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# Etching and passivation effects on boron-doped amorphous silicon carbide *p* layer of amorphous silicon solar cell by hydrogen treatment using a mercury-sensitized photochemical vapor deposition method

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Etching and passivation effects of hydrogen treatment of boron-doped hydrogenated amorphous silicon carbide (*a*-SiC:H) film used as a *p* layer of *p-i-n* type amorphous silicon based solar cells using a mercury-sensitized photochemical vapor deposition method were investigated. For the hydrogen treatment of the *p*-layer film, longer *p*-layer deposition time was needed to obtain the same thickness as for no hydrogen treatment because of hydrogen etching effect. However, the cell performance was improved by ~7% due to an increase in the open circuit voltage ( $V_{oc}$ ) and fill factor (FF) although the *p*-layer thickness was nearly identical in both cases. The increase in the  $V_{oc}$  and FF could be explained by an increase in the built-in potential due to a decrease in the film activation energy. Moreover, the electrical property improvement of the film was well explained by the passivation effect of a SiH<sub>2</sub>/SiH ratio decrease and a hydrogen content increase calculated from Fourier transformed infrared absorption measurements. © 1997 American Institute of Physics. [S0003-6951(97)02039-1]

A hydrogen plasma passivation technique has been used to obtain wide band gap intrinsic hydrogenated amorphous silicon (*a*-Si:H) without any decrease in the photoconductivity of the film<sup>1</sup> for *a*-Si:H solar cell application.<sup>2</sup> On the other hand, Nozaki *et al.* has carried out an etching study of intrinsic *a*-Si:H using mercury-sensitized H radicals in H<sub>2</sub> gas under ultraviolet (UV) light irradiation with a low pressure mercury lamp.<sup>3</sup> Recently, we have reported that a hydrogen treatment of the boron-doped amorphous silicon carbide (*a*-SiC:H) *p* layer of *p-i-n* type *a*-Si:H based solar cells using a mercury-sensitized photochemical vapor deposition (photo-CVD) is a novel technique to enhance the cell performance.<sup>4</sup> A hydrogen treatment at a proper hydrogen flow rate and treatment time made the open circuit voltage ( $V_{oc}$ ) and fill factor of the cells increase, resulting in higher performance. From the previous results, the boron-doped *p*-type *a*-SiC:H layer of the *a*-Si:H based solar cells seemed to be etched by hydrogen radicals. However, little has been reported about the passivation and etching effects of a hydrogen treatment on the boron-doped *a*-SiC:H *p* layer of the cells.

In this letter, we investigated both etching and passivation effects of the hydrogen treatment using the mercury-sensitized photo-CVD method on the boron-doped *a*-SiC:H *p* layer by measuring the solar cell characteristics as a function of *p*-layer deposition time for the no hydrogen treatment case and the hydrogen treatment case. Moreover, we show that an increase in the cell performance by the hydrogen treatment is due to a decrease in the activation energy of the boron-doped *a*-SiC:H film.

A three separated-chamber photo-CVD apparatus designed by our research group was used to deposit films and to fabricate *a*-Si:H based solar cells. Fabricated solar cells have a simple structure of glass/TCO(Asahi *U*-type SnO<sub>2</sub>)/

*p-i-n* metal (Al). The cell area is 0.031 cm<sup>2</sup>. Boron-doped *a*-SiC:H, intrinsic *a*-Si:H, and phosphorus-doped microcrystalline silicon ( $\mu c$ -Si:H) films were used as *p*, *i*, and *n* materials, respectively. Detailed deposition conditions of the each *p*, *i*, and *n* layer are presented in Ref. 4. A hydrogen treatment was successively performed on the *p* layer for 15 min by the photo-CVD method after *p*-layer deposition in the *p* chamber without destroying the vacuum. The hydrogen treatment condition was as follows: the hydrogen flow rate was 100 sccm, the substrate temperature was 250 °C, the total pressure was 1 Torr, and the temperature of the mercury bath was 20 °C. In order to assess fabricated *a*-Si:H solar cells, their photocurrent versus voltage (photo *I*-*V*) characteristics and collection efficiencies were measured under AM 1.5, 100 mW/cm<sup>2</sup> irradiation of a solar simulator. A constant energy spectrophotometer was used in collection efficiency measurements.

