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Development of textured ZnO-coated low-cost glass substrate with very high haze ratio for silicon-based thin film solar cells

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ABSTRACT

Zinc oxide (ZnO) films with a very high haze ratio and low resistivity were developed on soda–lime glass substrate by using reactive ion etching (RIE) treatment with carbon tetrafluoride (CF_4) to modify the substrate surface morphology before the deposition of ZnO films. We found that the surface morphology of the ZnO films deposited by metal organic chemical vapor deposition (MOCVD) technique could be modified by varying the glass treatment conditions and the gas pressure was a key parameter. With increasing glass-etching pressure, the surface morphology of the ZnO films changed from conventional pyramid-like single texture to greater cauliflower-like double texture, leading to significant increases in root mean square roughness and haze ratio of the films. By employing the developed high-haze ZnO films as a front transparent conductive oxide (TCO) layer in microcrystalline silicon solar cells, an enhancement in the quantum efficiency in the long-wavelength region has been achieved. Experimental results have verified that our unique and original glass etching treatment is a simple and effective technique to improve the light-scattering properties of the ZnO films while preserving their good transparency and electrical properties. Thus, the ZnO films deposited on etched soda–lime glass have a high potential for the use as a front TCO layer in thin-film Si solar cells.

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1. Introduction

Conductive zinc oxide (ZnO) thin films are one of the most promising materials for use as a front transparent conductive oxide (TCO) layer in thin-film silicon solar cells [1,2], because it has been recognized that ZnO film has high stability against hydrogen plasma exposure as compared to other TCO materials [2–4]. Moreover, their surface morphology can be easily modified by several methods [5–7]. To improve the efficiency of solar cells through the photocurrent, light trapping is very important because it can enhance the optical path length of light inside a solar cell structure, and thus results in an increment of the photocurrent in the absorber layer of the solar cell [8–10]. To further enhance the light trapping effect, particularly in the long-wavelength region and near-infrared wavelength range, root mean square (rms) surface roughness and haze ratio of ZnO films which are measures of texture size and optical scattering of the films need to be increased. In general, roughness and haze ratio are affected by the surface morphology [9–12]. Large surface grain size allows high rms roughness and high haze ratio, which leads to a better light-scattering of ZnO films [12–14].

Recently, textured ZnO films with a high haze ratio were prepared by using a pre-dry-etch process on the Corning glass before the film deposition [14]. The surface morphology and rms roughness of the ZnO films can be controlled by changing the glass-etching times. The performance of the solar cells using the etched substrates was found to be superior to those using flat substrates. In addition, similar studies have been performed on textured glass by other research groups [15,16]. Additionally, another method to achieve efficient textured ZnO films by using wet-chemical etched Corning glass as a substrate has already been reported [17]. However, the surface roughness of these wet-chemical etched glasses is relatively low compared to that of the dry etched substrate, and an acid etching at raised temperature comes up to the worries of safety rules.

The cost of solar cells is a critical issue in present-day Japan [18], and a way to reduce the production cost and improve efficiency of solar cells simultaneously is strong required. Using a low cost glass substrate with efficient textured TCO layer can be expected to resolve the cost issue. The objective of the present work is to modify the surface morphology of the ZnO films on low cost soda–lime glass by carrying out glass-substrate etching process prior to the film deposition in order to improve the optical scattering properties of the films. The effects of etching parameters on the properties of ZnO films were investigated and hydrogenated microcrystalline silicon (µc-Si:H) solar cells were also fabricated to verify potential of the textured ZnO coated low cost glass substrate developed in this study.

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2. Experimental details

2.1. Preparation of glass substrates

1 mm thick soda–lime glasses from Asahi Glass Co., Ltd. with an area of 10×10 cm^2 squared shape were used in this study. The initial roughness of these glasses is less than 1 nm. A typical composition of soda–lime is as follows: 60 to 70 wt.% silicon dioxide (SiO$_2$), 12 to 16 wt.% sodium oxide (Na$_2$O), 8 to 15 wt.% calcium oxide (CaO), 0 to 6 wt.% magnesium oxide (MgO) as well as aluminum oxide (Al$_2$O$_3$) and other trace elements. In addition, these glasses possess high thermal expansion coefficient, thus their resistance to chemical corrosion and sudden temperature changes is relatively poor.

