Recycling rejected silicon wafers and dies for high grade PV cells
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Abstract—The recent return of the US to the Paris Climate Accord, massive increase in solar panel production and energy storage solutions has resulted in pressure on supply for solar cell materials and recycling of panels installed in the 90’s and beginning of the 2000’s which have reached their end of life. In this work we focus on recycling silicon wafers and dies by stripping previous structures from the die using potent acids after which its base material is characterized and binned. We demonstrate the process for silicon p-type substrates where n-type doping is attained by using a simple solution of phosphoric acid, which is diffused into the substrate using a furnace thus creating a PN junction. In case the substrate is n-type it could be replaced by boric acid. This is followed by deposition of a conductive antireflective coating, bus bars and rear wafer metal coating. The initial demonstrated laboratory results indicate the feasibility of recycling wafers using simple low cost standard industrial methods.

Index Terms—PV, Silicon Recycling, solar cell recycling

I. INTRODUCTION

Renewable energy sources for electrical energy generation has become an increasing concern of most countries due to the environmental impact associated with the use of fossil fuels. In addition, reducing a countries dependence on fossil fuel further increases its self reliance and improves a nations balance of trade, thus boosting its economy. Some countries have initiated programs increasing economic incentives to companies and individual households for developing, improving efficiencies or increasing capacity of renewal energy sources. In a recent report [1] the International Renewable Energy Agency estimates the current cost of PV electrical generation at optimal locations, is 30 USD/MWh and predicts that by 2022 it will reach prices that are comparable to the lower end of fossil fuel costs. The various steps of manufacturing solar panels from raw materials is energy intensive and includes the use of large amounts of water and toxic chemicals. Therefore, expecting the rapid growth of silicon use for solar energy generation since the late 90’s of the previous century, research was conducted for initiating environmentally benign solar cell manufacturing [2]. The predicted increase in solar panel production and installations [1] and the 25 year life expectancy of a solar panel has initiated various End of Life (EOL) management programs [3], [4], [5], [6]. The rapid growth of solar energy generation having a capacity of 222 GW in 2015 and expected to rise up to 4,500GW by 2050 [6] will result in an increase of PV panel waste. The dominant technology which has developed rapidly since the 70’s of the previous century is the photovoltaic solar cell technology. Since the mid 90’s of the previous century, due to the leading industrialized countries governmental policies, silicon solar photovoltaic energy generation has become commercially viable. Most silicon solar cells are based on single crystal silicon (monocrystals) grown by the Czochralski technique and polycrystalline silicon casting. While there are more efficient materials for photovoltaic energy generation than single crystal silicon, they are not commercially viable for large area application. In 2015, crystalline silicon had approximately 93% of the market share of solar modules, with 24% going to the monocrystals and 69% going to the polycrystalline solar cells [7]. The larger market share of the polycrystalline solar cells is due to the significantly lower production costs, but this comes at a price of lower efficiency compared to the single crystal silicon. For most uses, where space or weight are not a concern the polycrystalline solar cells are appropriate. In places where space and weight are restricted, single crystal silicon, due to their higher efficiency are better suited. When dealing with monocrystal based photovoltaic cells, higher

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quality crystals result in higher conversion efficiency, but it comes at an economical price. Integrated circuit grade silicon is probably the most efficient base material for fabricating silicon solar panels due to its low defect density, but the lengths and costs for obtaining it, is prohibitive for its wide application in terrestrial energy generation, where the capital investment per Watt is the key driving force. In order to reduce costs of solar grade silicon monocrystals with a much higher level of defects and impurities are being introduced [5, 4]. Another concern which needs to be addressed is recycling of the panels when they reach their end of life (EOL). In this respect, rare metals and the silicon cells retain their value and should be salvaged using various techniques [5], [4]. One untapped resource of high quality near defect free silicon, are rejected dies and wafers. With an estimated 90% yield during full production [9] we are left with 10% rejected dies. Currently, major fabs are producing integrated circuits with wafer diameters larger than 400 mm. This provides an abundant supply of silicon for producing high quality solar panels. In this article we will present a relatively environmentally friendly method for recycling silicon from the rejected wafers. In a following article, we will present a method for assembling an efficient solar panel from the salvaged wafers.

II. MATERIALS PREPARATION

This work based on experiments conducted by our groups, suggests a method for recovering rejected silicon dies, wafers and residual silicon which resides on the rims of the processed wafers. In order to keep the text clear, we shall generally refer to all the recovered silicon as dies. The process results in PN photovoltaic structures composed of $In_2O_5Sn/n-Si/p-Si$ ITO, $n$-type silicon, $p$-type silicon.

