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On the origin of the changes in the opto-electrical properties of boron-doped zinc oxide films after plasma surface treatment for thin-film silicon solar cell applications

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ABSTRACT

The modification of the steep and sharp valleys on the surface of the boron-doped zinc oxide (BZO) front electrodes by plasma surface treatment is a critical process for avoiding a significant reduction in the electrical performance of thin-film silicon solar cells. In this work, we report the origin of the changes in the electrical and optical properties of the BZO films that occur after this process. On the basis of an analysis of the chemical states, we found an improvement of the carrier concentration along with the treatment time that was mainly due to an increase of the oxygen vacancy. This indicated a deficiency of the oxygen in the BZO films under argon-ion bombardment. The red-shift of the A_1 longitudinal optical mode frequency in the Raman spectra that was attributed to the existence of vacancy point defects within the films also strengthened this argument. The significant reduction of the haze ratio as well as the appearance of interference peaks on the transmittance spectra as the treatment time was increased were mainly due to the smoothing of the film surface, which indicated a degradation of the light-scattering capability of the BZO films. We also observed a gain of the visible-region transmittance that was attributed to the decrease of the thickness of the BZO films after the plasma surface treatment, instead of the crystallinity improvement. On the basis of our findings, we have proposed a further design rule of the BZO front electrodes for thin-film silicon solar cell applications.

1. Introduction

Among the photovoltaic technologies, the thin-film silicon solar cell is a powerful candidate thanks to its low production cost, larger scale commercialization, and its potential for further efficiency improvement [1–4]. A low efficiency that is mainly due to a low short-circuit current density (J_{sc}) is a main factor to limit the competitiveness of the thin-film silicon solar cells in comparison with the conventional crystalline silicon solar cells that dominate the solar-cell market, with a share of 90% [5,6]. Recently, light-trapping techniques have been widely applied to the thin-film silicon solar cells as an effective method for the improvement of the cell efficiency [7–11]. By increasing the light-beam path in the active layer, the light-trapping techniques significantly improve the incident photon absorption of the thin active layer, resulting in a gain of the J_{sc}.

In the superstrate-type thin-film silicon solar cells where the incident light first reaches the substrate, the light-trapping effect strongly relies on the transparent conductive oxide (TCO) front electrodes [10,12–14]. These electrodes simultaneously contribute to the transmission and scattering of incident light into the active layer, the process of the charge-carrier collection, and the growth of subsequent silicon layers via their surface morphology. In terms of its use as the front electrode in the thin-film silicon solar cells, an ideal TCO film should simultaneously fulfill the following six requirements: (1) an appropriately textured surface for effective light-scattering without any detrimental effects on the quality of the subsequent silicon layers, (2) a high transmittance in the absorption range of the active layer, (3) a low sheet resistance (R_{sh}) (< 10 Ω/sq for single-junction cells, and < 20 Ω/sq for multi-junction cells) to minimize series resistance losses, (4) high durability under exposure to the strongly reducing hydrogen ambient, (5) a low fabrication temperature for flexible substrate based thin-film silicon

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solar cells, and (6) a good uniformity for large-area fabrications (up to the meter-scale). Among the various TCO films used as front electrodes, it is likely that the boron doped zinc oxide (BZO) films deposited by metal-organic chemical vapor deposition (MOCVD) meet all of the above criteria. The highly textured surface of the as-deposited BZO films allows for an effective light-scattering. Unfortunately, the steep and sharp valleys on the surface of such BZO films, known as V-shaped valleys, is the main reason for the generation of stripelike defect regions in the active layer that leads to significant degradations of open circuit voltage (V_{oc}) and fill factor (*FF*) [15–18]. This phenomenon has been observed in both hydrogenated amorphous silicon (a-Si:H) and microcrystalline silicon (μc-Si:H) solar cells where the BZO films were used as front electrodes. Therefore, a smoothing of the V-shaped valleys on the surface of BZO front electrodes is an integral process for the avoidance of a significant reduction in the electrical performance of the thin-film silicon solar cells. There are several manners of surface modification of the BZO films [19–22]. Among these techniques, plasma surface treatment using argon (Ar) gas is generally used as an effective method to turn typical V-shaped valleys of the BZO front electrodes into U-shaped valleys [15,18,23]. Besides the surface modification, the electrical and optical properties of the BZO front electrodes are changed as side-effects of the plasma surface treatment. These changes affect the optimization of the BZO films, and hence affect the control of the fabricating conditions of the BZO films for cell applications. To the best of the authors' knowledge, a study on the origin of these changes has not been reported previously.

In this work, we analyzed the changes in the opto-electrical properties the BZO films before and after the plasma surface treatment. We also correlated this analysis with the changes of the crystal structure, the microstructure, and the chemical composition to suggest the origin of the changes in the opto-electrical properties of the BZO films.

