Identification and Suppression of Si-H_2 Bond Formation at P/I Interface in a-Si:H Films Deposited by SiH_4 Plasma CVD*)

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Light-induced degradation is an important problem concerning hydrogenated amorphous silicon (a-Si:H) solar cells. A-Si:H films of lower Si-H_2 bond density exhibit less light-induced degradation. In this study, Raman spectroscopy measurements of a-Si:H films with P-layer/I-layer structure reveal that high-density Si-H_2 bonds exist in the I-layer within 60 nm of the P/I interface. These Si-H_2 bonds originate from surface reactions of SiH_3 radicals, as the alternative origin (i.e., cluster incorporation) is considerably suppressed by a multi-hollow discharge plasma chemical vapor deposition method. For an I-layer thickness of 20 nm, the density ratio of Si-H_2 and Si-H bonds in the I-layer decreases from 0.133 to 0.053 as the substrate temperature increases from 170°C to 250°C. Fine tuning of the substrate temperature during the initial stage of I-layer deposition is thus effective in suppressing Si-H_2 bond formation at the P/I interface.

Keywords: plasma CVD, Si-H_2 bond, a-Si:H, solar cell, Raman spectroscopy

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1. Introduction

Recently, there has been a rapid expansion of the Internet of Things (IoTs), which has led to high energy consumption. However, the challenge of supplying power to an enormous number of IoT devices remains unresolved [1]. Hydrogenated amorphous silicon (a-Si:H) thin film solar cells have attracted attention due to their thin and flexible features and a relatively low production cost compared with other solar cells [2]. A critical challenge for a-Si:H solar cells is the suppression of light-induced degradation, as this degradation leads to a significant reduction in the efficiency of the solar cells [3, 4].

A-Si:H films are deposited by SiH_4 plasmas in which a-Si:H nanoparticles in a size range below 10 nm (clusters), higher-order silane Si_mH_n ($m < 4$, $n < 2m + 2$), and SiH_3 radicals are generated [5–10]. A lower density of Si-H_2 bonds in a-Si:H films leads to higher stability of the films. Cluster incorporation into films contributes to Si-H_2 bond formation in the films [11–15]. SiH_3 radicals are the main deposition precursors for high-quality a-Si:H films, while Si-H_2 bonds are also formed by surface reactions of SiH_3 radicals [16–18]. Therefore, suppressing cluster incorporation as well as tuning the surface reactions of SiH_3 radicals is required to form highly stable a-Si:H films.

A multi-hollow discharge plasma CVD (MHDPCVD) method has been developed together with a cluster-eliminating filter to suppress cluster incorporation [19–25]. Clusters in the discharge region are transported to the vacuum pump by fast gas flow, leading to the deposition of highly stable a-Si:H films. We also have succeeded in evaluating the density ratio I_{SiH2}/I_{SiH} of Si-H_2 and Si-H bonds in films in B-doped Si films (P-layer), intrinsic Si films (I-layer) and their interfaces of PIN a-Si:H solar cells using Raman spectroscopy [26]. In this study, we measured the I_{SiH2}/I_{SiH} ratio at the P/I interface to identify the region of high-density Si-H_2 bonds and suppress the Si-H_2 bonds in this region.

2. Experiment

As illustrated in Fig. 1, an MHDPCVD reactor with a cluster-eliminating filter was used for the deposition of a-Si:H films. Intrinsic I-layer were deposited on 5 cm × 5 cm SnO_2-coated glass substrate (Asahi-VU), on which P-layer was deposited in advance. Pure SiH_4 gas was fed into the reactor at 84 sccm, and the total pressure was 0.08 Torr. The discharge frequency and power were 110 MHz and 20 W, respectively. The substrate temperature was 170°C, 200°C, 220°C, and 250°C, and the thickness of the I-layer was 20 - 130 nm. Most clusters generated in plasmas are transported to the downstream region because their diffusion velocity is less than the gas velocity. Therefore, incorporation of clusters into films deposited in the upstream region is significantly suppressed compared with the downstream region.