Before the ZnO film deposition, the glass substrates were etched by a standard reactive ion etching (RIE) vacuum system using carbon tetrafluoride (CF$_4$) as the etchant gas. The CF$_4$ plasma was produced by supplying a radio frequency (RF) power supply with a maximum operating power of 300 W. The cathode with a 5 inch diameter size in the system was maintained at 20 °C by circulation of a chilled coolant. The internal diameter of the reactor chamber was 31 cm, whereas the turbo molecular pump backed by a rotary pump was used to keep the required pressure in the reactor chamber. Here, we did not use any pre-treatment before the etching process. To investigate the effects of glass-etching conditions on the properties of the ZnO films, the power density for the glass etching process was varied from 0 to 1.9 W/cm^2, while the flow rate of CF$_4$ gas and gas pressure were kept constant at 16 sccm and 7 Pa, respectively. The etching time was held constant at 40 min. The effect of gas pressure was also examined by varying in the range between 0 and 13 Pa. The flow rate of CF$_4$ gas, power density and etching time were fixed at 16 sccm, 1.5 W/cm^2 and 40 min, respectively.

2.2. Preparation of ZnO films

Before the ZnO deposition, the etched soda–lime glass substrates were ultrasonically cleaned in acetone and ethanol, respectively. Then, the ZnO films were deposited onto the etched glass substrates by metal organic chemical vapor deposition (MOCVD) technique using water as an oxidant for diethylzinc [1,7]. The 1%-hydrogen-diluted diborane was employed as a dopant gas. The thickness of the ZnO films was about 1.6 μm. The details of the ZnO growth procedure were described elsewhere [7].

2.3. Characterization of glass substrates and ZnO films

The etching rates of soda–lime glasses were evaluated by using a Dektak-150 surface profiler. The surface morphology and surface roughness of the glass substrates and ZnO films were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). To obtain clear SEM images, the surfaces of all samples in this work were coated with a thin platinum–palladium film by ion sputter coater using the argon gas. The rms roughness and lateral feature size of the sample surface were estimated from three-dimensional AFM data taken at a scan area of 10×10 μm^2 using a non-contact (tapping) mode. The total transmittance (T_t), diffuse transmittance (T_d) and reflectance (R) spectra of the ZnO films were measured by using a spectrophotometer with an integrating sphere in the wavelength range from 300 to 1500 nm. In order to measure the transmittance and reflectance spectra of highly textured ZnO films accurately in this work, an immersion method was employed [19]. Dichloromethane (CH$_2$Cl$_2$) was used for the refractive index matching in the total transmittance and reflectance measurements. The structure of the samples fabricated for the total transmittance and reflectance measurements was glass substrate/textured ZnO films/CH$_2$Cl$_2$/quartz. From the obtained transmittance spectra, spectral haze ratio of the ZnO films, which is defined as the ratio of diffuse transmittance and total transmittance, was

calculated. Then, an absorptance (A) of the ZnO films was calculated through the relation $A = 1 - R - T_t$. Hall measurement using four-point probe in van der Pauw configuration was used to evaluate the electrical properties of the obtained films. Additionally, we also prepared the samples with structure of glass substrate/textured ZnO films/intrinsic μc-Si:H (i-μc-Si:H)/Al for the purpose of observing influence of glass etching on the reflectance behavior of the ZnO films in the solar cells. The conventional p–i–n-type μc-Si:H solar cells with an area of 0.086 cm^2 were also fabricated using boron-doped ZnO (ZnO:B) films deposited on etched and flat glass substrates as a front TCO layer. The structure of these solar cells was glass substrate/textured ZnO:B/p-μc-SiO:H/i-μc-Si:H/n-μc-Si:H/ZnO:B/Ag/Al and glass substrates did not use anti-reflective coatings. The thicknesses of p and n-layers were fixed at 35 and 40 nm, respectively, while the i-layer thickness was about 1 μm. The photocurrent–voltage (J–V) characteristics of the fabricated solar cells were measured under standard test conditions (25 °C, AM 1.5, 100 mW/cm^2). Quantum efficiency (QE) measurement was also performed to estimate the spectral response of the solar cells.

