**Photo-stability of a-Si solar cells fabricated by “Liquid-Si printing method”
and treated with catalytic generated atomic hydrogen**

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Abstract

The film properties and solar cell performances of hydrogenated amorphous silicon (a-Si:H) fabricated by a newly developed non-vacuum process, “Liquid-Si printing method” were systematically investigated with comparing to the conventional plasma-CVD method. The as-printed a-Si:H films showed relatively high Urbach-tail characteristic energy (E_{ch}), high $[Si-H_2]/[Si-H]$, and low photoconductivity ($\sim 10^{-7}$ S/cm). However, the $[Si-H_2]/[Si-H]$ decreased, and the photoconductivity was improved to the device grade level ($\sim 10^{-5}$ S/cm) after appropriate catalytic-generated atomic hydrogen treatment. It was also found that the light-induced degradation of the photoconductivities and the solar cell efficiencies of the printed samples were less than half of the conventional a-Si:H case.

Keywords

Amorphous Si, Solar cells, Stability, Liquid-Si, Cyclopentasilane, Atomic hydrogen treatment, Cat-CVD

1. Introduction

Such thin-film Si as hydrogenated amorphous silicon (a-Si:H) and microcrystalline silicon (μ c-Si:H) are important materials for cost-effective solar cells. We have been developing thin-film Si solar cells with high deposition rates and high conversion efficiencies for very cost-effective photovoltaic systems. We successfully made a stabilized a-Si:H/ μ c-Si:H tandem solar module with a high efficiency of 10.7% on a 1100*1300 cm² glass substrate by developing an original localized plasma confinement chemical vapor deposition (CVD) method [1]. The a-Si:H films deposited by plasma-CVD have already been systematically investigated, and the deposition criteria for high quality films has been reported [2-6].

We are also developing non-vacuum fabrication techniques to reduce the cost of such vacuum equipment as plasma-CVD or sputtering, both of which are limiting factors of photovoltaic module cost [1, 7]. Si ink materials make it possible to fabricate a-Si:H films by non-vacuum processes. Liquid-Si materials, which are constituted by SiH₂ polymer types, were previously demonstrated in TFT fabrication [9]. It was also reported that the photoconductivities of a-Si:H films fabricated by Liquid-Si showed 0.9×10^{-5} S/cm, and the conversion efficiency of a-Si solar cells, which used a-Si:H films by Liquid-Si in all the Si layers, was 0.51% [10]. Since the a-Si:H films fabricated by Liquid-Si had high photoconductivities and worked in thin-film Si solar cells, this Liquid-Si printing method is a candidate for the process in cost-effective solar cells.

Catalytic-generated atomic hydrogen (Cat-H*) effectively improved the photoconductivities of a-Si:H films fabricated by Liquid-Si. Their photoconductivities increased from 10^{-7} S/cm to 10^{-5} S/cm by Cat-H* [10]. As an effect on a-Si:H films of hydrogen treatment by Cat-CVD, etching

and crystallization were also reported [11]. However, the effects of Cat-H* treatment on a-Si:H fabricated by plasma-CVD and liquid-Si printing haven't been demonstrated.

Since the source materials and the fabrication processes of the Liquid-Si printing method are different from the plasma-CVD method, new guidelines for Liquid-Si printing method are needed to obtain high quality a-Si:H films for solar cells. In this study, as the first step to obtain the guidelines, we compared the film properties and the photostabilities of a-Si:H fabricated by the Liquid-Si printing method to those of the device grade a-Si:H deposited by a conventional plasma-CVD to extract the differences between these two methods.

2. Experimental

Non-doped a-Si:H films about 100 nm thick were prepared by the Liquid-Si printing method (L-a-Si:H) and the RF plasma-CVD method (P-a-Si:H). Liquid-Si ink was a mixed solution of solvent and SiH₂ polymer (polydihydrosilane) [10]. The polydihydrosilane ($M_w = 10^2 \sim 10^7$) was synthesized by the photo-induced ring-opening polymerization of cyclopentasilane (CPS) [12]. The wavelength, the intensity, and the irradiation time were 365 nm, 15 mW/cm², and 10-60 min, respectively. The Liquid-Si printing method consists of the printing of Liquid-Si ink, the pyrolyzing, and the Cat-H* treatment [10]. The Liquid-Si ink was spin-coated on glass (Corning Eagle XG) substrates at 2000 rpm for 30 sec and pyrolyzed at 430°C for 15 min on a hot plate. The Liquid-Si printing method fabricated a-Si:H in a non-vacuum process, but it fabricated a-Si:H by a complicated three-dimension reaction and needed temperature over 400°C, which was much higher than the around 200°C needed for the plasma-CVD.

