Extended Abstracts of the 2011 International Conference on Solid State Devices and Materials, Nagoya, 2011, pp1359-1360

Effect of Hydrogen Radical-Injection on Growth Property and Crystallinity of Microcrystalline Silicon Thin Film

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1. Introduction

Microcrystalline silicon (μc-Si:H) thin films are promising materials for the bottom cell of a tandem solar cell, since they can absorb higher wavelength light towards the infrared region of solar spectrum and have excellent stability against light soaking compared to amorphous silicon (a-Si:H) thin films used for the top cell [1]. Plasma-enhanced chemical vapor deposition (PECVD) processes at low temperature were commonly used to deposit μc-Si:H films. However, in general, process margin to obtain optimal crystallinity of μc-Si solar cell absorber layers is extremely narrow and close to the amorphous-Si (a-Si) growth region [2]. Radicals such as SiH_3, SiH_2, H and so forth, which expose onto the growth surface of thin film silicon in PECVD, are one of dominant factor to determine the film properties. A capacitively coupled plasma (CCP) has been widely used for μc-Si growth. However, a conventional CCP has a limitation in controlling the density ratio of radicals.

In this study, we proposed a PECVD with hydrogen (H) radical-injection (RI) system for deposition of thin silicon films. The RI system enables to control the density ratio of radicals [3]. Hydrogen (H) radicals are recognized as a determining factor of crystallinity of thin silicon films in the case of the PECVD. During thin silicon film deposition, H radicals cover the growth surface and induce local heating through its recombination to hydrogen molecule. These two events occurring on the surface enhance the surface diffusion of SiH_x precursors. As a result, the SiH_x precursors can find stable adsorption sites and make stable Si-Si bonds [4]. H radicals will etch weakly-bonded Si atoms in an amorphous phase and reconstruct Si-Si bond network in a H-rich subsurface region [4]. Based on such the considerations, the growth characteristics and crystallinity of the thin Si films synthesized by the PECVD with and without the RI system were evaluated in this study.

2. Experimental and results

Figure 1 is schematic illustrations of conventional capacitively-coupled plasma (C-CCP) source and CCP source with a RI system (RI-CCP). The both sources have shower head VHF electrode to which a 60 MHz VHF power was applied and lower grounded (GND) electrode. SiH_4/H_2 plasma was generated between them. The RI-CCP source has an additional shower head-type upper GND

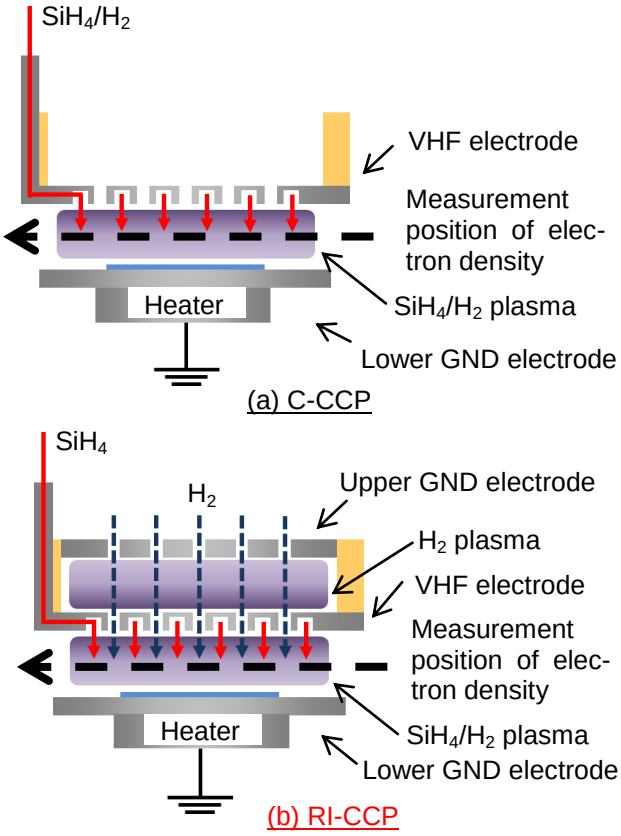

Fig. 1 Schematic illustrations of (a) C-CCP and (b) RI-CCP systems.

electrode above the VHF electrode. In the case of the C-CCP, H_2 gas introduced through the VHF electrode with SiH_4 gas. In the case of RI-CCP, H_2 gas was introduced through the upper GND electrode in order to generate H_2 plasma between the upper GND and VHF electrodes. The SiH_4/H_2 gas mixture ratio was 3% and total gas flow rate was 1000 sccm in the both cases. Total pressure was 9 Torr (1197 Pa). The distance between the VHF and lower GND electrodes was 10 mm, and that between the VHF and upper GND electrodes was 5 mm. The substrate temperature was 373 K. Two kinds of substrates, glass and quartz were placed on the lower GND electrode. The electron density in the SiH_4/H_2 plasma region was measured using a 35 GHz microwave interferometer [5]. The crystallinity and defect density (n_D) of the deposited films were analyzed by Raman spectroscopy and electron spin resonance (ESR), re-