3. Results and discussions

3.1. Influence of glass etching

Fig. 1 displays the etching rates of soda–lime glasses as functions of power density and gas pressure. It was found that the etching rate increased with increasing power density. The maximum etching rate was about 60 nm/min, where the power density was 1.9 W/cm^2. The increment of etching rate of the glass could be understood in terms of the productive ion bombardment in dry-plasma etching, which was highly affected by increasing the ion energy. The high energy ion bombardment led to a high removal rate of non-volatile elements [20–24], and thus resulted in an increase of the glass etching rate. The etching reaction of glass in CF$_4$ plasma under this etching condition is considered to be dominated by physical sputter-etching as described in the literature [25,26]. As seen in Fig. 1, the etching rate also increased as the gas pressure increased up to 10 Pa. The increment of the etching rate under this etching condition can be attributed to fluorine-rich radical concentrations in CF$_4$ plasma, which then led to an increase in the etching rate. Here, the etching reaction is dominated by an active abundance of neutral etchant species [20]. However, the etching rate slightly decreased when the gas pressure was higher than 10 Pa. This may be caused by the reduced ion bombardment effect at a high gas pressure [20,21]. It should be noted that the etching rates of soda–lime glass, as shown in Fig. 1 were relatively low compared to other glasses such as Corning and quartz glasses [20]. This is probably due to the fact that the soda–lime glass contains a great amount of non-volatile components and metallic impurities [22,26].

The SEM micrographs and the rms roughness of the surface of soda–lime glasses prior to the ZnO film deposition with various etching
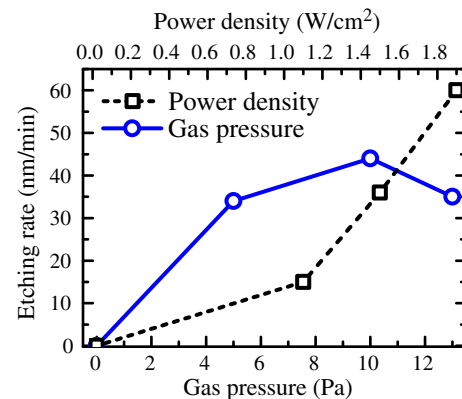

Fig. 1. Etching rates of soda–lime glasses as functions of power density and gas pressure.

conditions are shown in Fig. 2. With an increase in the power densities from 0 to 1.5 W/cm^2, the surface of glass changed from a smooth flat surface to small craters with lateral feature size of 200 to 700 nm. However, the surface of the glass became smoother when the power density was 1.9 W/cm^2, where its rms was about 3 nm. This was probably caused by the difference in the energetic ion bombardments [25], which affected etching kinetic and allowed smooth surfaces. The rms roughness of the glasses slightly increased as the power density is increased to 1.5 W/cm^2, and showed a rapid drop at the power density of higher than 1.5 W/cm^2. These results indicate that the etching with high power density under a constant pressure leads to a smooth surface of soda–lime glass.

According to Fig. 2c and d, it can be seen that the surface morphology of the glasses changed significantly with varying pressures. The glass surface morphology changed from a flat surface to large craters with lateral feature sizes between 4000 nm and 6000 nm, and the rms roughness increased from 0.6 to 360 nm as the gas pressure increased from 0 to 13 Pa. The different surface textures at different gas pressure conditions may be caused by the variation of gas radical concentrations, i.e. ion-radical and neutral etchant species in the dry plasma [20,25]. Since these factors have a significant impact on the kinetics of reactive ion etching, then the changes in the surface feature are observed. We can expect that the roughness of the ZnO films would increase when depositing on the textured glass with high rms, as presented in Fig. 2d. The optimum etching condition for preparing the textured soda–lime glass in this work was obtained at the pressure of 13 Pa and the power density of 1.5 W/cm^2.