Figure 2 presents the structure of the P and I layers. Measurements of the I_{SiH2}/I_{SiH} ratio were performed with a Raman spectroscope (JASCO, NRS-3100) equipped with a HeNe laser ($\lambda = 632.8$ nm). The focus position was set to

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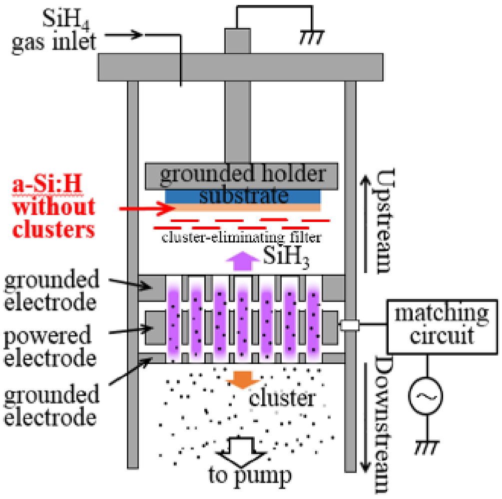

Fig. 1 Multi-hollow discharge plasma reactor with cluster-eliminating filter.

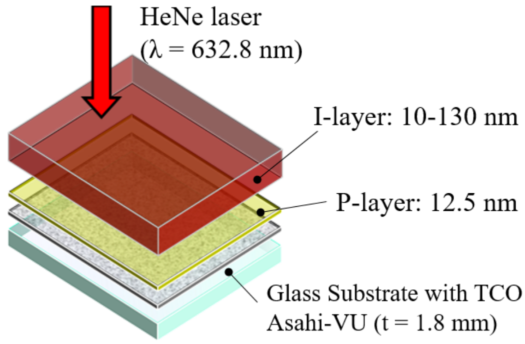

Fig. 2 Structure of P- and I-layers together with laser excitation of Raman spectroscopy.

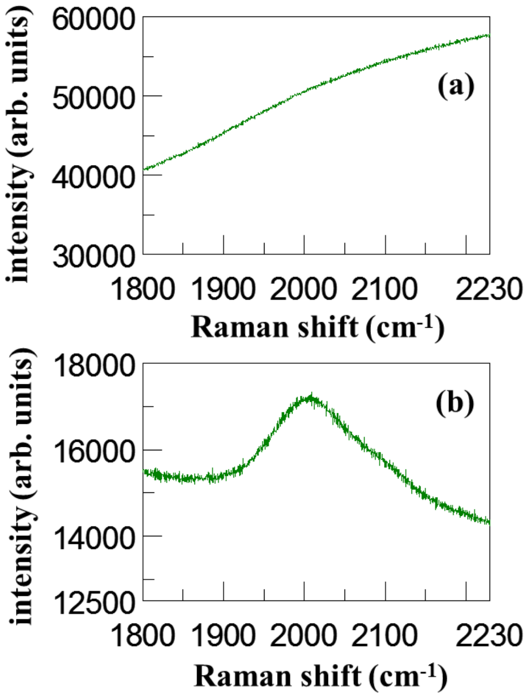

Fig. 3 (a) Spectrum of a single P-layer. (b) Spectrum of a PI-layer.

a surface of the I-layer. The scan time was 100 s, and there were three cumulative measurements. The diameter of the probe laser was 1 μm. Raman spectra were deconvoluted around 2000 - 2090 cm^{-1} of a-Si:H films into two peaks corresponding to Si-H bonds (2000 cm^{-1}) and Si-H_2 bonds (2090 cm^{-1}). The I_{SiH2}/I_{SiH} ratio was then deduced from the deconvoluted results [26–29].

We then measured the Raman spectra of a single P-layer and PI-layer, as presented in Figs. 3 (a) and (b), respectively. The I-layer thickness was 60 nm. No Raman peak was obtained for the single P-layer, while a clear peak was obtained for the PI-layer. The band gap of the P-layer was wider than that of the I-layer to suppress light absorption loss in the P-layer, namely, the window layer of PIN solar cells. Therefore, HeNe laser light of 632 nm was hardly absorbed in the P-layer, leading to no Raman peak, while the P-layer had a large number of Si-H_2 bonds [30, 31]. HeNe laser light was efficiently absorbed in the I-layer, leading to a clear Raman peak. Thus, the peak in Fig. 3 (b) originated from the I-layer.