For the Cat-H* treatment, Cat-CVD was used. The equipment was nearly identical to that previously described [13]. A 0.5 mm diameter, 100 cm long tungsten wire was used as a catalyzer and heated to 1850 °C. Hydrogen gas was introduced into the chamber at 20 sccm flow rate for 15 min. The chamber pressure and the substrate temperature were maintained at 0.2 Pa and 200 °C. For comparison, L-a-Si:H and P-a-Si:H were treated with Cat-H*.

The optical absorption coefficient (α) was determined from transmittance (T) and reflectance (R) spectra, where the optical interference effects were suppressed using $T/(1-R)$ [14]. The optical gaps were determined from the $(\alpha h\nu)^{1/3}$ versus $h\nu$ plot, which provides a better measurement of the properties of a-Si:H than Tauc's plot [14]. Photothermal deflection spectroscopy (PDS) was used to measure α in the low photon energy region. The IR absorption spectra were measured to confirm the hydrogen contents (C_H) bonded as Si-H and Si-H₂ using an ATR/FT-IR spectroscopic technique. We used mixed Gaussian and Lorentzian peak functions for this analysis.

3. Results and Discussions

3-1. Film properties

Figure 1 shows the α spectra of P-a-Si:H and L-a-Si:H before and after the Cat-H* treatment. The α spectra in the visible region of L-a-Si:H resemble those of P-a-Si:H. In contrast, the Urbach-tail slope of L-a-Si:H is larger than that of P-a-Si:H; the band-edge fluctuation of the L-a-Si:H is large. Their large band-edge fluctuations probably result from the distributions of the length and the angle of the Si-Si bonds.

Table 1 shows the optical gaps and the conductivities of L-a-Si:H and P-a-Si:H before and after the Cat-H* treatment. The effects of the Cat-H* treatment on the α spectra seem small; however, L-a-Si:H's optical gap, which is about 0.2 eV lower than that of P-a-Si:H, increased after the Cat-H* treatment. Even though the photoconductivity of L-a-Si:H was very low before the Cat-H* treatment, it improved to 5×10^{-6} S/cm after the Cat-H* treatment, which nearly equals that of P-a-Si:H. L-a-Si:H is relatively easily influenced by Cat-H*. Figure 2 shows the optical gap plotted against C_H . The optical gaps of P-a-Si:H have been reported to be proportional to C_H [15]. The relationship between the optical gap and the C_H of L-a-Si:H approximately consists of P-a-Si:H, but L-a-Si:H has a lower optical gap and a lower C_H than device grade P-a-Si:H.

Figure 3 shows the IR absorption spectra of P-a-Si:H and L-a-Si:H. Even though Si-H bonds are dominant in P-a-Si:H, Si-H₂ bonds are dominant in L-a-Si:H. Furthermore, although the Cat-H* treatment increases the Si-H bonds and decreases the Si-H₂ bonds in L-a-Si:H, it decreases the Si-H bonds in P-a-Si:H. The effects of Cat-H* treatment on the hydrogen bonding configurations are different between P-a-Si:H and L-a-Si:H.

Figure 4 shows [Si-H₂]/[Si-H] plotted against C_H. It was reported that the relationship between [Si-H₂]/[Si-H] and C_H for P-a-Si:H deposited from hydrogen-diluted silane was comparable to the continuous random network (CRN); however, the [Si-H₂]/[Si-H] of P-a-Si:H deposited from non-diluted silane increased with additional C_H [6]. By contrast, while L-a-Si:H's C_H is very low, [Si-H₂]/[Si-H] is very high. The rich Si-H₂ bonds in L-a-Si:H probably result from the molecular constitution of polydihydrosilane.