3.2. Surface properties of ZnO films

Fig. 3 shows the cross-sectional SEM micrographs of ZnO films deposited on soda–lime glasses with various glass-etching conditions.

The rms roughness of each film is also shown. As shown in Fig. 3a and b, the surface morphology of ZnO films did not change with glass-etching power density, where the conventional pyramid-like single texture was observed. The rms roughness and lateral feature size of the most films were 80 and 560 nm, respectively, at the power density of 1.5 W/cm^2.

As exhibited in Fig. 3c and d, it can be clearly observed that the surface morphology of ZnO films changed significantly from conventional pyramid-like single texture to greater cauliflower-like double texture when the gas pressure reached 13 Pa. The rms roughness of the ZnO films increased evidently to 270 nm and the lateral feature size of these films exceeded 4000 nm, as shown in Fig. 3d. More efficient light scattering at the TCO and p-Si-layer interface can be expected when the ZnO films with high rms roughness and large feature size are applied to thin-film solar cells [11,13]. It should be noted that the ZnO films deposited on the etched soda–lime glass, as shown in Fig. 3d had a higher rms roughness and larger feature size than those deposited on the etched Corning glasses as previously reported [14]. This is supposed to be due to the difference in the feature shapes of the post-etch glass surface. These results clearly showed that the surface morphology of the deposited ZnO films could be modified by controlling the surface morphology of the glass-substrate. According to the experiment results, we can conclude that a unique patterned surface-texture of the ZnO films can be obtained on soda–lime glass substrates, which are etched under high gas pressure condition.

3.3. Optical properties of ZnO films

Fig. 4a shows the total transmittance, absorptance and reflectance of the ZnO films deposited on soda–lime glasses with various glass-etching conditions. From this figure, the total transmittances
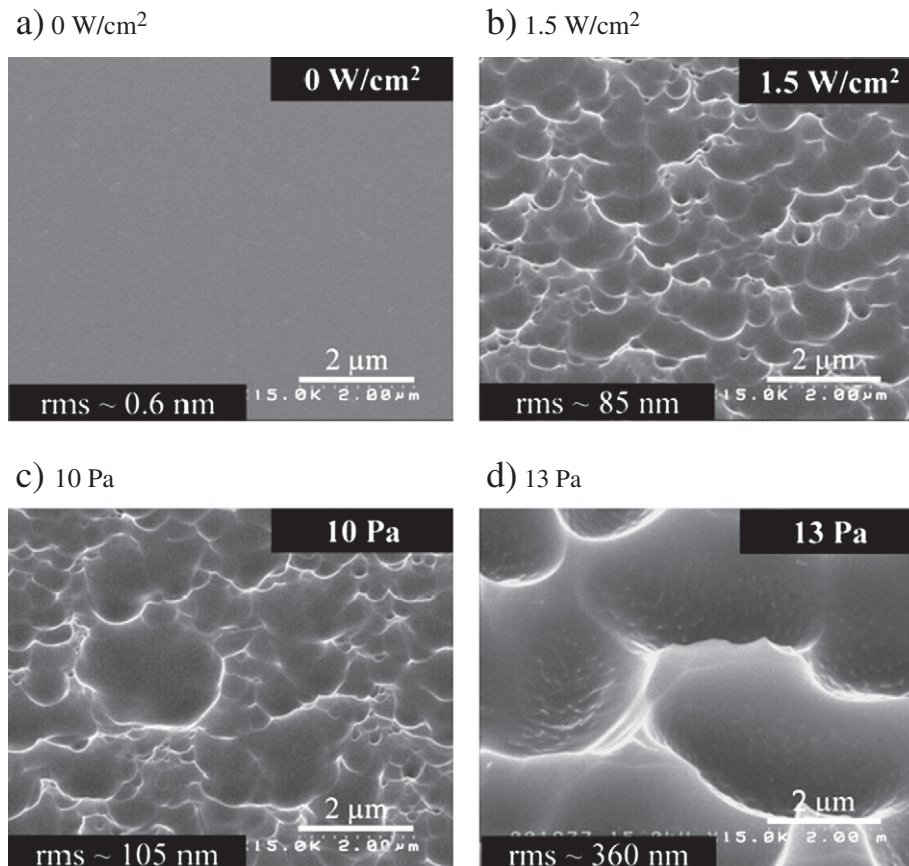

