TiO$_2$ nanoparticle/SiO$_2$ composite back reflector for solar cells

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Abstract

We have investigated a scattering back reflector (BR) using a TiO$_2$ nanoparticles (NPs)/SiO$_2$ composite film. The binder SiO$_2$ is made from Perhydropolysilazane (PHPS), which is a organosilicate polymer consisting of cyclic (SiH$_2$-NH)$_n$ units. The PHPS changes into pure SiO$_2$ by heat treatment less than 450°C, which can be easily coated on a substrate by spin coat. Compare to the conventional organic binders, SiO$_2$ is quite stable and has a good transparency. The composite BR showed more than 90% of absolute reflectance at near infrared region. To improve a passivation property of BR, we inserted a thin liquid source SiO$_2$ layer between the silicon surface and the composite BR. The composite BR using Al coated TiO$_2$ NPs showed high effective lifetime with a combination of thin SiO$_2$ passivation layer. This paper describes the light reflection property of TiO$_2$ NPs/SiO$_2$ composite film and the effect of inserting thin liquid source SiO$_2$ passivation layer between the silicon surface and the composite BR layer on effective lifetime.

Keywords: Back reflector, passivation, nanoparticle, PHPS

1. Introduction

A pigment based reflectors with high refractive index nanoparticles in a low refractive index media attracted a lot of attention in solar cell applications [1,2]. The strong scattering property of TiO$_2$ nanoparticle BR is attractive for the applications of thin film solar cells and recent thin bulk crystalline silicon solar cells [3,4]. By introducing light confinement structures, thin solar cells have effectively thick optical structures to maintain high light absorption. Cost reduction and high efficiency are indispensable in the process of cost competitive solar cells. The reduction of semiconductor thickness is an important option in cost reduction. The reduction of the absorber thickness requires an effective BR structure as well as an effective passivation property. As the thickness of devices become thinner, rear reflections of solar cells are going to be more important due to the high transmission losses [5-7]. The conventional back reflectors using planar Si/SiO$_2$/Al or Si/Al structures mirror the non absorbed long wavelength...
back into the cell. However, the small reflect angle causes the escaping of light at the front surface. The metal reflector with Lambertian rear surface is another option to enhance light trapping effect in bulk crystalline solar cells, however, this needs high process cost [8]. The light scattering reflection enables a large angle rear reflection, leading a long pass length and light confinement effect of the back reflected light. This method has a potential to obtain effective light confinement with low cost.

We have developed the light scattering BR using TiO$_2$ NPs/SiO$_2$ composite film. The liquid source SiO$_2$ was introduced as a binder material of the TiO$_2$ NPs/SiO$_2$ composite BR. The refractive index of TiO$_2$ is 2.78~2.53 in near infrared area (750~1100 nm). In contrast, the SiO$_2$ has 1.47. This combination enables an effective scattering [9-10]. Compare to the conventional organic binders, SiO$_2$ is quite stable and has a good transparency. We introduced the PHPS as a low cost liquid source material for binder SiO$_2$. The PHPS is an organosilicate polymer consisting of cyclic (SiH$_2$-NH)$_n$ units, which changes into pure SiO$_2$ by heat treatment less than 450 °C, which can be easily coated on a substrate by spin coat. We have introduced the liquid source SiO$_2$ passivation on silicon surface as a low cost passivation process for silicon solar cells and obtained over 3 ms of effective lifetime with the combination of hot steam annealing, which is higher than that of the chemical passivation using quinhydrone methanol solution [11]. In this experiment, we inserted the liquid source SiO$_2$ passivation layer between TiO$_2$ NPs/SiO$_2$ composite film and the silicon substrate surface to develop an interface property of the composite BR. This paper describes the light reflection property of TiO$_2$ NPs/SiO$_2$ composite film and the effect of inserting thin liquid source SiO$_2$ passivation layer between the silicon surface and the composite BR layer in effective lifetime.

2. Experimental

Figure 1 shows the schematic of BR using TiO$_2$ NPs/SiO$_2$ composite film with the liquid source SiO$_2$ passivation. We prepared this structure by a two step process. The experimental condition is shown in Table 1. Firstly, thin SiO$_2$ passivation layer was prepared by spin coat method, followed by the hot steam annealing. The film thickness of SiO$_2$ passivation layer was controlled by the concentration of PHPS and spin coat rotation speed. After dried at room temperature, the hot steam annealing was carried out at 600 °C. The SiO$_2$ thickness is 100 nm. The TiO$_2$ NPs/SiO$_2$ composite film was coated on the SiO$_2$ passivation layer using a TiO$_2$ NPs/PHPS mixed solution. A 20% PHPS in xylene solution was used to prepare thick TiO$_2$ NPs/SiO$_2$ composite film. The concentration of TiO$_2$ NPs in the PHPS was 1 g/ml. In this experiment, TiO$_2$ NPs/SiO$_2$ composite layer was coated repeatedly to obtain thick film over 20 μm in thickness. The film thickness was controlled by rotation speed of spin coat, PHPS concentration and repeat number of coating. Three different type of TiO$_2$ NPs were tested; 0.27 μm, 0.27 μm(Al coated) and 1~2 μm.
Table 1. Experimental conditions.

