Ultra-low reflective silicon surfaces for photovoltaic applications

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Abstract

Silicon based photovoltaic cells still remain a mainstay in the industries due to its relatively low cost for manufacturing and implementation. A good knowledge base of the material has also been built up over the years and there is no doubt that silicon based photovoltaic cells would continue to lay the basis for renewable energy for many years to come. However, it is widely known that conventional silicon photovoltaic cells have relatively lower power conversion efficiencies as compared to its next generation counterparts. This is partly due to the high optical losses on surfaces, resulting in poor harvesting of energy from incident light. In this work, an ICP process was developed to fabricate ultra-low reflective silicon surfaces for photovoltaic applications. An Ar + H\textsubscript{2} feedstock was used to texture nanocones on the surface of silicon wafers, reducing the reflective losses and forming a high quality pn junction simultaneously. Reflectivity of the samples were characterised with a Zolix SCS10-X150-DSSC UV-Vis spectrometer with an attached integrating sphere, while the photovoltaic properties were measured with a PV characterization suite from Sinton instruments. The low reflectivity with promising electronic properties of the processed materials shows propitious potential for applications in the field of photovoltaics.

Keywords: Plasma ; Materials processing; Silicon; Nanocones; Low-reflectivity

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1. Introduction

In recent years, there has been much concern over the continual depletion of non-renewable energy reserves such as coal and oil [1, 2]. With the rapid advancement in technology in industries bringing sophisticated digital products which consume a large amount of energy to the consumer on a personal level, the global energy crisis is becoming an increasingly relevant problem that has yet to be solved thoroughly. On the other hand, huge concern has also arisen while trying to meet the energy demands of consumers in the form of environmental degradation [3-5]. Conventional forms of energy conversion involves burning of fossil fuels which give rise to many associated problems in damage to the environment and as a result, the health of the population living in areas which are unable to mitigate the negative toxic byproducts of the conventional combustion of fuels.

Photovoltaics (PV) has received a renewed interest in recent years as a viable source of renewable energy [6]. A few reasons which can be attributed to the popular reception of PV would be its relatively well developed field of research which has seen large increments in power conversion efficiencies over the years [7, 8], as well as the small environmental footprint that it has during the process of energy conversion, harnessing just incident light from an external source, and converting it into usable energy for the masses without the need for combustion, leaving behind undesirable byproducts [9-11]. In recent years, there has been a huge paradigm shift in the designs of PV modules, with interesting novel metamaterials and tandem cells being studied and produced for high-efficiency harvesting of solar energy [7, 12, 13]. However, industries still prefer to fall back on the conventional silicon based PV modules for large-scale applications and implementation. This is due to the relatively low cost of silicon which drives down the costs of fabrication of modules, and the "cost per watt" that would be borne by the industries and eventually, the consumer. Silicon is also a mature semiconductor material and has a rich database of research in its backlog [14-16]. As such, there is no doubt that silicon based PV modules will continue to remain a mainstay in both the market as well as a key area of research in laboratories globally.

However, silicon based PV modules as compared to its next-generation counterparts, does not perform as well in terms of power conversion efficiencies (PCE). A few sources which contribute to the decreased PCE in silicon based PV modules would be optical losses [17] as well as the inability of the PV module to successfully convert the absorbed light in the material into usable light-generated charged carriers for production of a photocurrent. Bare silicon has optical losses due to reflection on the surface which amounts to about 35% of incident light [18]. To reduce optical losses from surface reflection, a common technique involving texturing [19-21] of the surface of substrates are usually employed to increase the probability for light collection in the absorber material. When photo-generated carriers are produced in the absorber layer, a high-quality pn junction is required to sweep the carriers to the different ends of the PV cell for collection and production of a photo-current. Conventional methods for incorporating these functions in PV cells involve fabrication through wet chemical processes which require copious amounts of reagents for processing, as well as a large amount of accumulated waste from washing and post process treatment of substrates [22].