a) 0 W/cm^2

b) 1.5 W/cm^2

c) 10 Pa

d) 13 Pa

Fig. 2. SEM micrographs of soda–lime glasses with various etching conditions: a) 0 W/cm^2; b) 1.5 W/cm^2; c) 10 Pa; and d) 13 Pa.
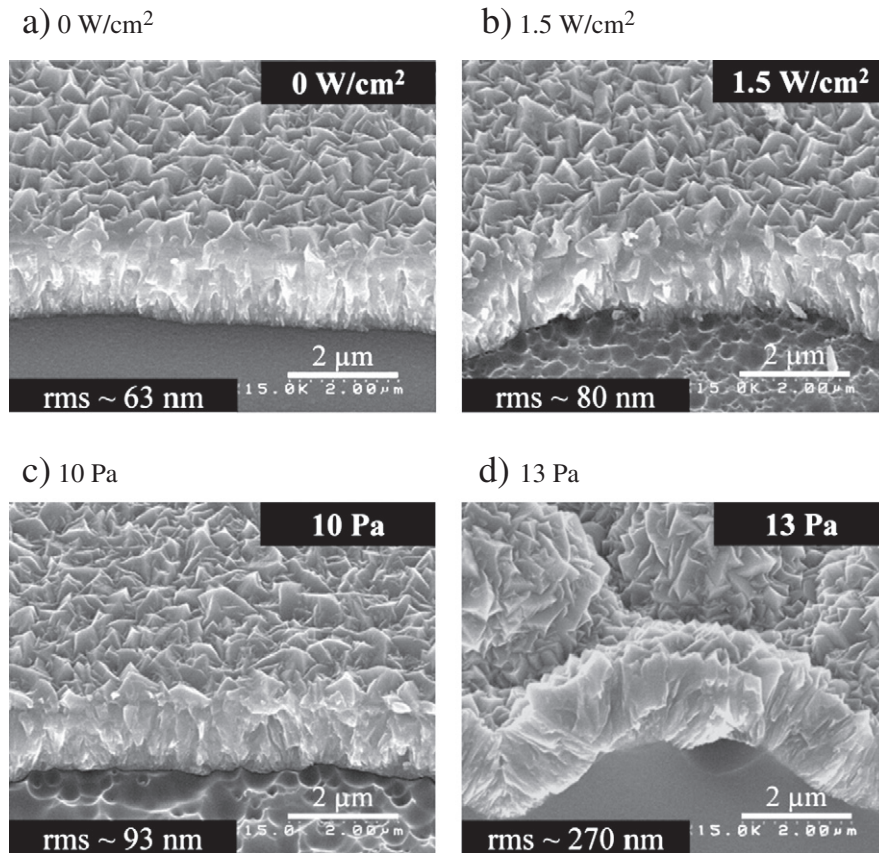
Fig. 3. Cross-sectional SEM micrographs of ZnO films deposited on soda–lime glasses with various glass-etching conditions: a) 0 W/cm^2; b) 1.5 W/cm^2; c) 10 Pa; and d) 13 Pa.

of all samples were higher than 80% over a wide wavelength region. However, the transmittances tended to decrease gradually in the long-wavelength range above 1000 nm because of the absorption of free carriers in the boron doped films [27,28]. The total transmittance, absorptance and reflectance of the ZnO films did not show obvious change with varying glass-etching conditions. It should be noted that the total transmittances of the ZnO deposited on soda–lime glass in this study are lower than those of the ZnO films deposited on Corning glass as previously reported elsewhere [14]. This is because the soda–lime glass contains a large amount of metallic impurities, thus it absorbs more light. These results clearly showed that the additional glass-substrate etching process had no negative effect on the transmittance of the ZnO films.

