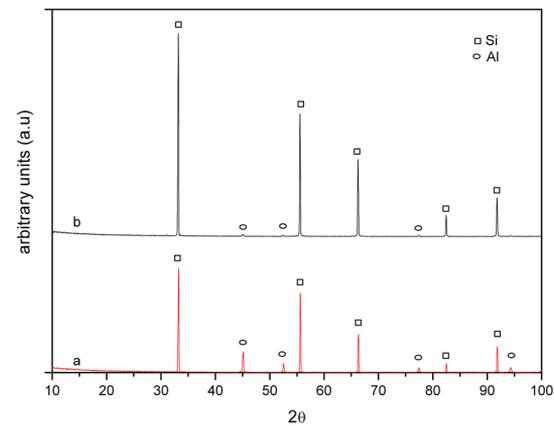
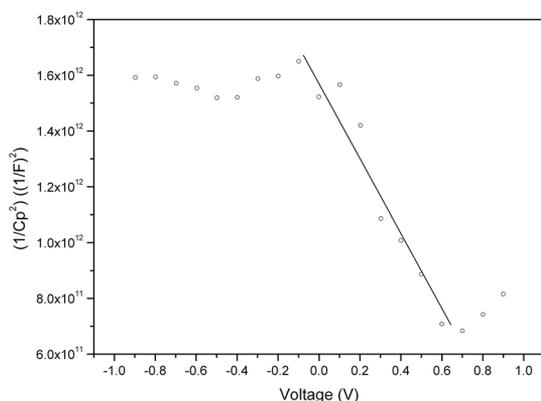
Possibly, the high contact resistance between the surface of the TCO and the sample was responsible for the low efficiency values (Table 1). The addition of the electrolyte film tends to diminish the influence of contact resistance, but, for high values of light intensity, the electrolyte loses efficiency and the charge recombination dominates the system. However, the obtained data permits to infer that TCO has potential to be included in the recycling cycle of silicon photovoltaic cells.

The previously data were only for samples with antireflection layer. This way, samples without antireflection layer were placed between the TCOs of the SnO_x:F and were tested under the same light intensity conditions previously cited. However, the photovoltaic effect was not observed for this system. To understand this behavior, samples with and without antireflection layers were characterized by X-rays diffraction and fluorescence. In addition, after the removal of the antireflection layer, the Mott-Schottky analysis technique was used.

The X-rays diffraction and fluorescence analysis have been used to identify the components of photovoltaic modules made with silicon cells^{1,2}. Figure 3 shows the X-rays diffractograms for samples with and without antireflection layer, respectively. First of all, it came to attention the presence of silicon (Si)

Table 1. Photovoltaic parameters for both systems.

	System I				System II			
	V_{oc} (V)	FF	J_{sc} (mA/cm ²)	η (%)	V_{oc} (V)	FF	J_{sc} (mA/cm ²)	η (%)
0.025 W/cm ²	0.49	0.31	3.82	2.34	0.50	0.50	3.55	3.52
0.050 W/cm ²	0.54	0.27	5.64	1.65	0.53	0.42	7.11	3.13
0.075 W/cm ²	0.55	0.27	6.39	1.25	0.55	0.36	10.25	2.68
0.100 W/cm ²	0.56	0.26	6.78	1.00	0.56	0.33	12.88	2.35

**Figure 2.** Current density versus voltage profiles of system II: a) 0.025 W/cm², b) 0.050 W/cm², c) 0.075 W/cm² and d) 0.100 W/cm².**Figure 3.** X-rays diffraction profile for samples: a) with antireflection layer and b) without antireflection layer.**Figure 4.** Characterization by Mott-Schottky.

and aluminum (Al) in both samples. The removal of the antireflection front and conductive back layers reduces the aluminum presence, but not completely (Figure 3b).

In addition to the X-rays technique, the fluorescence method was used as an auxiliary tool. The fluorescence data demonstrate that after removing the antireflection and aluminum electrical contact layers the purity of the silicon sample was about 98%. The impurity caused by the presence of the Al atoms was identified by X-rays diffraction was also detected in X-rays fluorescence analysis. The presence of Al atoms can be due to the weak removal process or because Si had been obtained from the aluminothermic reduction. The silicon gained by aluminothermic reduction from the quartz sand (SiO₂) has a significant amount of impurities¹⁵.

In a silicon photovoltaic cell, the solar energy conversion is only possible because the presence of the p-n junction¹⁵. The n-type is obtained by the addition of pentavalent atoms into silicon and the p-type by the addition of trivalent atoms. But, as the DRX and FRX were not capable to determine if the samples with and without antireflection layer had p-n junction, the Mott-Schottky technique was used to complement the obtained data.

The characterization by Mott-Schottky plots allows verifying if the material is a semiconductor of the p-type or n-type from the plot of the reciprocal capacitance square versus applied voltage¹⁷⁻²¹. Figure 4 shows the profile of reciprocal capacitance square versus applied voltage. The linear region with negative slope indicates that the silicon is a p-type semiconductor.

The Mott-Schottky technique revealed that the antireflection layer mechanical removal process used in this work was capable to extract the n-layer of the silicon cells. Thus, the removal of the n-layer, which caused the destruction of the p-n junction, explains why the TCO/SAMPLE/TCO surface was not sensitized by the light intensities. Additionally, works, investigated in this study, proposing the development of methods to deposit n-type layer, obtained from removal mechanical process, on p-type silicon have potential for future researches.

4. Conclusion

The photovoltaic effect was observed only in the OCT/SAMPLE/OCT system with broken silicon cells containing the p-n junction. But, from the obtained data, it could be

assumed that there is potential for the insertion of TCOs in the recycling cycle of silicon photovoltaic cells. Besides, the Mott-Schottky characterization identified the destruction of the p-n junction as a result of the antireflection layer removal. Additionally, the removal process of the cell antireflection layer had as collateral effect the obtaining of silicon in metallurgical degree (98% of purity).

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