In this work, a unique method of processing silicon substrates in a low frequency inductively coupled plasma (ICP) was developed for improving the optoelectronic properties of silicon substrates for PV applications. A compound feedstock of Ar and H₂ was used in a plasma discharge in an ICP reactor. Polycrystalline p-type wafers that were subjected to the discharge were found to have dense nanocone structures etched onto the surface. The nanocones were found to decrease the reflective losses to yield ultra-low values similar to that of black silicon. On top of that, exposure to the discharge also simultaneously caused a "p-to-n type conductivity conversion" (PNTCC) which resulted in a formation of a high-quality p-n junction in the material [23, 24], essential for the separation of photo-generated carriers in a PV cell. The advantages of plasma processing as compared to the conventional wet chemical processing include unprecedented control of discharge parameters to tailor the optoelectronic properties of the resulting material to suit their applications, as well as the massive reduction of unwanted toxic byproducts through treatment and washing in chemical processes. This truly makes the entire approach to utilizing PV modules
as not only a viable alternative for renewable energy, but at the same time incorporating it as an environmentally friendly source of energy from fabrication to implementation.

2. Experimental methods

A low frequency ICP reactor as shown in Fig. 1. was used exclusively in this work. The reactor is fully evacuated to a base pressure of < 10^-4 Pa with the aid of a 2 stage rotary and turbo-molecular pump set up. The reactor was constructed out of stainless steel and feature double walls which enable coolants to flow throughout the sides of the chamber. 4 portholes line the reactor radially, and enable the insertion of diagnostic probes and visual diagnosis of the discharge process. Samples are loaded onto a processing stage which is connected to an external high voltage DC power supply which enables a bias to be applied to the stage. A heating element was also attached to the sample stage, enabling external heating of the substrates during processing. Feedstock gases are introduced into the chamber through inlets which line the top of the reactor, and their flow rates are controlled with MKS 1100 mass flow controllers externally. A RF coil, which enables the provision of 4000 W of power through a 460 kHz RF power generator and matching network system, sits on top of an alumina lid which seals the reactor with a Viton O-ring. The RF coil also features coaxial tubes to allow coolants to circulate to prevent over-heating and damage of the coil and the reactor.

![Fig. 1. Schematic of the ICP reactor used in this work.](image)

3.0 cm x 3.0 cm boron-doped p-type polycrystalline silicon wafers were used exclusively in this work. Samples were first washed with the standard RCA 1 clean prior to being placed in the loading transfer chamber, leading to transfer onto the processing stage. Feedstock gases of Ar and H₂ were introduced through the gas inlets, and the base
pressure of the reactor was varied manually through altering the width of the pump out valve. The discharge conditions were kept constant throughout this work with the RF power supplied at 2000 W, temperature of 500 ºC, process time of 30 minutes, and the base pressure of the discharge at 1.7 Pa. Only the ratio of Ar : H₂ in the feedstock recipe was varied for studies on how they affect the resulting optoelectronic properties of the processed samples.

After processing, the surface morphology of samples were characterized with a JEOL JSM-6700F field emission scanning electron microscope. This revealed details with regards to the type of nanostructures obtained, the corresponding aspect ratios, and the density of the nanostructures through planar, tilted and cross-sectional analysis. The reflectivity of the substrates were derived with a Zolix QE-C2 integrating sphere attached to a UV-VIS spectrometer which was selected to analyze the wavelengths of light corresponding to that from the solar spectrum and within the range which is above the band gap of silicon (400 nm – 1100 nm). The PV properties of the samples were measured with a Sinton instruments WCT-120 and a Suns-Voc add-on stage. This enabled the measurement of the open-circuit voltage (V_oc) of the samples without requirement of deposition of external electrodes. Finally, the fill factor (FF) of the samples were obtained with a Keithley 4200-SCS semiconductor characterization system with the Keithley interactive test environment for I-V characteristics. A Peccell PEC-L01 portable solar simulator was used to simulate the conditions of an AM 1.5 spectrum.