Two kinds of substrates, about 1200-Å-thick thermal-oxide-grown crystalline silicon (*c*-Si) wafer and Corning 7059 glass, were used to deposit the *p*-layer films. All the film thicknesses before and after a 15 min hydrogen treatment were measured using a spectroscopic phase modulated ellipsometer (Jobin-Yvon, UVISSEL). The ellipsometric angles ( $\psi, \Delta$ ) were collected over a spectral range of 1.5–4.0 eV and the results were fitted by the amorphous dispersion model<sup>5</sup> varying the parameters which denote optical properties of the film. In order to obtain more well-fitted results, film roughness was also considered. The roughness was modeled by Bruggeman's effective medium approximation (EMA)<sup>6</sup> with hemispherical shape. The ( $\psi, \Delta$ ) were fitted well over the entire spectral range of measurement. The thickness of the films deposited on the oxide-grown *c*-Si wafer was from 70 to 400 Å. These films were used to investigate the etching effect by the hydrogen treatment. The film roughness was 7–10 Å regardless of hydrogen treatment. The conductivity and activation energy were measured

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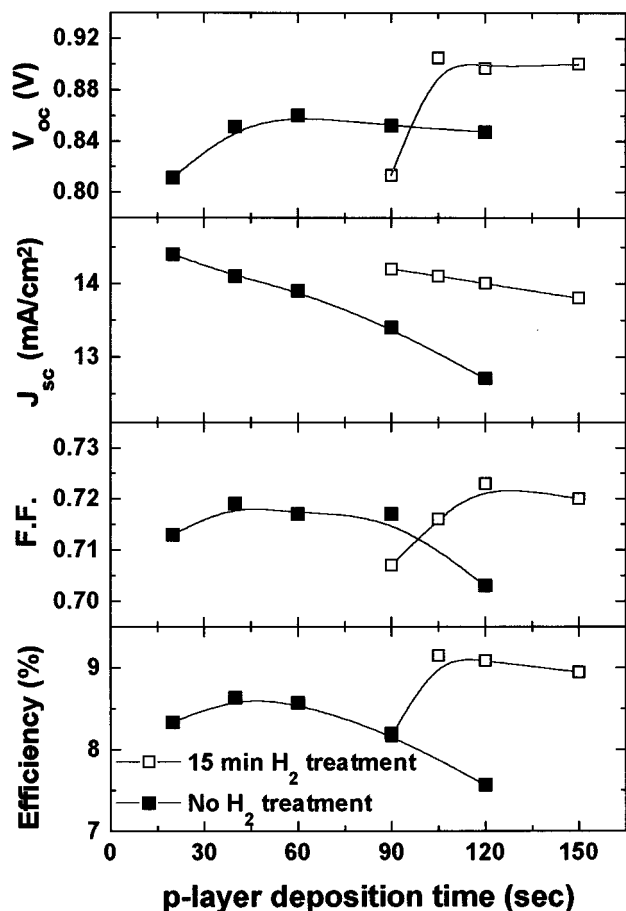


FIG. 1. Cell characteristics under AM 1.5, 100 mW/cm<sup>2</sup> illumination when *p*-layer deposition time is varied for the case of no hydrogen treatment (solid) and the case of a 15 min hydrogen treatment on the *p*-layer (open).

for 5000- to 6000-Å-thick films deposited on Corning 7059 glass substrates using coplanar electrodes. Fourier transformed infrared (FTIR) spectroscopy measurements were performed on these samples.

Solar cell characteristics as a function of *p*-layer deposition time are shown in Fig. 1. The *p*-layer deposition time was varied from 20 to 120 s for no hydrogen treatment case, and from 90 to 150 s for hydrogen treatment case. The cell characteristics show the same tendency for both cases except that the characteristics for hydrogen treatment case were horizontally shifted by about 65 s along the abscissa (*p*-layer deposition time) compared with the no hydrogen treatment case.

Boron-doped *a*-SiC:H *p*-layer deposition time versus film thickness before and after a 15 min hydrogen treatment is shown in Fig. 2. It can be seen that for the hydrogen treatment, longer deposition time is necessary to obtain roughly same thickness as for the no hydrogen treatment due to an etching effect of the hydrogen treatment. The deposition time of 20–90 s before the hydrogen treatment corresponds to that of 90–150 s after a 15 min hydrogen treatment. From these data, the etch rate under the hydrogen treatment conditions used in these experiments is about 10 Å/min. In *a*-Si:H based solar cell fabrication, the *a*-SiC:H film is deposited on textured transparent conducting oxide (TCO), therefore, the film thickness in *a*-Si:H solar cell may differ from that deposited on thermally grown SiO<sub>2</sub> due to