Fig. 4b illustrates the spectral haze ratio of the ZnO films with various glass-etching conditions. It was found that the haze ratio of the ZnO films at a wavelength of 800 nm slightly increased from 15 to 23% as the power density increased up to 1.5 W/cm^2, and started decreasing at the power density of 1.9 W/cm^2. This may be due to relatively low surface roughness and small lateral feature size of the films deposited on the glass etched at high power density condition as mentioned in Section 3.1. The haze ratio of ZnO films drastically increased with increasing gas pressure. The haze ratio enhanced as high as 92% has been obtained at a wavelength of 800 nm with the gas pressure of 13 Pa. These results revealed that the glass-etching pressure was a key parameter to control the light-scattering properties of the ZnO films.

3.4. Electrical properties of ZnO films

These results of Hall measurement indicated that the electrical properties of the ZnO films did not depend on the glass-etching
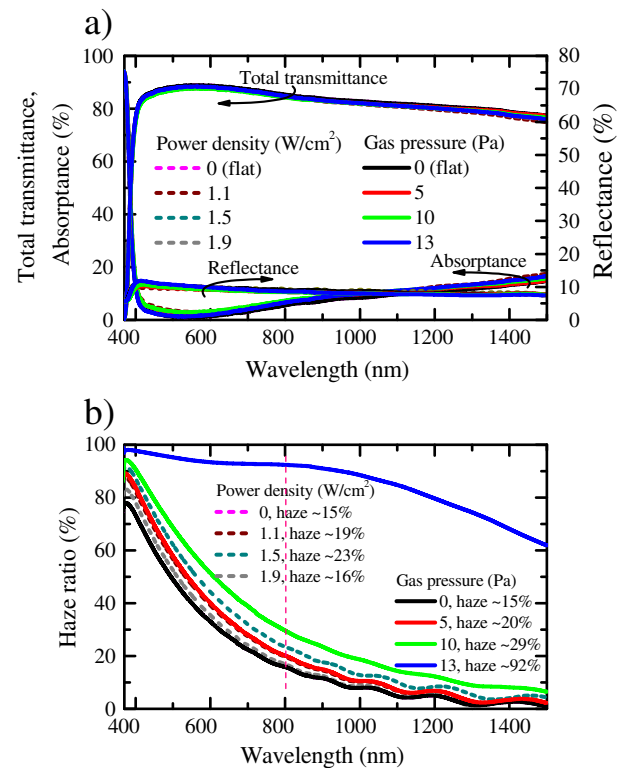

Fig. 4. Optical properties of ZnO films deposited on soda–lime glasses with various glass-etching conditions: a) total transmittance, absorptance and reflectance and b) spectral haze ratio. The spectral haze ratio at the wavelength of 800 nm for each film is also shown.

condition. The carrier concentration, mobility, and sheet resistance of all samples were approximately 3.11×10^{20} cm^{-3}, 18.21 cm^2/ (V · s), and 8.83 Ω/square, respectively. These results illustrated that the glass-substrate etching using RIE method allows the modification of surface properties of the ZnO films while maintaining their good electrical properties.

