Identification and Suppression of Si-H$_2$ Bond Formation at P/I Interface in a-Si:H Films Deposited by SiH$_4$ Plasma CVD$^*$

Kazuma TANAKA, Hisayuki HARA, Shota NAGAISHI, Liu SHI, Daisuke YAMASHITA, Kunihiro KAMATAKI, Naho ITAGAKI, Kazunori KOGA and Masaharu SHIRATANI

Kyushu University, Fukuoka 819-0395, Japan

(Received 3 January 2019 / Accepted 21 April 2019)

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$^\circ$C to 250$^\circ$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

DOI: 10.1585/pfr.14.4406141

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$_m$H$_n$ ($m\leq4$, $n<2m+2$), 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$_2$ 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 ISiH$_2$/ISiH 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 ISiH$_2$/ISiH 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 $\times$ 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$^\circ$C, 200$^\circ$C, 220$^\circ$C, and 250$^\circ$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 ISiH$_2$/ISiH 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...
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.

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 $I_{\text{SiH}_2}/I_{\text{SiH}}$ on the thickness of the I-layer. $I_{\text{SiH}_2}/I_{\text{SiH}}$ 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 $I_{\text{SiH}_2}/I_{\text{SiH}}$ ratio of a single P-layer using a Raman spectroscope equipped with the second harmonics of a YAG laser ($\lambda = 532$ nm), as a single P-layer is so thin that a Raman peak cannot be obtained with a HeNe laser. The $I_{\text{SiH}_2}/I_{\text{SiH}}$ ratio of a single P-layer was 0.60, indicating the existence of high-density Si-H$_2$ bonds in the P-layer.
The P/I interface is also known to contain hydrogen-rich bonds and many dangling bond defects, which may have an influence on Si-H2 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 ISiH2/ISiH 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, ISiH2/ISiH 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-H2 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 ISiH2/ISiH. Figure 5 illustrates the dependence of ISiH2/ISiH on I-layer thickness as a parameter of substrate temperature. At a film thickness of 20 nm, ISiH2/ISiH 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 ISiH2/ISiH 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, ISiH2/ISiH remains constant at 0.069 irrespective of the I-layer thickness from 20 to 130 nm, indicating that Si-H2 bond formation at the P/I interface is significantly reduced.

The average diffusion length of SiH3 radicals on a-Si:H films is expressed as $\Lambda = \sqrt{D\tau}$, where $D$ is the diffusion coefficient and $\tau$ is the lifetime of SiH3 radicals on the surface [34, 35]. Here, $D$ is dependent on the substrate temperature. As the substrate temperature increases, the surface diffusion of SiH3 radicals increases, and the H-abstraction reaction is promoted [36]. Therefore, Si-H2 bond formation is suppressed for a P/I interface thickness of less than 60 nm by controlling the substrate temperature.

4. Conclusions

In this study, we examined the Si-H2 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-H2 bond density and to suppress the Si-H2 bond density in that region. In the I-layer on the P-layer, the Si-H2 bond density was high for a thickness of less than 60 nm. To suppress the Si-H2 bond density in this region, we examined the effects of substrate temperature on ISiH2/ISiH. ISiH2/ISiH decreased from 0.133 to 0.053 as a result of increasing the substrate temperature from 170°C to 250°C. The activation energy $E_a$ for converting Si-H2 bonds into Si-H bonds by surface reactions of SiH3 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.

Acknowledgments

The authors are grateful to Mr. Kimitaka Keya, Kyushu University for their help in sample preparation. This work was partly supported by National Institute of Advanced Industrial Science and Technology (AIST) and JSPS KAKENHI Grant Number JP26246036.
[1] H. Jayakumar, K. Lee, W. Suk Lee, A. Raha, Y. Kim and V. Raghunathan, Proceedings of the 2014 international symposium on Low power electronics and design, ACM (2014).

[2] T. Matsuhi, H. Sai, A. Bidiville, H.J. Hsu and K. Matsubara, Solar Energy 170, 486 (2018).

[3] D.L. Staebler and C.R. Wronskj, Appl. Phys. Lett. 31, 292 (1977).

[4] T. Matsui, H. Sai, K. Saito and M. Kondo, Jpn. J. Appl. Phys. 41, 10NB04 (2012).

[5] Y. Watanabe, M. Shiratani, Y. Kubo, I. Ogawa and S. Ogi, Appl. Phys. Lett. 53, 1263 (1988).

[6] K. Koga, N. Matsuoaka, K. Tanaka, M. Shiratani and Y. Watanabe, Appl. Phys. Lett. 77, 196 (2000).

[7] K. Koga, N. Kaguchi, M. Shiratani and Y. Watanabe, J. Vac. Sci. Technol. A 22, 1536 (2004).

[8] M. Shiratani, K. Koga, N. Kaguchi, K. Bando and Y. Watanabe, Thin Solid Films 506-507, 17 (2006).

