High-Rate Deposition of Intrinsic Amorphous Silicon Layers for Solar Cells using Very High Frequency Plasma at Atmospheric Pressure

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1. Introduction

Hydrogenated amorphous silicon (a-Si:H) is expected as a useful material for thin film solar cells. In order to increase the competitiveness with the conventional energy sources, improvement of deposition rate and higher source gas utilization are required for a further reduction in the production cost of solar cells. Generally, a-Si:H films are prepared by low-pressure plasma chemical vapor deposition (CVD) technique. Silane (SiH₄) is typically used with inert gases or hydrogen. However, high-rate deposition of device-quality films has not actually been realized by the conventional low-pressure plasma CVD.

In order to make an a-Si:H film at high rate on a large-area substrate, we have originally been developing the atmospheric pressure plasma CVD (AP-PCVD) technique [1]. In this paper, we investigated the electrical and optical properties of a-Si:H films prepared at extremely high deposition rates by the AP-PCVD. Additionally, we applied the films to the intrinsic layers of a-Si:H solar cells, and evaluated the I-V characteristics of the cells.

2. Experimental details

Figure 1 schematically shows the AP-PCVD apparatus used in this study. The apparatus is almost the same as that described in our previous report [1]. A cylindrical rotary electrode with 300 mm diameter and 200 mm width was placed in the reaction chamber. The atmospheric pressure plasma was generated in the gap between the rotary electrode and the substrate by supplying 150 MHz



Fig. 1 Schematic illustration of the AP-PCVD apparatus.

VHF power. A Si film was deposited in a rectangular region without substrate scanning. The deposition rate in this paper was defined at the smallest gap in Fig. 1. By scanning the substrate, a uniform Si film could be deposited in the area having the width of plasma and the substrate scanning distance.

In order to study electrical and optical properties of the a-Si:H films, a set of samples with thickness of 200 to 500 nm was prepared on 0.7 mm thick Corning #1737 glass substrates (100mm×100mm) under a constant process pressure of 1×10^5 Pa. A different set of samples was prepared for fabricating p-i-n single-junction a-Si:H solar cells. The cell structure was glass substrate/textured SnO₂/p/i/n/metal electrode. Only the i-layers of 230 or 350 nm thickness were deposited by the AP-PCVD, and the p- and n-layers with thickness of about 50 nm were formed by conventional low-pressure plasma CVD. On the other hand, all the layers were prepared by conventional plasma CVD for reference cells. The process gases used in this study were He (the base gas), H₂ and SiH₄ (the reactive gases). During deposition, the smallest gap between the rotary electrode and the substrate was fixed at 200 µm. The substrate scanning distance was 80 mm.

The initial photoconductivity (σ_{ph}) and dark conductivity (σ_d) of the a-Si:H films were measured at room temperature in the Ohmic region with a coplanar cell using aluminum electrodes with 1mm spacing. σ_{ph} of the a-Si:H films and the initial I-V characteristics of the solar cells (cell area: 1cm²) were measured under AM1.5, 100mW/cm² illumination.

3. Results and discussions

Figure 2 shows the VHF power dependence of σ_{ph} , σ_d and the photosensitivity (σ_{ph}/σ_d) of the films prepared with 0.5% SiH₄ and 0.5% H₂ (H₂/SiH₄=1). In Fig. 2, σ_{ph} greatly increases with the VHF power and attains value greater than 10⁻⁵ Ω^{-1} cm⁻¹ over 800W. Since σ_d monotonously increases with the VHF power, the maximum photo- sensitivity is given at 800W. The maximum deposition rate was 184 nm/s at 500W, which corresponded to the average deposition rate of 0.92 nm/s for the substrate scanning distance of 1 m.

Investigating a significant number of films deposited with various deposition conditions, we have found that the VHF power is a very important parameter governing the dissociation of SiH_4 molecules and the structural relaxation of the film. At low VHF power, Si-Si network structure is sparse and hydrogen content in the film is high due to insufficient dissociation of SiH_4 molecules. While, when too much VHF power is supplied, SiH_4 molecules excessively decompose, and highly dissociated precursors polymerize in gas phase and cause formation of silicon particles, resulting in deterioration of electrical properties and decrease in deposition rate of the films. From these facts, both excellent film property and extremely high deposition rate can be obtained in the AP-PCVD.

Figure 3 shows the H₂ concentration dependence of the optical gap (E_{opt}) of the a-Si:H films prepared with 0.5% SiH₄ at the substrate temperature of 220°C. E_{opt} of the films was derived from reflection and transmission spectra according to the method free from the optical interference effect [2]. Diluting SiH_4 with H_2 is generally understood as an effective means for suppressing gas-phase polymerization and forming a denser network structure [3]. In Fig. 3, E_{opt} tends to decrease with increasing H_2 concentration, implying that hydrogen content of the film decreases with increasing H₂ concentration. It is considered that hydrogen radicals incident to the substrate eliminate the bonded H atoms and enhance Si-Si bond formation on the film-growing surface. Since the form of precursor may be affected by the H₂ concentration in the plasma, further study is required to know the details of the deposition mechanism in the AP-PCVD process.

Figure 4 summarizes the relationship between the conversion efficiency of the solar cells normalized by that of the reference cells and E_{opt} of the i-layer. σ_{ph} of the i-layer is also shown in the figure. In Fig. 4, no appreciable deterioration in σ_{ph} is observed even when E_{opt} becomes large, while the normalized efficiency is greatly affected by E_{opt} . Thus, the present study suggests that further reduction in E_{opt} is necessary to improve the efficiency. At the present stage, an initial efficiency of 8.25% has been achieved. This is the highest efficiency ever achieved for an a-Si:H solar cell of which i-layer is prepared at a deposition rate of more than 100 nm/s.

4. Conclusions

The AP-PCVD process was applied to the fabrication of device-quality a-Si:H films and the i-layer of singlejunction amorphous silicon solar cells. Supplying the optimum VHF power, E_{opt} of the a-Si:H films could be controlled without appreciable deterioration in σ_{ph} by changing H₂ concentration in the plasma. It was shown that E_{opt} of the i-layer strongly affected the energy conversion efficiency of the solar cell, suggesting that further study on reducing E_{opt} is necessary to improve the efficiency. As a result, an initial efficiency of 8.25% was obtained for the a-Si:H solar cell with an i-layer prepared at an extremely high deposition rate of more than 100 nm/s.

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References

[1] Y. Mori, K. Yoshii, H. Kakiuchi and K. Yasutake: *Rev. Sci. Instrum.* **71**, 8 (2000) 3173.

- [2] Y. Hishikawa, N. Nakamura, S. Tsuda, S. Nakano, Y. Kishi and Y. Kuwano: *Jpn. J. Appl. Phy.* **30**, 5 (1991) 1008.
- [3] A. Matsuda, M. Takai, T. Nishimoto, M. Kondo, Sol. Energy Mater. Sol. Cell. 78 (2003) 3.



Fig. 2 VHF power dependence of photo- and dark conductivity and photosensitivity of the a-Si:H films prepared at the substrate temperature of 220°C. The SiH₄ concentration was 0.5% and H₂/SiH₄ ratio was 1. The electrode rotation speed was 1700 rev./min.



Fig. 3 H_2 concentration dependence of the optical gap (E_{opt}) of the a-Si:H films prepared at the substrate temperature of 220°C. The SiH₄ concentration was 0.5% and the VHF power was 800W. The electrode rotation speed was 1700 rev./min.



Fig. 4 Photoconductivity (σ_{ph}) of the i-layer and the normalized energy conversion efficiency of the solar cell as a function of E_{opt} of the i-layer.