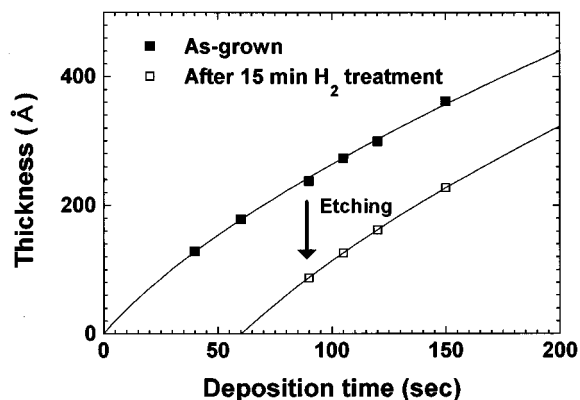


FIG. 2. Boron doped *a*-SiC:H *p*-layer deposition time vs film thickness before and after a 15 min hydrogen treatment.

roughness of the TCO. However, it is known that the effective thickness is virtually identical for both cases from the results of the real time spectroscopic ellipsometry (RTSE) measurement.<sup>7</sup>

In Figs. 1 and 2, although the *p*-layer thickness was identical, the  $V_{oc}$  and fill factor of the cells with hydrogen treatment were higher than those without hydrogen treatment except for the case of 90 s *p*-layer deposition time which is the case of very thin *p*-layer thickness. Thus, a maximum efficiency of the hydrogen treatment case (9.14%) was increased by 6.5% compared with that of no hydrogen treatment case (8.63%). The above results indicate that the electrical properties of boron-doped *a*-SiC:H film is improved due to passivation by hydrogen radicals. The activation energy and dark conductivity of the film before and after the hydrogen treatment were measured in order to clarify the passivation effect. Figure 3 shows the results as a function of hydrogen treatment time. The activation energy decreases from 0.467 to 0.441 eV and the conductivity increases by about two times from  $3.7 \times 10^{-7}$  to  $7.4 \times 10^{-7}$  S cm<sup>-1</sup> as the hydrogen treatment time increases from 0 (without hydrogen treatment) to 20 min. However, the activation energy increases again for 40 min hydrogen treatment time. From these results, the increase in  $V_{oc}$  by the posthydrogen treatment can be explained by an increase in the built-in voltage of *a*-Si:H solar cell. Figure 4 displays a band diagram explaining the increase in the built-in voltage by the posthydro-

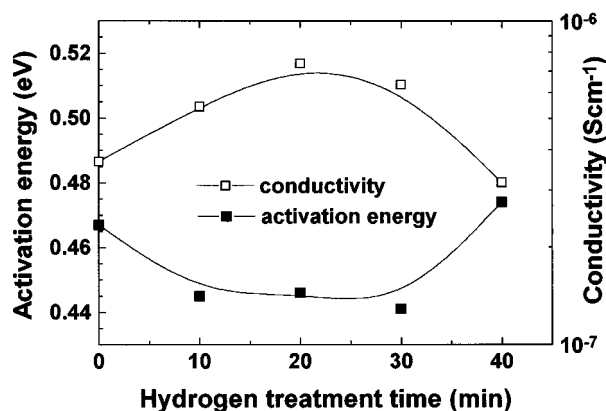


FIG. 3. Variation of activation energy and dark conductivity as a function of hydrogen treatment time.

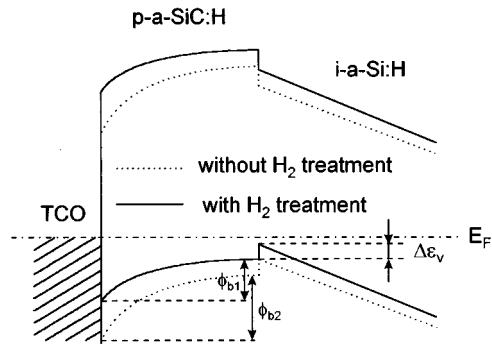


FIG. 4. Band diagram which explains the increase in the built-in voltage by a 15 min hydrogen treatment. The built-in voltage of *a*-Si:H solar cell increases by (i) the decrease in activation energy ( $\Delta\epsilon_v$ ). (ii) the decrease in surface barrier potential ( $\phi_{b2} - \phi_{b1}$ ) between the TCO and *a*-SiC:H film by the hydrogen treatment.

gen treatment. First, the built-in voltage increases due to the decrease in activation energy by the hydrogen treatment ( $\Delta\epsilon_v$ ). However, the increase is about 30 meV from Fig. 3 though the increase in  $V_{oc}$  is about 40 meV from Fig. 1. The remaining 10 meV is considered to be caused by a decrease in surface barrier potential ( $\phi_{b2} - \phi_{b1}$ ) between the TCO and *a*-SiC:H film due to an increase in conductivity of the *a*-SiC:H film by the hydrogen treatment.

