Cerium oxide and hydrogen co-doped indium oxide films for high-efficiency silicon heterojunction solar cells

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ABSTRACT

CeO_2 and hydrogen co-doped In_2O_3 (ICO:H) films deposited by ion plating with dc arc-discharge were used as a transparent conducting oxide (TCO) electrode in hydrogenated amorphous silicon (a-Si:H)/crystalline silicon (c-Si) heterojunction (SHJ) solar cells. Incorporating ICO:H instead of conventional Sn-doped In_2O_3 (ITO) films and hydrogenated In_2O_3 (IO:H) films, improved the fill factor (FF) and short-circuit current density (J_{sc}) simultaneously. The best SHJ cell (243.4 cm^2) containing ICO:H films had a conversion efficiency of 24.1%, open-circuit voltage of 745 mV, J_{sc} of 38.8 mA/cm^2, and FF of 83.2% because of their high Hall mobility of 140 cm^2/V s. We have clarified the following design principles for ICO:H films: (i) the Ce species substituted for In atoms acts as a donor and (ii) CeO_2 and H decrease the residual strain and the contribution of the grain boundary scattering to carrier transport. This co-doping method can produce high conversion efficiencies in all solar cells containing TCO with resistive emitters.

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1. Introduction

Hydrogenated amorphous silicon (a-Si:H)/crystalline silicon (c-Si) heterojunction (SHJ) solar cells are currently the focus of much research because they can achieve very high conversion efficiencies with simple processes [1–15]. The highest reported short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF) for this type of cell are 40.1 mA/cm^2, 750 mV, and 0.832, respectively [1]. As for all solar cells with resistive emitters, the conversion efficiency of SHJ solar cells is increased by low electrical resistivity and low optical absorption loss at wavelengths from the visible to the near-infrared (NIR) spectral regions of the transparent conducting oxide (TCO) layers. Although Sn-doped In_2O_3 (ITO) films have been widely used in solar cells [16,17], the light absorption loss in the TCO layers in the NIR region arising from free carrier absorption (FCA), which results from the high carrier density (N) causing plasma oscillations, must be addressed for light management [18]. In addition, the thermal stability of SHJ cells is usually limited to 200 or 250 °C [19,20]. Therefore, high-mobility TCO films deposited at temperatures below 200 °C must be compatible with high current properties and low ohmic losses without degrading the passivation properties.

Various metals have been used to dope polycrystalline In_2O_3 films to decrease the intragrain defects. W [21–23], Zr [24,25], Mo [26,27], Ti [28]-doped In_2O_3 films show high Hall mobility (μ_H) exceeding 80 cm^2/V s. In addition, Koida et al. showed that highly H-doped In_2O_3 (IO:H) films obtained by using H_2O vapor exhibited μ_H exceeding 100 cm^2/V s and good transparency in the NIR region [29–32]. Libera et al. reported the performance of IO:H films deposited by atomic layer deposition at 100–250 °C with O and H_2O vapor [33], similar to IO:H films produced by Koida. Although the electrical resistivity (ρ) in highly H-doped ITO films is decreased [34], doping pure In_2O_3 with H is more effective for decreasing the intragrain defects compared with conventional ITO. N of IO:H films [29–32] containing more than 2 atom % H exceeds 1.0×10^2 cm^{-3} because the H atoms act as shallow donors [35,36].

We have reported 100-nm-thick CeO_2-doped hydrogenated In_2O_3 (ICO:H) films with superior μ_H values of 130–145 cm^2/V s and low N values of less than 3×10^{20} cm^{-3} [37]. Our strategy of co-doping with CeO_2 and H is based on two factors [37]. (i) The effective ionic radius of tetravalent Ce donors with a coordination number of 6 (0.101 nm) is close to that of trivalent In with a coordination number of 6 (0.094 nm) [38], producing little change in microstrain around the dopant sites. (ii) The density of O vacancies (V_O) can be decreased by doped CeO_2 with a large standard enthalpy of formation compared with In_2O_3, improving the crystallinity. Analyzing the relationship between μ_H and N of ICO:H films showed that the main factor limiting the carrier

transport of the films is the intragrain ionized impurity scattering mechanism [37].

Here, we report the advantages of SHJ solar cells containing ICO:H films over the solar cells with conventional TCO films. We show that ICO:H films improve FF and J_{sc} simultaneously compared with conventional ITO films and IO:H films. We fabricated SHJ solar cells with an efficiency of 24.1% after fully optimizing all process steps. In addition, we propose the design principles for ICO:H films with superior μ_H based on Ce L_3 X-ray absorption near edge structure (XANES) spectra measurements and analysis of those films.

2. Materials and methods

ICO:H films were deposited by ion plating with dc arc-discharge, also called high-density plasma-enhanced evaporation (HPE) [39,40], at a low growth temperature of 150 °C. Commercially, HPE is suitable for depositing TCO layers in high-efficiency SHJ solar cells because its ion bombardment is lower than conventional sputtering, and its growth rate of typically 5.5 nm/s in our experimental setup is high. The ultimate vacuum pressure of the process chamber before the deposition was 6.0×10^{-5} Pa. The deposition gases were Ar, O_2, and H_2. The total gas pressure during film deposition was 0.45 Pa.