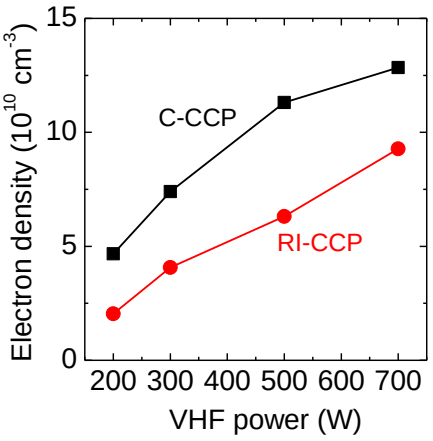

Fig. 2 Electron density in SiH_4/H_2 plasma region as a function of VHF power.

spectively.

Figure 2 shows the electron density in the SiH_4/H_2 plasma regions as a function of VHF power. The electron density increases with increasing the VHF power in both sources. The densities in the case of RI-CCP are lower than that in the C-CCP case; they are 44-72% of the C-CCP case. This indicates that the VHF power is applied to not only SiH_4/H_2 plasma but also H_2 plasma at the RI-CCP case.

Figure 3 shows the deposition rate as a function of VHF power. The deposition rate in the C-CCP case slightly increases from 2.8 to 3.2 nm/s with increasing the VHF power from 200 to 500 W and tends to saturate. Similarly, the deposition rate in the RI-CCP case increases from 2.0 to 3.0 nm/s with increasing the VHF power from 200 to 500 W and tends to saturate. The differences of the deposition rates between the C-CCP and RI-CCP cases are only 6-21%, although the differences of the electron densities are 28-56%. It is attributed to the fact that the H radicals supplied from the upper H_2 plasma could generate the SiH_3 radicals, which are dominant precursor, through the below reaction.

$$H + SiH_4 \rightarrow H_2 + SiH_3 \qquad (1)$$

Figure 4 shows the peak intensity ratios of I_c to I_a, which correspond to crystalline and amorphous Si regions, respectively in Raman spectra, as a function of the VHF power. Values of n_D are also indicated as a right axis. At VHF powers of 500 and 700 W, the I_c/I_a ratio in the RI-CCP case is higher than that of the C-CCP case. This indicates that the crystallinity of thin Si film is enhanced by the H radical injection at the RI-CCP case. On the other hand, n_D of RI-CCP is lower than that of C-CCP. It is well-known that short lifetime species such as SiH_2 and SiH cause the defects. In the C-CCP, it is guessed that the short lifetime species increases with the VHF power, since SiH_4, the scavenger of such the short lifetime species, is depleted. In the case of RI-CCP, it is deduced that the depletion of SiH_4 is hard to occur because the electron density is lower than that in the C-CCP case. Therefore, in the case

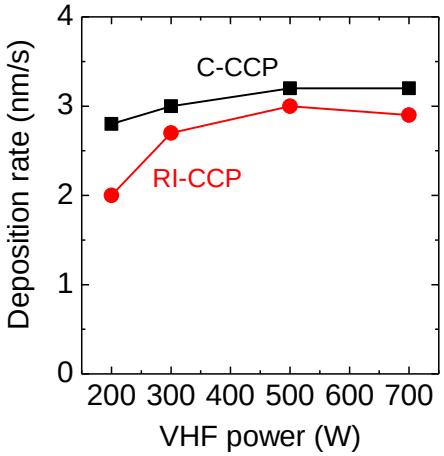

Fig. 3 Deposition rate as a function of VHF power.

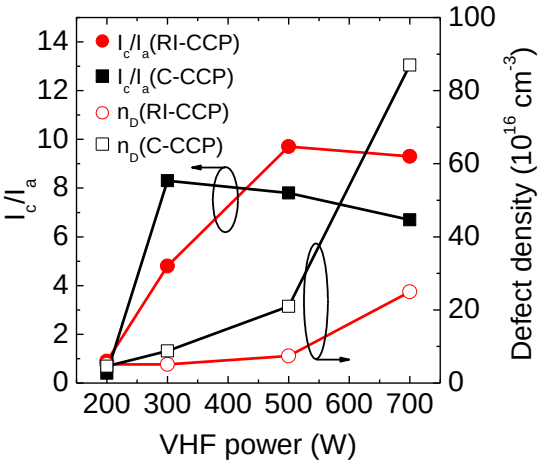

Fig. 4 I_c/I_a and n_D as a function of VHF power.

RI-CCP, the density of short lifetime species is suppressed by the H radical injection, while enough H radicals are supplied from the upper H_2 plasma. As the result, the high crystallinity of thin Si film is kept without increase of the n_D.

3. Conclusions

The PECVD with the RI system was proposed for deposition of thin Si films. It is demonstrated that the RI system can simultaneously realize the lower defect density and higher crystallinity of thin μc-Si films compared with the conventional PECVD.

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