In order to explain the decrease in the activation energy and the increase in the conductivity, C–H and Si–H bond configuration ( $\text{SiH}_2/\text{SiH}$  ratio) of boron-doped *a*-SiC:H film was calculated from FTIR absorption measurements. The C–H bond configuration and total hydrogen content bonded with carbon were nearly unchanged as the hydrogen treatment time varied. Figure 5 shows the total hydrogen content bonded with silicon and  $\text{SiH}_2/\text{SiH}$  ratio as a function of hydrogen treatment time. When the hydrogen treatment were performed, the hydrogen content clearly increases for a short hydrogen treatment time (about 10 min) but decreases again as the hydrogen treatment time increased. On the other hand,

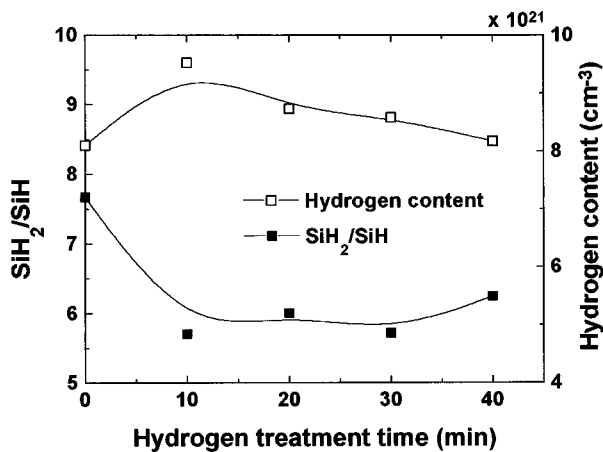


FIG. 5.  $\text{SiH}_2/\text{SiH}$  ratio and total hydrogen content bonded with silicon of the boron-doped *a*-SiC:H film vs hydrogen treatment time.

$\text{SiH}_2/\text{SiH}$  ratio rather decreases for the 10–30 min hydrogen treatment time and increases again for 30 min treatment time. Therefore, it can be known that the hydrogen incorporated in the film by the hydrogen treatment using the photo-CVD method mainly contributes to Si–H stretching mode bond configuration which passivate the defects of the film.<sup>1</sup> These results are well consistent with the data of Fig. 3. The decrease in the activation energy and increase in the conductivity are correlated to the increase in the Si–H bond configuration by the hydrogen treatment.

From secondary ion mass spectroscopy (SIMS) data, the diffusion coefficient ( $D$ ) of deuterium in boron-doped *p*-type *a*-Si:H film is about  $\sim 10^{-14} \text{ cm}^2 \text{ s}^{-1}$  at our posthydrogen treatment temperature of 250 °C.<sup>8</sup> Using this value of the  $D$ , the characteristic length,  $2(Dt)^{1/2}$ , is 500 Å for a 10 min hydrogen treatment and 980 Å for a 40 min hydrogen treatment in the *p*-type *a*-Si:H film. For *p*-type *a*-SiC:H film, the dangling bond density is more than 100 folds higher than that of *a*-Si:H. Therefore, the characteristic length may be more than tenfolds higher than that of *a*-Si:H because hydrogen atoms diffuse via hopping between dangling bond sites of amorphous network and the  $D$  is proportional to the dangling bond density of the film.<sup>9</sup> Moreover, the diffusivity of hydrogen is somewhat larger than that of deuterium. From the above discussion, it can be considered that the changes of the film occur in the bulk of the *p*-type *a*-SiC:H film.

In conclusion, the boron-doped *a*-SiC:H *p* layer of *p*-*i*-*n* type *a*-Si:H based solar cells was etched and passivated simultaneously by the hydrogen treatment using a mercury-sensitized photo-CVD when the treatment was performed on the *p*-layer after the deposition of the layer. For the hydrogen treatment of the *p*-layer film, longer *p*-layer deposition time was needed to obtain the same thickness as for no hydrogen treatment because of hydrogen etching effect. The passivation effect caused the  $V_{oc}$  and FF to increase, resulting in the cell performance improvement. The increase in  $V_{oc}$  and fill factor could be explained by an increase in the built-in potential due to a decrease in the activation energy of the boron-doped *a*-SiC:H *p* layer. Moreover, the improvement of film electrical property was well explained by the bond configuration ( $\text{SiH}_2/\text{SiH}$  ratio) and hydrogen content of the film calculated from FTIR spectra.

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