3. Results and Discussion

Figure 4 illustrates the dependence of I_{SiH2}/I_{SiH} on the thickness of the I-layer. I_{SiH2}/I_{SiH} decreases by increasing the thickness from 10 to 60 nm, and becomes constant for a thickness above 60 nm, indicating that high-density Si-H_2 bonds exist at the P/I interface. These Si-H_2 bonds originate from surface reactions of SiH_3 radicals, as the alternative origin (i.e., cluster incorporation) is considerably suppressed by the MHDPCVD method and cluster-eliminating filter. Keya *et al.* [26] measured the I_{SiH2}/I_{SiH} ratio of a single P-layer using a Raman spectroscope equipped with the second harmonics of a YAG laser (λ = 532 nm), as a single P-layer is so thin that a Raman peak cannot be obtained with a HeNe laser. The I_{SiH2}/I_{SiH} ratio of a single P-layer was 0.60, indicating the existence of high-density Si-H_2 bonds in the P-layer.

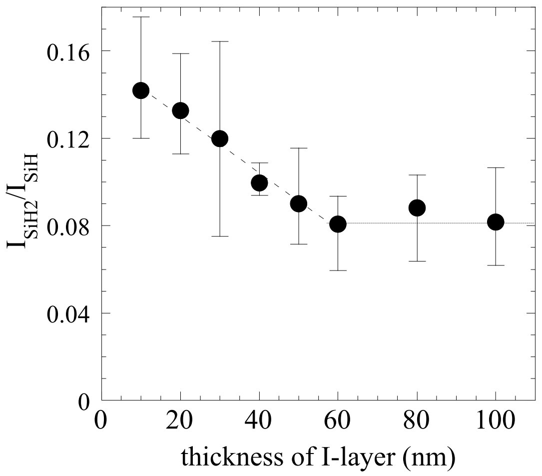

Fig. 4 Dependence of I_{SiH2}/I_{SiH} on thickness of I-layer.

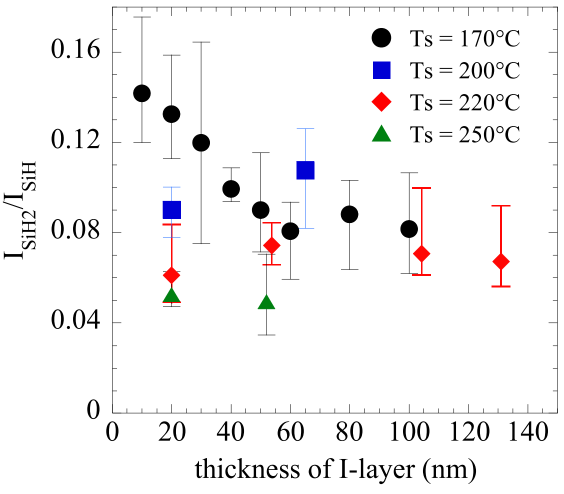

Fig. 5 Dependence of I_{SiH2}/I_{SiH} on thickness of I-layer and substrate temperature.

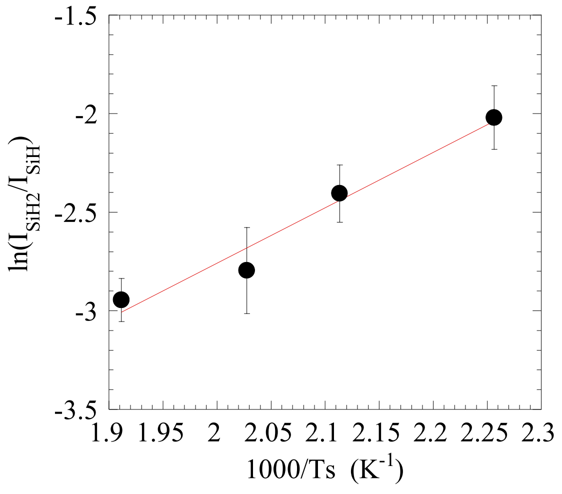

Fig. 6 Arrhenius plot (ln(I_{SiH2}/I_{SiH}) vs. 1000/T_s) for a thickness of 20 nm.