3. Experimental results and discussion

Fig. 2. shows the SEM micrographs of the resulting silicon surfaces after being exposed to the Ar + H₂ ICP discharge at different Ar : H₂ ratios. The figure shows the arrangement of nanostructures in increasing order their Ar : H₂ ratios. Table 1.1 summarizes the results from through SEM analysis. It is found that as the Ar : H₂ ratio was kept low, the size of the nanocones produced were coarse and less sharp. The densities of the nanostructure distribution were relatively low initially, but increased gradually with Ar : H₂ ratio. Similarly, the aspect ratios (height: width) increased with Ar : H₂ ratio.

![Fig. 2. SEM micrographs of nanostructures produced at the following Ar : H₂ ratios (a) 0.10; (b) 0.20; (c) 0.30; (d) 0.40.](image-url)
Table 1. Surface morphology of samples processed at different Ar : H₂ ratio.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Ar : H₂ ratio</th>
<th>Physical appearance</th>
<th>Aspect ratio (height : width)</th>
<th>Nanostructure density (x 10¹⁰ cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>Sparsely distributed nanostructures.</td>
<td>2</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>Dense nanostructures. Not well defined.</td>
<td>3</td>
<td>4.0</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>Dense nanocones with moderate heights</td>
<td>4</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>Well-defined sharp tipped nanocones</td>
<td>6</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The resulting surface morphology as a result of Ar + H₂ plasma processing is well understood by the different roles and mechanisms that the radicals in the discharge play during fabrication [21, 23-26]. There are 3 main species in the reactor which dynamically influence the resulting morphology of the samples. In the discharge, silicon may be found after being removed from the surfaces of the samples through etching by the reactive species and high impact sputtering. The silicon may go into the plasma phase as part of the discharge and may be re-deposited back on the substrate again, forming new silicon structures. However, it is also important to note that the re-attachment of silicon atoms is only possible on unpassivated surfaces (where dangling bonds are present). During plasma treatment, Ar plays a major role of sputtering on the surface, thereby impacting the substrate at high energies resulting in removal of material, whereas hydrogen plays the role in terminating the dangling bonds, and passivating the surfaces. This is in agreement with experimental results. While the removal of material from the surface is due to the presence of Ar species in the discharge, it is observed that with an increase in Ar in the feedstock ratio, the nanocones are moulded to have high aspect ratios with sharp tips due to the rapid sputtering rate. As the concentration of Ar in the feedstock recipe increases, the H₂ concentration decreases consequently. This results in the decreased hydrogen species present in the bulk which would be able to terminate the dangling bonds on the material. This in agreement with experiments through the observations made when increasing the Ar : H₂ ratio further (0.50), where the nanocones are no longer seen on the surface. This can be attributed to the increased unpassivated sites on the surface of the substrate which enable the re-deposition of sputtered silicon back onto the substrate, hence causing a less defined nanostructure array. The densities of the nanostructures were also observed to decrease as a result of having more well defined nanocones with high aspect ratios, since more material would be removed, giving rise to sharper nanocones with larger bases as compared to the less defined nanostructures which are densely distributed throughout the surface.

Fig. 3. Reflectance spectra of the samples processed under different conditions in comparison with an untreated Si wafer.

The purpose of the nanostructures on the surface of the material was to reduce surface reflection. The reflectivity of the samples and an untreated silicon wafer are shown in Fig. 3. It is shown that as the concentration of Ar in the
feedstock increases, the aspect ratio increases accordingly, and it is the increase in aspect ratio which has a large influence over the reflectivity of the samples as compared to the density of the nanostructures on the surface. The results show that ultra-low reflective losses were conceivable with careful manipulation of the Ar : H₂ ratio to be at 0.40 in order to obtain reflective losses of less than 2% (black silicon) [19, 22, 27].

