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Passivation of silicon wafers by Silicon Carbide (SiC$_x$) thin film grown by sputtering

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Abstract
Silicon Carbide films for silicon solar cell application were deposited by means of RF sputtering process. Films were deposited from mixed Silicon – Graphite target onto silicon Cz <100> wafers. Samples were characterized by Photo Conductance Decay (PCD) method to measure the effective lifetime. The thickness and refractive index of the films deposited were measured using a spectroscopic Ellipsometer. X-Ray Diffraction (XRD) was performed to measure the crystallinity of the samples. Results have indicated that the deposited films were mainly amorphous. The crystalline fraction was present in samples with a better passivation level. Results from PCD show that the effective lifetime improved up to 38μs which corresponds to a Voc=641mV. Deposition rates up to 30nm/min were obtained for samples at 0.9kW bias power.

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Keywords: Silicon Carbide, surface passivation, sputtering, minority carrier lifetime

1. Introduction
Recent rapid growth of photovoltaic(PV) industry has led to increased interest in device development. The biggest challenge for the PV devices is the cost of energy generation. In order to achieve this the efficiency of devices must be increased, together with a decrease in manufacturing costs.

For crystalline silicon technology a big part of the cost is that of the raw material itself[1]. This can be reduced by making the cells thinner, but this increases the surface to volume ratio. The surface is a crucial part of the device, since an abrupt end of the crystalline structure causes many defects to be present[1]. These defects introduce recombination centers for charge carriers and thus decrease device efficiency. In order to prevent losses the surface has to be passivated, this is normally achieved by applying a thin film dielectric layer. This film also plays an important role as an antireflective coating. The coating in

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industrial silicon solar cells is deposited by Plasma Enhanced Chemical Vapour Deposition (PECVD)[2]. This method can deliver coatings of excellent quality[2-4] however, it has the drawback of using highly hazardous silane gas as a precursor[5]. This problem can be avoided by utilizing sputtering as the deposition method which still offers the possibility of high quality coating preparation without the expensive and hazardous precursors, as they are replaced by relatively inexpensive targets and noble working gas. High Target Utilization Sputtering (HiTUS) offers further reduction of cost through 90% target utilization[6]. The remote plasma lunch system offers a deposition technique where the deposited film is not bombarded by ions, which leads to better surface passivation[3], this combined with a high density low energy plasma gives the possibility of preparing high quality films.

Silicon Carbide (SiC) is a material which has been proven to work as a passivation layer for silicon. It has been deposited by CVD and sputtering methods[7-9]. Refractive indexes in the range 2.25-2.7[10,11] have been reported. SiC material has a widely tunable band gap 1.5-3eV[8,12], which guarantees no light absorption above 400nm at 3eV. SiC has also been recognized as an excellent semiconductor material in other applications due to its thermal and mechanical stability[8].

2. Experimental

SiC films were deposited on p-type 1-2Ωcm, 230µm thick Czochralski crystalline silicon wafers (c-Si). Prior to the deposition of the coating the wafers were given a saw damage etch, in 10% NaOH at 90°C for 5 minutes. This step was followed by anisotropic etching in an Iso-Propyl Alcohol (IPA) / NaOH solution at 90°C for 15 minutes. This resulted in the creation of a random pyramidal structure on the wafer’s surface. Wafers then were loaded into a diffusion furnace where at 850°C, shallow n-type region was doped from POCl₃, resulting in 0.3µm doped region characterized by 100Ω/□ sheet resistivity on both sides of the wafer. Wafers were then etched in 5% HF solution to remove Phosphosilicate glass (PSG), grown during the doping process, and rinsed in DI water before drying. The samples were tested using PCD (WTC-100 Sinton lifetime tester) in QSS mode (quasi steady state) to record the effective minority carrier lifetime. Optical attenuation factor was set to 0.8 since the wafers were textured. Wafers were then loaded into the sputtering chamber where the SiC film was deposited on the front surface of the wafer. Effective minority carrier lifetime was again measured after the deposition. Optical properties were checked using ellipsometry (Horiba Jobin Yvon UVISEL iHR320FGAS). The process diagram is presented in Figure 1.

Films were deposited in HiTUS sputtering process using a remote plasma source. During the experiments such parameters as RF plasma discharge power, target bias, Ar and H₂ gas flows, deposition temperature, deposition pressure were varied. High purity metallic Si target (99.995%) was used, onto which graphite strips (99.995% purity) were placed. The Si to C ratio was varied in the range 25-40% (C surface area coverage), which was previously reported to deliver stoichiometric SiC films[13]. Ar was used as the inert sputtering gas. The plasma was ignited remotely in a plasma lunch system, using a 3kW RF power supply, another 1kW RF power source is used to bias the target. A schematic of the sputtering system used is presented in Figure 2.

