Formation of High Light Scattering Texture on Glass Substrates Using Spherical Silica Particles and Spin-on-Glass for Thin Film Si Solar Cells

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A high light scattering morphology on glass was used as a substrate for thin film solar cells was fabricated using spherical silica particles and spin-on-glass. After deposition of Al-doped ZnO thin films, a hemispherical morphology appeared at the surface, and a high haze value of 77% (λ = 800 nm) was obtained when the cover ratio of the silica particle was 44%. The quantum efficiency of microcrystalline thin film Si solar cells was improved at wavelengths over 700 nm due to the textured morphology formed by the silica particles and spin-on-glass.


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Thin film Si solar cells based on hydrogenated amorphous Si and hydrogenated microcrystalline Si have been considered to have a reduced manufacturing cost compared with crystal type Si solar cells due to their reduced use of Si materials. However, the conversion efficiency of thin film Si solar cells is much lower than that of crystal Si solar cells owing to their lower photo absorption in the near infrared region, which can be attributed to their indirect-transition type absorption and thin Si layer thickness. In order to increase the conversion efficiency of thin film Si solar cells, improvement in the optical path length in the near infrared region is necessary. In order to confine the light and thereby increase the optical path length within the solar cells, a textured morphology has been formed on a transparent conductive oxide (TCO) substrate.1–3 Such a textured morphology induces scattering and the confinement of the incident light within the solar cells. Consequently, the optical path length and total amount of optical absorption in the thin film Si solar cell are increased significantly. Many types of textured morphologies prepared by various methods have been proposed,4–9 the light scattering characteristics of which are determined by their textured width and height.9 Hongsinthong et al. reported that a cauliflower-like textured TCO substrate with different sized texturing formed on textured glass etched by a reactive ion etching method achieved high light scattering characteristics in the visible and near infrared region.10 The formation of such a textured morphology on a glass surface is considered to be an effective method for improvement of the optical confinement properties of the solar cells. However, different-sized textured TCOs have not yet been commercialized due to the difficulties in their large-scale fabrication at sufficiently low cost. Plasma-etching techniques have been widely used as a candidate methodology for the formation of a textured morphology on a glass surface. However, the production cost is too high for commercialization due to the high cost of the required vacuum equipment. Therefore, an alternative methodology yielding a low cost texturing process which could be applied to large scale substrates is required. In this study, we demonstrate the fabrication of a textured TCO substrate with high light scattering characteristics with a low manufacturing cost. The textured morphology was formed on a glass surface using spherical shaped silica particles (SSPs) and spin-on-glass (SOG) in air. Subsequently, Al-doped ZnO (AZO) thin films were deposited on the textured surface forming a TCO layer, thus, demonstrating the possibility of fabricating a textured morphology on a glass substrate without the use of expensive vacuum equipment, and thus reducing the fabrication cost.

The textured morphology was formed on Eagle XG glass substrates using SSPs (2 µm in diameter, HIPRESICA, UEXC Co.) and SOG (Liquid glass G-type, NARUSE SEIJOU Ltd.). First, SSPs mixed at 30 mass% in 2-propanol were coated on the glass substrate using a spin-coating method. The cover ratio of the SSPs on the glass surface was controlled using a varied rotation speed of spin-coating in the range of 1500–8000 rpm. Next, the SOG was deposited on the glass surface of dispersed SSPs by spin-coating at 4000 rpm. The SOG was then dried and solidified by a two-step annealing process for 120 min at 70°C in air using a constant-temperature drying oven, and for 120 min at 450°C in air using an electric furnace. AZO thin films were deposited on the textured SOG layer using a radio frequency magnetron sputtering method with a ceramic ZnO (1 mass% Al2O3 doped, 71 mm diameter) target. The deposition power, pressure, and heating substrate temperature were maintained at 100 W, 0.5 Pa, and 400°C, respectively. The thickness of the AZO thin films was approximately 1200 nm.