Table 2 shows the photovoltaic responses and reflectivities of the samples processed at different Ar : H₂ ratios. The results concur very well with previous work done on the origins of the conductivity conversion of p-type wafers when exposed to a plasma discharge containing hydrogen species. It is understood that the conductivity conversion occurs in a 2 step process. Firstly, impurity dopant atoms (boron in the case of this experiment utilizing p-type Si wafers) diffuse to the surface of the samples when initially being exposed to the plasma discharge from heating processes through ion, electron and radical related heating mechanisms as well as the sputtering with heavier Ar ions impacting the surface. The boron impurities are then removed from the surface of the samples through interaction with atomic hydrogen during the formation of volatile boron hydrides [28]. At the same time, weakly bonded interstitial hydrogen atoms as well as oxygen related thermal donors play a more significant role in determining the overall conductivity behaviour of the resulting materials, since the concentration of acceptor species have decreased significantly. This results in the observed PNTCC seen in the samples.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Ar : H₂ ratio</th>
<th>Reflectivity from 400 nm – 1100 nm (%)</th>
<th>FF (%)</th>
<th>V oc (mV)</th>
<th>Aspect ratio (height : width)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare wafer</td>
<td>-</td>
<td>35</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.10</td>
<td>2.5</td>
<td>72</td>
<td>525</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>2.0</td>
<td>74</td>
<td>528</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
<td>1.8</td>
<td>75</td>
<td>530</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>&lt;1.8</td>
<td>71</td>
<td>524</td>
<td>6</td>
</tr>
</tbody>
</table>

As can be seen in the Table 2, the resulting PV response in terms of V oc and FF increase generally with increasing aspect ratio. This can be attributed to the increased amount of available sites on the surface realized by the increased surface area to volume ratio, for the removal of substitutional acceptor (boron) atoms as they diffuse to the surface and get removed by impinging hydrogen atoms as boron hydrides. However, it is also noticed that as the aspect ratio increases beyond 4, the corresponding photovoltaic properties started to decline. This is due to the decreased concentration of hydrogen species present in the discharge recipe to obtain the increased aspect ratio. Hydrogen plays a vital role in determining the resulting conductive character of the sample. A decrease in hydrogen species results in reduced passivation of dangling bonds found on the surface, leading to trap states which reduces the minority carrier lifetimes, thereby influencing the resulting PV properties. The decrease in hydrogen also decreases the rate of removal of boron atoms on the surface, and the formation of hydrogen related shallow thermal donors [29]. This is illustrated in sample 4 where there is a relatively lower concentration of hydrogen present in the discharge resulting in a decrease in PV response which continued to degrade further as the Ar : H₂ ratio was increased further. It is therefore reasonable to conclude that an Ar : H₂ ratio of 0.30 would be the most practical for PV applications since it returns the best FF and V oc while retaining the ultra-low reflectivity properties which is only marginally higher than that processed with a ratio of 0.40 which compromises the resulting FF and V oc.

4. Conclusion

This work demonstrates the ability of an ICP process to simultaneously produce an array of nanostructures on silicon in order to reduce reflective losses as well as to form a pn junction which are vital requirements for high performance PV cells. The effect of the ratio of the discharge feedstock was investigated with respect to how it affected the resulting surface morphology which influences both the reflectivity as well as the PV response of the samples. It was found that Ar and H₂ both play important and competing roles in the dynamic process resulting in
the optoelectronic properties obtained. An optimum processing condition which balances the reflective losses with photovoltaic response was realised. Ultra-low reflective surfaces of 1.8% were obtained with relatively high FF and Voc. This paves way for exciting developments which could further reduce reflective losses through implementation of anti-reflection coatings [30], as well as to improve the FF and Voc by introducing novel structures which could increase the minority carrier lifetimes of the samples [31-34]. The processes are also highly controllable through variation of process parameters and scalable for large scale implementation in industrial fabrication lines. Most importantly, the entire approach towards fabrication is environmentally friendly which is in tandem with the ideals of a green renewable source of energy.

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