[9] S. Toko, Y. Torigoe, K. Keya, T. Kojima, H. Seo, N. Itagaki, K. Koga and M. Shiratani, Surf. Coat. Technol. 326, 388 (2017).

[10] T. Kojima, S. Toko, K. Tanaka, H. Seo, N. Itagaki, K. Koga and M. Shiratani, J. Plasma Fusion Res. 13, 1406082 (2018).

[11] T. Nishimoto, M. Takai, H. Miyahara, M. Kondo and A. Matsuda, J. Non-Cryst. Solids 299-302, 1116 (2002).

[12] K. Koga, M. Kai, M. Shiratani, Y. Watanabe and N. Shikatani, Jpn. J. Appl. Phys. 41, L168 (2002).

[13] W.M. Nakamura, H. Matsuizuki, H. Sato, Y. Kawashima, K. Koga and M. Shiratani, Surf. Coat. Technol. 205, S241 (2010).

[14] T. Matsui, H. Sai, K. Saito and M. Kondo, Prog. Photovoltaics 21, 1363 (2013).

[15] S. Toko, Y. Hashimoto, Y. Kanemitsu, Y. Torigoe, H. Seo, G. Uchida, K. Kamataki, N. Itagaki, K. Koga and M. Shiratani, J. Phys. Conf. Ser. 518, 012008 (2014).

[16] T. Nagai, A.H.M. Smets and M. Kondo, Jpn. J. Appl. Phys. 45, 8095 (2006).

[17] K. Koga, T. Matsuqaga, Y. Kim, K. Nakahara, D. Yamashita, H. Matsuzaki, K. Kamataki, G. Uchida, N. Itagaki and M. Shiratani, Jpn. J. Appl. Phys. 51, 01AD02 (2012).

[18] Y. Kim, K. Hatozaki, Y. Hashimoto, G. Uchida, K. Kamataki, N. Itagaki, H. Seo, K. Koga and M. Shiratani, Jpn. J. Appl. Phys. 52, 11NA07 (2013).

[19] K. Koga, T. Inoue, K. Bando, S. Iwashita, M. Shiratani and Y. Watanabe, Jpn. J. Appl. Phys. 44, L1430 (2005).

[20] W.M. Nakamura, H. Miyahara, H. Sato, H. Matsuzaki, K. Koga and M. Shiratani, IEEE Trans. Plasma Sci. 36, 888 (2008).

[21] H. Seo, Y. Wang, G. Uchida, K. Kamataki, N. Itagaki, K. Koga and M. Shiratani, Electrochimica Acta 95, 43 (2013).

[22] G. Uchida, H. Seo, K. Kamataki, N. Itagaki, K. Koga and M. Shiratani, Thin Solid Films 554, 93 (2013).

[23] Y. Hashimoto, S. Toko, D. Yamashita, H. Seo, K. Kamataki, N. Itagaki, K. Koga and M. Shiratani, J. Phys.: Conf. Ser. 518, 012007 (2014).

[24] G. Uchida, Y. Kanemitsu, D. Ichida, H. Seo, K. Kamataki, N. Itagaki, K. Koga and M. Shiratani, Proceedings of the 12th Asia Pacific Physics Conference JPS Conf. Proc. 1, 015080 (2014).

[25] S. Toko, Y. Torigoe, W. Chen, D. Yamashita, H. Seo, N. Itagaki, K. Koga and M. Shiratani, Thin Solid Films 587, 126 (2015).

[26] K. Keya, T. Kojima, Y. Torigoe, S. Toko, D. Yamashita, H. Seo, N. Itagaki, K. Koga and M. Shiratani, Jpn. J. Appl. Phys. 55, 07LE03 (2016).

[27] M.H. Brodsky, M. Cardona and J.J. Cuomo, Phys. Rev. B 16, 3556 (1977).

[28] I. Sakata, M. Yanamana and Y. Hayashi, J. Appl. Phys. 67, 3737 (1990).

[29] K. Kitaheara, S. Murakami, A. Hara and K. Nakajima, Appl. Phys. Lett. 72, 2436 (1998).

[30] H. Fujiwara, M. Kondo and A. Matsuda, Appl. Phys. Lett. 82, 1227 (2003).

[31] M. Lozac’h, S. Nunomura, H. Sai and K. Matsubara, Sol. Energy Mater. Sol. Cells 185, 8 (2018).

[32] N. Hata, S. Wagner, P. Rocai Cabarrocas and M. Favre, Appl. Phys. Lett. 56, 2448 (1990).

[33] S. Nunomura, I. Sakata and K. Matsubara, Appl. Phys. Express 10, 081401 (2017).

[34] K. Maeda, A. Kuroe and I. Umez, Phys. Rev. B 51, 10635 (1995).

[35] G.T. Dalakos, J.P. Plawsky and P.D. Persans, Phys. Rev. B 72, 205305 (2005).

[36] A. Matsuda, Jpn. J. Appl. Phys. 43, 7909 (2004).