Intentionally introduced H_2O vapor during TCO-film growth is generally used to incorporate H atoms into the TCO films deposited by sputtering. Residual H_2O vapor in the deposition chamber with HPE and conventional sputtering can affect the film properties. We monitored the gas during deposition using a quadrupole mass spectrometer (Prisma Plus QMG220, Pfeiffer Vacuum) with an ultra-high-vacuum differential pumping system at an ultimate partial pressure of H_2O of 10^{-7} Pa to investigate the effect of residual gas in a chamber. Fig. 1 shows the partial pressure of H_2O vapor (P_{H_2O}) and H_2 (P_{H_2}) during discharge as a function of H_2 gas flow ratio (Q_H). The O_2 gas flow ratio was fixed at 11%. The P_{H_2O} values were calculated from the spectrum peak of the mass-to-charge ratio (m/z) of 18, which eliminated the effect of the doublet ion of the argon isotope $^{36}Ar^{2+}$. H_2O vapor in the residual gas, with a P_{H_2O} of 1.6×10^{-4} Pa, acted as a H source during deposition. P_{H_2} increased slightly with increasing Q_H, in contrast to P_{H_2O}. Although H_2O vapor was used as a H source during sputtering deposition, this result suggests that H_2 gas can be used for H doping the TCO films by HPE. Using H_2 gas instead of H_2O vapor has the advantage that a complex system for deaerating H_2O vapor

to exclude carbon dioxide and avoid contamination is unnecessary. HPE uses arc discharge at a high pressure of around 100 Pa, whereas sputtering uses glow discharge at a low pressure of around 1 Pa. Arc discharge at a high pressure can produce a dc arc plasma with a low electron temperature (T_e) compared with glow plasma [41]. As T_e increases, the ion bombardment of the substrate increases with the difference in the potential between plasma and substrate. We speculate that high-energy hydrogen ions generated by glow discharge with high T_e increase the number of dangling bonds in TCO films, increasing the strain in the films. Consequently, using H_2 gas in HPE at low T_e produces high-quality TCO films, in contrast to conventional sputtering.

The source materials for TCO deposition in this study were pure In_2O_3, and In_2O_3 pellets containing 3% CeO_2 (ICO), 10% SnO_2, or 1% WO_3 (IWO). All pellets were produced by Sumitomo Metal Mining Co., Ltd. The ICO:H, ITO and IO:H films were deposited on glass substrates (EAGLE XG, Corning) for electrical and optical characterization and structural analysis. The film compositions were analyzed by Rutherford backscattering spectrometry (RBS) and hydrogen forward scattering (HFS) with a custom-built RBS system from CEA. Electric conductivity and Hall voltage were measured with a Hall effect measurement system (ResiTest 8300, Toyo Technica). To analyze the optical band gap and assess the absorbance in the NIR region of TCO films, optical spectra were measured at wavelengths from 250 to 2500 nm with a grating spectrometer (V-770, JASCO). The chemical states of Ce dopants in ICO:H and non-H doped ICO films were evaluated from L_3-XANES spectra. Ce L_3-XANES spectra were obtained by the conversion He^+ yield method at BL11 of Kyushu Synchrotron Light Research Center [42]. The measurements were carried out at energy intervals of about 0.19 eV.

The cell structure was metal grid/TCO/a-Si:H p/a-Si:H i/c-Si n/a-Si:H i/a-Si:H n/TCO/blanket metal. The cell size was 243.4 cm^2. Both sides of the TCO layer were deposited with the same materials and process conditions. The thicknesses of the a-Si:H layers and TCO layer on each side of the wafers were approximately 10 and 70 nm, respectively. The total thickness of the a-Si:H layers was determined by transmission electron microscope measurements.

We used Czochralski (CZ) wafers as absorbers for the SHJ solar cells. The Si(100) wafers had a ρ of 2.0 Ω cm. The as-grown wafers were textured in alkaline solution and wet-chemically cleaned before they underwent thermal donor killer annealing. The textured wafers were dipped in 5% HF solution just before plasma-enhanced chemical vapor deposition (PECVD). The final wafer thickness of the CZ Si was approximately 130 μm. The SHJ solar cells contained thin a-Si:H films as a wide gap layer on both sides of the c-Si wafers that passivated the front heterojunction emitter, which collects minority-carriers, and the back contact, which collects majority-carriers. Intrinsic and doped a-Si:H layers were deposited on the whole wafer surfaces at 150–200 °C using mixtures of SiH_4, PH_3, B_2H_6, and H_2 in an automated parallel-plate industrial PECVD reactor at 40.68 MHz. TCO films were deposited by HPE on the front and back of the solar cells. Silver reflectors were deposited on the back of the cells by sputtering. Front fingers with no busbars were screen-printed with low-temperature silver paste. Finally, the cells were cured at 200 °C for 30 min.

The J–V characteristics of SHJ cells were measured with a Spot^{LIGHT} cell tester with a Grid^{TOUCH} contacting system (Pasan, Meyer Burger Technology Ltd.). The Grid^{TOUCH} system ensured a homogeneous pressure distribution across all fingers for FF measurement via its slightly bent bottom plate and an adapted load on the 35 wires perpendicular to the cell fingers. The voltage measurement was carried out using 5 of the 35 wires, distributed over the entire cell, while the other 30 were used to extract the current. J_{sc} was inversely proportional to the number of wires because of the shadowing effect of the wires on the cell. J_{sc} with no
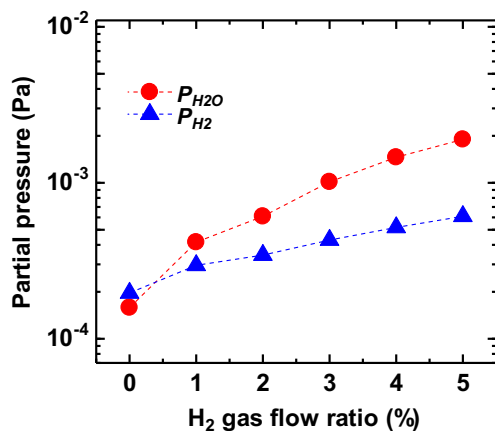

Fig. 1. Partial pressure of water vapor (P_{H_2O}) and H_2 (P_{H_2O}) as a function of Q_H during discharge.