A. Stripping

The dies were etched in $HF$ after which the conductivity and type were measured. This assists us with defining the type of base material to deposit prior to diffusion (Phosphorous/Arsenic or Boron/Gallium). Similar die types are binned together. In this article we shall describe the process for a $p$-type substrate. Standard cleaning recipe was applied to the dies with an optional oxide strip using $HF$ between the first step (SC-1) and the second step (SC-2). When using those steps, the rare metals can be recovered using the processes described in [4].

B. Donor/Acceptor diffusion

The samples were spin coated using a solution of 1:1 ratio of phosphoric acid and ethanol ($H_3PO_4 : C_2H_5OH$). If the substrate is n-type one can replace the phosphoric acid with boric acid ($H_3BO_3$). The samples were place in a furnace with an ambient atmosphere pre-baking them at a temperature of $150^\circ C$ for 10 minutes drying the newly applied coating. The temperature was raised to a temperature of $900^\circ C$ for 6 hours slowly cooling it to a level of $600^\circ C$, this procedure allows for proper diffusion while reducing destructive glass phases. Dopant concentration was evaluated using ICP-OES [10] which can trace down to approximately $N_d \sim 10^{14}[cm^{-3}]$.

C. Transparent Conductive Oxide coating

Although much work was conducted in the past 20 years, on the topic of environmentally sustainable, indium free Transparent Conducting Oxides (TCOs), for example [11], [12], in this work we used ITO with the standard application methods.

Transparent conductive films of $In_2O_5Sn$ were deposited by RF sputtering using an ITO ceramic (90 wt % $In_2O_3$, 10 wt % $SnO_2$). Substrates were cleaned using ultra pure deionized water isopropyl alcohol and acetone in an ultrasonic cleaner bath for 20 minutes. This was followed by drying using a flow of nitrogen gas. The RF sputtering chamber was purged with Ar and a working pressure of 100 mTorr was maintained. Surface oxidation was removed in the pre-sputtering stage. A film of approximately 250nm was deposited on the surface of the materials with the procedure tested using microscope slides prior to the actual deposition. The deposited film was annealed in a tube furnace in an oxygen saturated environment supported by a 0.5 sccm $O_2$ gas flow at a temperature of $400^\circ C$. Optical transparency of the $In_2O_5Sn$ films was measured in the UV/VIS using a Jasco V-730. Additionally, it was used in reflective mode to measure the film thickness using the SLM-907 specular reflectance accessory. Figure illustrates the transmission of the glass substrate and the ITO deposition on the glass substrate.
Figure 1. Optical transmission of the ITO on a glass substrate compared to the transmission of the glass substrate.

The optical transmission of the ITO excluding the glass substrate in the 420-1100nm range is given in figure 2.

Figure 2. Optical transmission of the ITO excluding the glass substrate

As can be seen in figure 2, the optical transmission at 500nm is 93.6% which compares favorably with published data. Inkjet printing of the collector bus bar and finger aluminum electrodes were tested with inconclusive results. As a result we opted for the traditional method of applying aluminum electrodes by thermal evaporation deposition.

A four-point measurement of the $In_2O_5Sn$ deposited layer resistance was conducted before and after the diffusion validating the resistivity of the layer. Figure 3 illustrates the resistivity obtained using three different samples from three different batches.

Figure 3. Resistivity of the ITO deposited layer of three different batches as extracted from a four point measurement

The resistivity results correspond with published data [14]. A hot probe experiment identified the type of semiconductor layer after the diffusion process a detailed account of the measurement can be found in [15]. During the various processes the surface structure was studied and documented using a metallurgical microscope.

A standard photovoltaic structure with a thin emitter fabricated at the top surface using a p-type substrate is demonstrated in figure 4.

EXPERIMENTAL RESULTS
The wavelength dependent short circuit current is approximated by

\[ J_{SC}(\lambda) = \frac{q\phi(\lambda)(1 - R_f)\alpha L_p}{\alpha^2 L_p^2 - 1} \Phi_e \quad (1) \]

with \( \Phi_e \) presenting an emitter factor which depends on doping levels and depth of doping:

\[ \Phi_e = \frac{S_p L_p}{D_p} + e^{-\alpha h_e} \left( \frac{S_p L_p}{D_p} \cdot \cosh(h_e/L_p) + \sinh(h_e/L_p) \right) \]

\[ - \alpha L_p e^{-\alpha h_e} \}

\[ \Phi_e = \frac{S_p L_p}{D_p} \sinh(h_e/L_p) + \cosh(h_e/L_p) \quad (2) \]

where:

\( \phi(\lambda) \) phonon flux \([\text{photons/sec-m}^2]\)

\( R_f \) reflectance of the active surface of the cell

\( \alpha \) absorption coefficient of the semiconducting material \([\text{cm}^{-1}]\)