3.5. Performance of thin-film silicon solar cells

p–i–n type μc-Si:H solar cells were fabricated on etched and flat glass substrates in order to evaluate performance of the ZnO film as a front TCO film. Prior to the solar cell fabrication, all samples were briefly exposed for 10 min to Ar plasma to make the surface more suitable for good silicon deposition [29]. By employing the developed ZnO films on etched glass with the rms roughness of about 270 nm, up to now a cell efficiency of 8.14% with open-circuit voltage (V_{oc}) of 0.492 V, short-circuit current (J_{sc}) of 24.70 mA/cm^2 and fill factor (FF) of 0.67 has been obtained. These results were better than those of the cells fabricated on flat glass substrate, whose efficiency was 7.16% (V_{oc} = 0.497 V, J_{sc} = 21.85 mA/cm^2 and FF = 0.66). The efficiency of the solar cell with etched substrate increased, mainly owing to the enhancing of J_{sc}, which was ascribed to the higher rms roughness and higher haze ratio of the ZnO films, as previously mentioned in Section 3.2.

Fig. 5 exhibits the QE and reflectance of two typical μc-Si:H solar cells fabricated on ZnO coated glass substrates with different roughnesses. The QE of the solar cell on the etched glass in the wavelength region of higher than 600 nm was obviously greater than that of cell on flat glass. The improvement of QE, particularly in the long-wavelength region is supposed to be due to a better light scattering of the ZnO films deposited on etched glass. As mentioned previously, ZnO films with high surface roughness can improve light scattering at the ZnO/ p-layer interface [11,13], thereby enhancing light trapping in the long-wavelength region. The reflectance of the solar cell using high-haze ZnO on etched glass substrate was lower than that of the cell using conventional ZnO on flat substrate, which is possibly due to the anti-reflective properties of rougher interfaces [11]. The excellent QE results have verified that the high-haze ZnO on etched glass was effective in enhancing the light absorption in the microcrystalline silicon absorber layer by means of increasing light trapping together with a reduction of light reflection at the surface of the thin-film solar cells.

4. Conclusions

We have developed ZnO:B films with a very high haze ratio and low resistivity by carrying out a pre-etching process on soda–lime glass before the ZnO deposition. The effects of glass-etching conditions on the properties of the ZnO films were investigated. We found that the gas pressure was a key parameter to control the surface morphology of
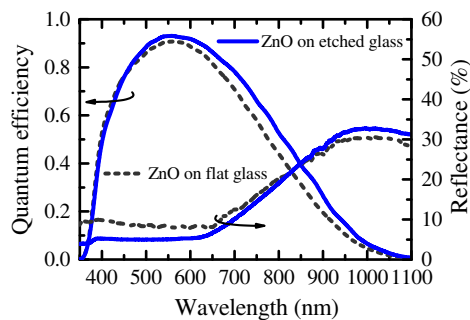
the soda–lime glass. The surface with large crater and high rms roughness could be obtained at the gas pressure of above 13 Pa. It was found that the surface morphology of the ZnO films grown on the glass strongly depended on the glass-substrate etching conditions. The rms roughness of the glass as high as 360 nm enables the surface morphology of the ZnO films to change from conventional pyramid-like single texture to greater cauliflower-like double texture, whose the rms roughness and haze ratio were relatively high. The ZnO film with the haze ratio of over 92% at the wavelength of 800 nm was achieved, while their good transparency and electrical properties of the ZnO films were maintained. When the developed ZnO films with a very high haze ratio were applied as a front TCO film in the μc-Si:H solar cells, the quantum efficiency of the solar cells particularly in the long-wavelength region improved. Up to now the highest cell efficiency of 8.14% with the J_{sc} as high as 24.70 mA/cm^2 has been achieved. It can be concluded that our unique and original glass etching process is effective in improving the light-scattering properties of the ZnO films while preserving their good transparency and electrical properties. Experimental results have verified the potential of the ZnO coated low cost glass substrate with very high haze ratio as the TCO coated glass for thin-film Si solar cells.

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Fig. 5. Quantum efficiency and reflectance of two typical μc-Si:H solar cells using ZnO films deposited on etched glass (rms ~270 nm) and flat glass (rms ~63 nm) as a front TCO film.