3-2. Photo-stabilities

One of the main problems in a-Si:H is the photodegradation due to an increase in the number of metastable defects in a-Si:H during light irradiation [16]. To compare the photostabilities, the films and solar cells that used L-a-Si:H and P-a-Si:H were exposed to light with an intensity of 500 mW/cm² at 25°C for 180 min and annealed at 80°C to confirm the thermal recovery behavior. We prepared the solar cells that used P-a-Si:H and L-a-Si:H as i-layers. The cell structure was glass/TCO(flat)/a-Si:H(nip)/metal. The doped-Si layers were deposited by plasma-CVD. The photodegradation of the solar cells that used L-a-Si:H was considerably less than those that used P-a-Si:H. The photodegradation of the L-a-Si:H films was less than half of those of the P-a-Si:H films even if their photoconductivities are comparable to those of the L-a-Si:H films. Figure 5 shows the photodegradation and the thermal recovery behaviors. The photoconductivity ratios of the light degradation and the thermal recovery of the films that used L-a-Si:H to those that used P-a-Si:H are comparable to those of the ratios of the conversion efficiencies. This result demonstrates that the photoconductivities and the conversion efficiencies of L-a-Si:H have high photostability.

The light-induced degradation of the photoconductivities and the defect densities decreased when the Si-H₂ bond densities decreased in the P-a-Si:H films [5]. Hydrogen motion and structure flexibility, both of which are related to Si-H₂ bonds, may be associated with a light-induced effect. L-a-Si:H has rich Si-H₂ bonds and high photostabilities, probably because the hydrogen atoms in it are difficult to move due to very low C_H.

4. Conclusions

We systematically compared the properties of L-a-Si:H to those of P-a-Si:H and summarized them as follows: (1) As film properties, the similarities were α in the visible region and high photoconductivities, and the differences were α in the Urbach-tail region, C_H, and [Si-H₂]/[Si-H]. (2) Cat-H* largely improved the photoconductivities and increased the optical gaps of L-a-Si:H, increased the Si-H bonds, and decreased the Si-H₂ bonds. The effects on the hydrogen bonding configurations were in contrast with the case of P-a-Si:H. (3) The photoconductivities and the conversion efficiencies are stable against light soaking.

High photoconductivities and high photostabilities are valuable properties for solar cells with a-Si:H. L-a-Si:H is expected to be improved for use in cost-effective and high performance solar cells with a-Si:H, such as a-Si:H solar cells and hetero junction solar cells.

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Table 1 The film properties of P-a-Si:H and L-a-Si:H before and after Cat-H* treatment.

Fig. 1 The absorption coefficient (α) spectra of P-a-Si:H and L-a-Si:H before and after Cat-H* treatment.

Fig. 2 The optical gap (E_{opt}) as a function of the hydrogen contents. Rounds ($\bigcirc$) indicate P-a-Si:H and triangles ($\blacktriangle$) indicate L-a-Si:H. Some plots are referenced from [4].

Fig. 3 The IR absorption spectra of P-a-Si:H and L-a-Si:H before and after Cat-H* treatment.

Fig. 4 $[\text{Si-H}_2]/[\text{Si-H}]$ as a function of C_H . Rounds ($\bigcirc$) indicate non-diluted P-a-Si:H squares ($\square$) indicate hydrogen-diluted P-a-Si:H and triangles ($\blacktriangle$) indicate L-a-Si:H.

Fig. 5 (a) the normalized photoconductivities and (b) the normalized conversion efficiencies plotted against light induced time and annealed time. Rounds ($\bigcirc$) and dashed lines indicate P-a-Si:H and triangles ($\triangle$) and solid lines indicate L-a-Si:H.

Figure 1

Table 1

	Hydrogen treatment	Thickness [nm]	Optical gap [eV]	Conductivity [S/cm]		photo/dark
				photo	dark	
Plasma-CVD	before	67	1.63	1.1E-05	7.1E-12	1.5E+06
	after	64	1.65	1.6E-05	7.1E-12	2.3E+06
Liquid-Si printing	before	83	1.45	5.7E-08	4.4E-11	1.3E+03
	after	80	1.51	5.1E-06	3.7E-11	1.4E+05

Figure 2

Figure 3

Figure 4

Figure 5