\( L_p \) diffusion length of the minor charge carriers in the emitter \( L_p = \sqrt{D_p \cdot \tau_p} \quad [\text{cm}] \)

\( S_p \) surface recombination velocity for minor charge carriers \([\text{cm/s}]\)

\( h_e \) depth of the emitter \([\text{cm}]\)

\( D_p \) diffusion coefficient of minor charge carriers in the emitter \([\text{cm}^2/\text{s}]\)

\( J_{ph}(\lambda) \) the photon flux current is referred to as the photon flux which is the current given that every photon generates an electron hole pair. In order to get a grasp of the behavior of the short circuit current (equation (1)) one has to observe that the emitter factor (equation (2)) has the form

\[ \Phi_e \approx C - Be^{-t} \quad t \to \infty \]

In which \( C \) is a constant depending on the minor charge carrier attributes \((L_p, D_p)\) which are donor density dependent, the depth \( h_e \) and the surface recombination velocity \( S_p \). The surface recombination velocity depends on both the surface defects and doping levels. For a passivated surface the doping level is \( N_s \approx 10^{18} - 10^{19} \). The surface recombination velocity is given by \( S_p = 10^{-16} N_s \)

Figure 5 shows the calculated short circuit current as a function of the depth of the emitter.
This happens when the surface of the silicon and the applied coating are at a distance of $\lambda/4$, or

$$n_c d = \lambda/4$$

a further improvement (minimization of reflection losses) is obtained when the coating is the mean of the refractive indices i.e.

$$n_c(\lambda) = \sqrt{n_{air} \cdot n_{Si}}$$

one such material that is both transparent and which provides an appropriate solution over most of the visible range is ITO. Figure 6 displays the refractive index and the square root of the refractive index of the silicon compared to the refractive index of ITO.

![Figure 6. Comparison between the index of refraction of ITO and the square root of $n_{Si}$ and $n_{air}$](image)

Our peak wavelength is about 500nm and according to the graph $n_{ITO}(500) \approx 2.11$ thus a deposition thickness of 125nm is appropriate for our purpose. As was seen in figure 3 the low resistivity of the ITO film on our samples accommodates the conduction of charge to the fingers and bus bars.

### E. Post diffusion

The describe process’s weakness is that, to date, it is not a completely controlled process. While during the classic method the flow of the dopant gas is controlled, some of the spin coated material evaporates and we need to resort to ICP-OES measurements in order to estimate dopant concentration. The resistivity of the doped layer was measured using a four point measurement as shown in figure 7.

![Figure 7. A four point measurement of the doped (emitter) layer](image)

The resistivity result of $\sim 127 \Omega \cdot cm$ corresponds with a dopant density of $4 \times 10^{14} cm^{-3}$ [18] which was confirmed by the ICP-OES measurement which is approximately $5 \times 10^{14} cm^{-3}$ (close to the detection limit of the phosphorus). Following the resistivity characterization the I-V characteristic was measured at different temperatures. Figure 8 indicates that the material displays a regular PN junction behavior.

![Figure 8. Device I-V characteristic at several temperatures](image)

The calculated potential of the junction is 0.5 V while the actual open circuit voltage was found to be lower than 0.1 V. This is due to the high losses in this device which is in its preliminary research stages.

After depositing a 150nm ITO coating and adding the bus bar, fingers and back electrode, the photocurrent was measured under various intensities which
were controlled using a UNI-T UT383BT luxmeter. The measured illuminance was converted to irradiance based on a recent guide which tries to sort out the various conversion factors [19]. Based on their recommendation we used a \( \text{116 lux} \ T W/m^2\). Figure 9 displays the devices output power as a function of the irradiance.

\[
\begin{align*}
\text{Irradiance [W/m}^2\text{]} & \quad \text{Power [W/m}^2\text{]} \\
0 & \quad 0 \\
200 & \quad 2 \\
400 & \quad 4 \\
600 & \quad 6 \\
800 & \quad 8 \\
10 & \quad 10 \\
\eta & = 1.51\%
\end{align*}
\]

Figure 9. Device output power as a function of the irradiance

The slope of the graph shows the efficiency of the device, which is 1.51% in the above measurement.

### III. CONCLUSIONS

This work presents a viable method for recycling and re-purposing used silicon wafers for PV use. The preliminary work shows that standard stripping methods followed by a newly suggested method for diffusing dopants does provide a working PV cell. Both optical and electrical properties of the resulting device were presented. The output power density’s dependence on the incident irradiance resulted in a 1.51% efficiency, which is an order of magnitude lower than expected. As this work was intended as a feasibility study, the result shows promise. Following this work we intend to improve the efficiency of a single crystal wafer cell and extend the work for recycling polycrystalline wafers which are abundant in the ever increasing retired solar panels.

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