2. Experimental section

With the use of diethylzinc (DEZ, $Zn(C_2H_5)_2$) and de-ionized water (DI H_2O) as precursors, BZO films were deposited onto $5 \times 5\ cm^2$ Corning Eagle 2000 glass substrates using a MOCVD system. Diborane (B_2H_6) diluted in 99% H_2 was used as a dopant gas. The DEZ, DI H_2O, and B_2H_6 flows were set as 125, 150, and 75 sccm, respectively. All of the samples were fabricated at a substrate temperature of 150 °C and a working pressure of 800 mTorr. The surface of the as-deposited BZO films was treated under Ar plasma using an inductively coupled plasma reactive-ion etching system. The treatment times were 3, 9, and 15 min, and these are named as short treatment time (STT), optimal treatment time (OTT), and excessive treatment time (ETT), respectively. Meanwhile, the other conditions such as power, working pressure, and Ar gas flow rate were fixed. After the plasma surface treatment, the BZO films were used as the front electrodes in the a-Si solar cells. The p-i-n layers were subsequently fabricated using a cluster-type plasma-enhanced chemical vapor deposition. The cell area was defined by the back contacts that consist of 200-nm-thick silver and 300-nm-thick aluminum layers. Furthermore, the a-Si solar cells using the as-deposited BZO films were fabricated as a reference.

Field-emission scanning electron microscopy (FE-SEM) was employed to examine the surface morphology of the BZO films. The carrier concentration (n), resistivity (ρ), and Hall mobility (μ) of the BZO films were analyzed by the HMS-3000 Hall effect measurement system (Ecopia) for which the van der Pauw geometry was applied. The R_{sh} measurement was performed using a four-point probe. The optical characteristics such as the total, specific, and diffuse transmittance were measured by a haze-meter system (Scinco). The haze ratio that represents the light-scattering capability is defined by the diffuse-transmittance/total-transmittance ratio. The optical band gap energy (E_{opt}) was determined by Tauc's model for a direct band gap semiconductor, as given by:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

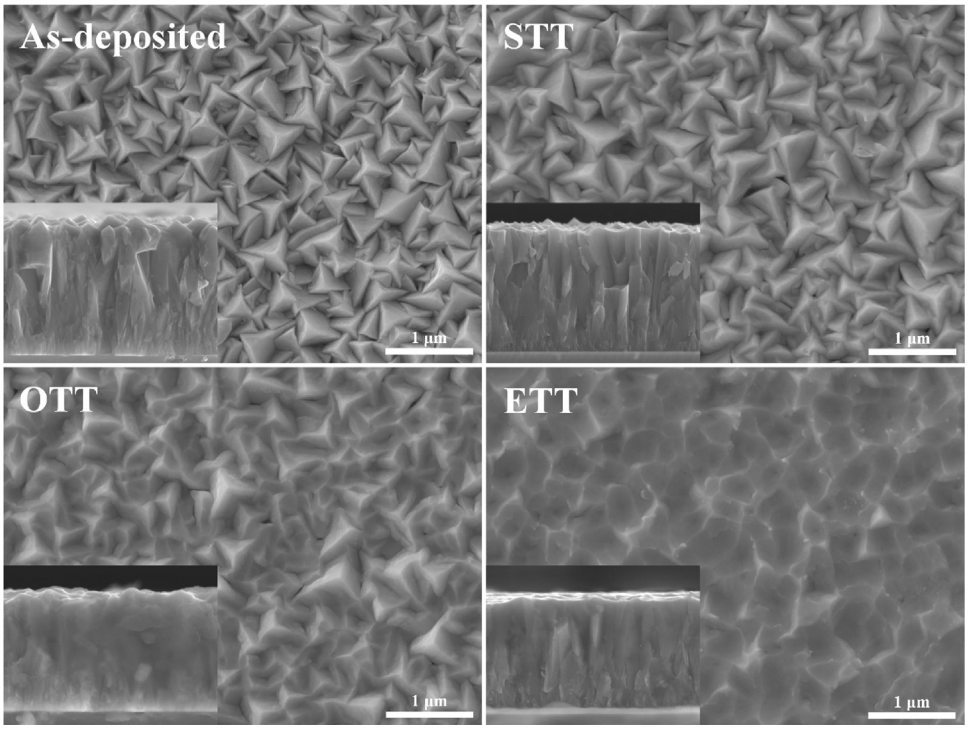

Fig. 1. FE-SEM images of the surfaces of the BZO films at various treatment times. The corresponding FE-SEM images of cross-sectional views of the BZO films are also shown in the insets of this figure.