The surface morphology and roughness of the substrates with the AZO films deposited on the SOG-coated SSPs (AZO-SSP) were analyzed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The cover ratio of the SSPs on the glass substrate was obtained from SEM images. We measured the total transmittance and the diffuse transmittance of all AZO-SSP substrates using a spectrophotometer equipped with an integrated sphere in
order to estimate their haze value. An immersion method using a contact liquid (n = 1.74 at 588 nm) was employed for accuracy of the transmittance measurements of the highly textured substrates.\(^{11}\) Electrical properties of the AZO films deposited on the textured substrates were also performed using Hall measurement.

The AZO-SSP substrates were applied to the fabrications of p-i-n type \(\mu\)c-Si:H single-junction solar cells (area: 0.25 cm\(^2\)). The solar cells consisted of the following layers: glass, textured SOG, AZO, p-i-n type \(\mu\)c-Si, second AZO, Ag, and third AZO. The i-layer thickness was approximately 1 \(\mu\)m. The photo \(J\)-\(V\) measurements of the fabricated solar cells were conducted at standard conditions under simulated solar light (25°C, 1-sun, AM 1.5, 100 mW/cm\(^2\)). The spectral responses of solar cells were measured using quantum efficiency (QE) measurement.

Figures 1(a)–1(c) shows the surface SEM images of the AZO-SSP substrates at the fabrication steps of (a) after the dispersion of SSPs on the glass substrate, (b) after the SOG coating on the SSPs, and (c) after the AZO film deposition on the textured substrate. In Figs. 1(a) and 1(b), spherical textured morphologies can be observed on the glass surface due to the SSPs and the spherical shapes were transformed to hemispherical shapes by the covering of SOG layer. The AZO deposition resulted in no significant change in the surface morphology as shown in Fig. 1(c). AFM measurements of the AZO-SSP substrates showed that the root-mean-square (RMS) roughness was approximately 140 nm when the cover ratio of SSPs was 44\%, which is much higher than that of AZO films deposited on glass substrates under the same conditions. According to the cross sectional SEM image of the AZO-SSP substrate, the SOG penetrated well between the AZO-SSP substrates, and no void like structures were observed, as shown in Fig. 1(d). This suggests that the dispersed SSPs were fixed on the substrates by the SOG coating.

Figures 2(a) and 2(b) show the transmittance and haze value spectra of AZO-SSP substrates with different cover ratios of the SSPs. Transmittance and haze value spectra of the AZO film deposited on the smooth glass substrate is also shown as a reference. As shown in Fig. 2(a), the AZO films prepared with and without the textured substrates have high transparency of over 80\% in a wavelength range of 400–1100 nm. This result suggests that the underlying textured SOG layer did not significantly affect the transmittance of the AZO-SSP substrates. Haze value spectra of the AZO-SSP substrates, shown in Fig. 2(b), suggests all AZO-SSP substrates had much higher light scattering characteristics than that of the smooth surface AZO film. In addition, the light scattering characteristics correlated with the cover ratio of the SSPs within the underlying SOG layer. The haze value in a wavelength range of 400–700 nm significantly increased with increase in the SSP cover ratio. Consequently, the haze value of AZO-SSP substrates at a wavelength of 500 nm significantly increased from approximately 51\% to 90\%. A feature of the haze value is that the haze value of AZO-SSP substrates reached a maximum value of 87\% at an SSP cover ratio of 39\%, and then decreased to 77\% at a cover ratio of 44\% owing to the reduction of the space among the SSPs. These results suggest that the formation of the textured morphology using the SSP and the SOG is effective in controlling the light scattering characteristics of TCO substrates.

We examined the electrical properties of the AZO films deposited onto the textured SOG layer and glass substrate, as shown in Table 1. The electrical property of the AZO-SSP substrate with an SSP cover ratio of 44\% is shown as an example. A reduction of the Hall mobility of the AZO-SSP substrates was observed as compared to the AZO film deposited on the glass substrate (28.7 cm\(^2\)/Vs). Thickness irregularity of the AZO film fabricated on the highly textured SOG layer can be considered to be the reason for this.
reduction. Most AZO-SSP substrates showed similar electrical properties, and the carrier density, Hall mobility, and sheet resistance were approximately $3 \times 10^{20}$ cm$^{-3}$, 20 cm$^2$/Vs, and 8 $\Omega$/sq, respectively.