The P/I interface is also known to contain hydrogen-rich bonds and many dangling bond defects, which may have an influence on Si-H_2 bond formation in the I-layer at the beginning of film formation [32, 33]. As the I-layer is formed from 10 to 60 nm on the P-layer, the influence of the P-layer on the I-layer gradually decreases, and I_{SiH2}/I_{SiH} decreases from 0.142 to 0.081. At a thickness greater than 60 nm, the I-layer is not affected by the P-layer and thus, I_{SiH2}/I_{SiH} is constant at 0.083. As a result, high-quality films are formed for a thickness greater than 60 nm. To achieve higher stability, it is important to suppress Si-H_2 bond formation for a P/I interface thickness of less than 60 nm.

To achieve this suppression, we examined the effects of substrate temperature on I_{SiH2}/I_{SiH}. Figure 5 illustrates the dependence of I_{SiH2}/I_{SiH} on I-layer thickness as a parameter of substrate temperature. At a film thickness of 20 nm, I_{SiH2}/I_{SiH} decreases from 0.133 to 0.053 as the substrate temperature increases from 170°C to 250°C. In addition, as the substrate temperature increases from 170°C to 250°C, the dispersion of I_{SiH2}/I_{SiH} in the I-layer decreases, and the uniformity of the film quality is improved for a higher substrate temperature. At a substrate temperature of 220°C, I_{SiH2}/I_{SiH} remains constant at 0.069 irrespective of the I-layer thickness from 20 to 130 nm, indicating that Si-H_2 bond formation at the P/I interface is significantly reduced.

The average diffusion length of SiH_3 radicals on a-Si:H films is expressed as $\Lambda = .\sqrt{D\tau}$, where D is the diffusion coefficient and τ is the lifetime of SiH_3 radicals on the surface [34, 35]. Here, D is dependent on the substrate temperature. As the substrate temperature increases, the surface diffusion of SiH_3 radicals increases, and the H-abstraction reaction is promoted [36]. Therefore, Si-H_2 bond formation is suppressed for a P/I interface thickness of less than 60 nm by controlling the substrate temperature.

Figure 6 presents an Arrhenius plot (ln(I_{SiH2}/I_{SiH}) vs. 1000/T_s) for a thickness of 20 nm. We used a substrate temperature range of 170 - 250°C. The slope of ln(I_{SiH2}/I_{SiH}), related to activation energy E_a, differs depending on the Si-H_2 bond density in the I-layer. The activation energy E_a for converting Si-H_2 bonds into Si-H bonds by surface reactions of SiH_3 is 0.242 eV. Using the MHDPCVD method with a cluster-eliminating filter, we succeeded in deriving the activation energy E_a under conditions of low cluster incorporation.

4. Conclusions

In this study, we examined the Si-H_2 bond density in the I-layer on the P-layer, deposited by the MHDPCVD method equipped with a cluster-eliminating filter, to identify a region of high Si-H_2 bond density and to suppress the Si-H_2 bond density in that region. In the I-layer on the P-layer, the Si-H_2 bond density was high for a thickness of less than 60 nm. To suppress the Si-H_2 bond density in this region, we examined the effects of substrate temperature on I_{SiH2}/I_{SiH}. I_{SiH2}/I_{SiH} decreased from 0.133 to 0.053 as a result of increasing the substrate temperature from 170°C to 250°C. The activation energyE_a for converting Si-H_2 bonds into Si-H bonds was deduced to be 0.242 eV from an Arrhenius plot (ln(I_{SiH2}/I_{SiH}) vs. 1000/T_s) for a thickness of 20 nm. Precise tuning of the substrate temperature is thus effective in suppressing Si-H_2 bond formation at the P/I interface.

Acknowledgments

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