<table>
<thead>
<tr>
<th></th>
<th>PHPS concentration</th>
<th>Spin coat rotation speed</th>
<th>Hot steam annealing temperature</th>
<th>Annealing time</th>
<th>TiO₂ particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ passivation</td>
<td>0.1-10 [%]</td>
<td>1500-3000 [rpm]</td>
<td>600 [°C]</td>
<td>2 [h]</td>
<td></td>
</tr>
<tr>
<td>TiO₂ NPs/SiO₂ composite</td>
<td>10-20 [%]</td>
<td>1000-2000 [rpm]</td>
<td>450 [°C]</td>
<td>1 [h]</td>
<td>0.27, 1-2 [μm]</td>
</tr>
</tbody>
</table>

The dried samples were annealed at 450 °C, 1 hour in air. When the samples after annealing had pores in the layer, we coated the PHPS over the composite layer to fill them. A N-type, CZ, <100> single side polished wafer was used as a substrate. The wafers were cleaned by soaking in H₂SO₄+H₂O₂ at 80 °C, followed by a 5% HF treatment. The absolute reflectance spectra were measured by using UV-Vis spectrophotometer (SHIMADZU MPC-2200). The effective lifetime was evaluated by MW-PCD.

3. Results and discussion

3.1 Reflectance spectra

Figure 2 shows the examples of cross sectional view of TiO₂ NPs/SiO₂ composite film. As shown in Fig2.(a), dense and thick film over 10 μm can be obtained without cracks.

![Image](a)

(b)

(c)

Fig.2 Crosse sectional view of the samples; (a) 0.27μm, (b)0.27μm( Al coated), (c)1-2μm.
In some cases, we observed the pores remain in the film as shown in Fig2(b), which are generated by volatilization of xylene solvent. Figure 3 shows the absolute reflectance spectra of the TiO$_2$ NPs BR as a function of film thickness. The reflectance of near infrared region strongly depended on the film thickness. Precipitous diminution at 420 nm is caused by bandgap absorption of TiO$_2$. Each sample showed more than 90 % of reflectance at optimized film thickness. The reflectance increased with film thickness, saturated at some point. The saturating thickness depended on the TiO$_2$ nano particle size. In the case of Fig.3(a), BRs using 0.27 $\mu$m TiO$_2$ NPs needed more than 40 $\mu$m to obtain high reflectance over 90 %. In this particle size, incident light was scattered by Rayleigh scattering condition. On the other hand, the film including 1-2 $\mu$m nano particles more effectively scattered the light, the increase of the reflectance saturated at 26.5 $\mu$m as shown in Fig3(c). The wavelength of light becomes 1/1.45 in SiO$_2$, which is shorter than the grain size of NPs. In this condition, the incident light was scattered by Mie scattering.

### 3.2 Passivation effect

Figure 4 shows the effective lifetime of the samples coated TiO$_2$ NPs/SiO$_2$ composite BR layer on both sides. The effective lifetime of liquid source passivation with the hot steam annealing is also shown as a reference. The effective lifetime of the samples without passivation layer was much lower than the reference. A direct contact of TiO$_2$ NPs to Si or impurities degraded the surface property of silicon. On the other hand, the effective lifetime much improved by inserting the liquid source SiO$_2$ layer, however the values were lower than the reference sample. This degradation can be explained by the effect of annealing in air to prepare the TiO$_2$ NPs/SiO$_2$ composite layer. By introducing low temperature process using PHPS with catalyst, this degradation can be avoided. In Fig.4, the composite BR using aluminium coated TiO$_2$ NPs showed highest value. The PHPS generates hydrogen in the reaction process. The thin aluminium layer on TiO$_2$ nano particle decomposes the hydrogen molecule generated by the equation (1). As a result, interface defects at TiO$_2$ NPs/SiO$_2$ were effectively terminated by hydrogen.
4. Conclusion

We developed a scattering back reflector (BR) using TiO$_2$ NPs/SiO$_2$ composite. The composite BR showed more than 90% of absolute reflectance at near infrared region. The composite BR using Al coated TiO$_2$ NPs showed high effective lifetime with the combination of thin SiO$_2$ passivation layer.

References