Finally, a $\mu$-Si:H thin film solar cell was fabricated on the AZO-SSP substrates which has the highest haze value in the wavelength range 400–700 nm with a silica cover ratio of approximately 44% (RMS: 140 nm). In addition, a solar cell was fabricated on a smooth AZO film (RMS: 7 nm) as a comparison standard. A short circuit current density ($J_{SC}$) of 16.2 mA/cm$^2$ was obtained from the AZO-SSP cell, which is 1.3 mA/cm$^2$ larger than that of the smooth AZO cell ($J_{SC}: 14.9$ mA/cm$^2$). Consequently, the efficiency of the solar cell improved from 5.45% (open circuit voltage; $V_{OC} = 0.49$, fill factor; $FF = 0.75$) to 5.98% ($V_{OC} = 0.50$, $FF = 0.74$). Figure 3 shows the QE spectra of both the smooth AZO and AZO-SSP cells. It is observed that the QE of the AZO-SSP cell improved at wavelengths over 700 nm compared with that of the smooth AZO cell. We considered that the increase of $J_{SC}$ occurred due to the improvement of the spectral response of the solar cell at wavelengths over 700 nm, and the improvement of the QE in the near-infrared light region is due to the high light scattering characteristics of the AZO-SSP substrates, as shown in Fig. 2(b). Despite the difference in the haze values of these substrates, the QE spectra of the AZO-SSP cell in a wavelength range of 500–600 nm showed a lower value than that of the smooth AZO cell. This is probably because the thickness of i-layer of the AZO-SSP cell was thinner than that of the smooth AZO cell due to the difference in their surface areas. In addition, it is well known that the scattering angle of light is reduced when the size of the particles or otherwise textured morphology is much larger than the wavelength of the light,1,12 as a result of which, the optical confinement properties within the solar cell are reduced. For these reasons, it is considered that the QE spectra of the AZO-SSP cell in the wavelength range of 500–600 nm is reduced compared with that of the smooth AZO cell. However, the optical confinement property of the solar cells in the visible wavelength region could be improved by forming a small textured morphology on the TCO surface with a high light scattering angle in the visible wavelength. Therefore, further improvement of the solar cell efficiency can be expected by increasing the amount of light absorption in the visible wavelength. Moreover, control of the light scattering characteristics at various wavelengths can be achieved by choosing the preferred size, shape, and the cover ratio of the silica particle and the thickness of the SOG layer.

In conclusion, we have successfully demonstrated fabrication of a large textured morphology on a glass substrate in air by using SSPs and SOG. After AZO film deposition, hemispherical shape AZO films were formed on the glass substrate. The haze value of the textured substrates was significantly influenced by the cover ratio of the SSPs. When the cover ratio was 44%, haze values of approximately 90% and 77% were obtained at wavelengths of 500 nm and 900 nm, respectively. The $\mu$-Si:H thin film solar cell fabricated on the textured substrate yielded a higher $J_{SC}$ than that of the smooth substrate, possibly due to an improvement in the spectral response at wavelengths over 700 nm without a significantly decrease in the $V_{OC}$ and $FF$. These results indicate that the formation of a texture using silica particles and SOG is an effective method for improving the light scattering characteristics of TCO substrates with a low fabrication cost.

Acknowledgement

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REFERENCES


Table 1 Electrical properties of the AZO-SSP substrate and AZO film deposited on a glass substrate. The electrical properties of the AZO-SSP substrate with a silica cover ratio of 44% is shown as an example.

<table>
<thead>
<tr>
<th></th>
<th>carrier density [cm$^{-3}$]</th>
<th>Hall mobility [cm$^2$/Vs]</th>
<th>sheet resistance [$\Omega$/sq]</th>
</tr>
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<tbody>
<tr>
<td>w/SSP</td>
<td>$3.3 \times 10^{20}$</td>
<td>21.0</td>
<td>7.6</td>
</tr>
<tr>
<td>w/o SSP</td>
<td>$3.4 \times 10^{20}$</td>
<td>28.7</td>
<td>5.4</td>
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