![Figure 1 Process diagram](image1.png)

![Figure 2 Schematic of deposition system](image2.png)
3. Results

The deposition process was initially optimized to maximize minority carrier lifetime. In the experiment: plasma discharge power, target bias, argon flow and deposition temperature were varied. Optimal deposition conditions were found to be: RF plasma discharge power = 2.7kW, Target Bias = 0.3kW, Ar flow=50ccm, deposition temperature T=200°C. Experiments showed that the deposition temperature was the most important parameter to obtain good surface passivation. Minority carrier lifetimes for films deposited at different substrate temperature is presented in Figure 1.

At the best conditions minority carrier lifetime reached 35μs at 1.5×10^{15}cm^{-13} minority carrier concentration. The film deposited at this condition has a refractive index of 3.37 at 550nm, the refractive index dispersion is shown in Figure 4.

The first absorption centre occurs at ~3.1eV. The deposition rate was 5nm/min, which is a major drawback, since other conditions could yield rates of up to 30nm/min. Deposition rates and refractive index measured for films deposited at different temperatures are presented in Figure 5. Attempts to increase deposition rate by increasing target bias did not give the expected results. Refractive index and deposition rate against target bias is presented in Figure 6.

![Figure 3 Minority carrier lifetime for films deposited at different substrate temperature](image1.png)

![Figure 4 Refractive index of film deposited at conditions resulting in highest minority carrier lifetime](image2.png)

![Figure 5 Deposition rate and refractive index at 550nm for different substrate temperatures.](image3.png)

![Figure 6 Deposition rate and refractive index at 550nm for different target bias levels.](image4.png)
Increasing target bias level led to a decrease in lifetime. Minority carrier lifetime and implied Voc measured for films deposited at different target bias level are plotted in Figure 7. Implied Voc reach 640mV at 0.3kW target bias level. Passivation quality depends on two mechanisms: reducing the number of trapping states at the surface by removing dangling bonds and, by repelling carriers from surface by built in field. The field is a function of charge fixed in the dielectric layer. It was previously reported that around 50nm is required to obtain maximum passivation layer[15]. A second film was deposited to check if any improvement could be obtained by growing a thicker film. Figure 8 presents the effective minority carrier lifetime measured for two films; 41nm and 76nm thick. The lifetime was increased up to 38μs and the implied Voc reached 641mV at 1sun.

X-ray diffraction measurement was carried out on the deposited films using Bruker D8 Advanced diffractometer with Copper 1.542 Å anode. During the measurement 1mm slit at the x-ray generator and 1mm slit at the Sol-X detector were used. Moreover a Ni filter which blocks Kβ but allows Kα1 and Kα2 components of the X-ray beam was used. No monochromator was used.

Table 1 Elements detected in deposited films

<table>
<thead>
<tr>
<th>Elements</th>
<th>Transition</th>
<th>Energy [eV]</th>
<th>Atom [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>2p</td>
<td>100.816</td>
<td>42.4</td>
</tr>
<tr>
<td>C</td>
<td>1s</td>
<td>284.7552</td>
<td>34.9</td>
</tr>
<tr>
<td>N</td>
<td>1s</td>
<td>399.1935</td>
<td>3</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>552.3876</td>
<td>19.7</td>
</tr>
</tbody>
</table>

Figure 9 XRD measured for samples deposited at different target bias.

Figure 10 XPS – sample deposited at 200°C, 0.3kW target bias

Figure 11 XPS - sample deposited at 200°C, 0.3kW target bias
The sample which gave the highest passivation level revealed twin peaks at 32.96° and 33.04° as presented in Figure 9. The peaks were identified as Si(100). The composition of deposited films was analysed utilising XPS technique (VG ESCALAB Mk I using Aluminium X-ray source), spectra measured for films with optimal passivation properties are presented in Figure 10. Detected elements are listed in Table 1. Si to C ratio is equal 1.21 in the deposited film, which is near the stoichiometric value. A second scan at greater resolution was performed around the peak corresponding to the carbon atom. Result of this scan is presented in Figure 11. This scan shows that there are actually two peaks at 283 and 285 eV – the presence of a second peak shows that there is a compound formation between silicon and carbon.

4. Summary

Silicon carbide films have been deposited in a silane free sputtering process. Films were deposited from mixed Si/C target. At 25% C coverage of the target the deposited films were found to be near stoichiometric composition SiC0.8. XPS data showed that compound formation had occurred.

Films deposited gave good passivation level of the silicon surface, providing minority carrier lifetime $\tau = 38 \mu s$ and implied Voc of 641 mV.

Films were characterized by refractive index in range 3.3-4 at 550 nm. At the optimal passivation level the film had a band gap of 3.1 eV. Deposition rates of 30 nm/min was achievable however, in order to deposit films with good passivation properties conditions have to be changed and the deposition rate is limited to 5 nm/min.

5. References