Mitsubishi Heavy Industries Ltd. (MHI) has been engaged in the development of high-efficiency, large-area, thin-film silicon photovoltaic (PV) modules using Very-High-Frequency (VHF) plasma enhanced Chemical Vapor Deposition (CVD) in line with the development plan for cost down to accelerate the spread of photovoltaic modules in Japan. MHI has already developed its independent ladder-shaped electrode in amorphous Si PV module, succeeding in a large-area solar module by VHF plasma. The tandem type PV module composed of amorphous Si/microcrystalline Si is currently under development, with the tandem cell efficiency of 13.1% achieved in the test using small-area glass substrate of 5 cm². With the consignment of New Energy Industrial technology Development Organization (NEDO), MHI is conducting research on the development of large-area tandem modules aiming at the conversion efficiency of 12% by reflecting the aforesaid technologies in large-area substrates.

1. Introduction

NEDO is currently taking positive steps in the development of cost-down (high cost performance) technology in order to accelerate the spread of PV modules in Japan. The thin-film Si PV modules with unlimited raw material are considered the most effective technology for low manufacturing cost. For the realization of this technology, however, the improvement in conversion efficiency and productivity is indispensable. Taking note of the effectiveness of tandem PV module composed of amorphous Si cell and micro-crystalline Si cell for higher efficiency, MHI already commenced production of amorphous Si PV module in 2002 as the first step. In order to realize high productivity, the plasma CVD large-area, high-speed film forming technology and the thin-film Si PV module film forming process are important, so that the development is under way, with due attention paid to the VHF plasma CVD process capable of high-speed, high-quality film forming.

Compared with the conventional RF plasma, the VHF plasma has higher density and less ion damage, and is applicable to high-speed, high-quantity film forming[1,2]. However, since VHF plasma has shorter magnetic wavelength, it was considered problematic for a large-area solar module. As a solution to this, MHI succeeded in large-area solar module by using the phase control method (phase modulation method)[3,4] of the VHF supplied to the electrode as well as the proprietary ladder-shaped electrode (Fig. 1). As a result, MHI succeeded in the development of a VHF plasma enhanced CVD system capable of high-speed film forming of amorphous Si at 1.0 nm/s on a large-area glass substrate of size 1.1 m x 1.4 m, the largest in the world in PV modules, establishing the large-area, high-speed film forming technique.

The tandem type PV module makes use of the high efficiency of high-quality film forming by using the VHF plasma enhanced CVD, and has achieved the initial efficiency of 13.1%[5] in the test using 5 cm² area glass substrate.

The development project is underway for a large-area tandem module with conversion efficiency 12% by applying the aforesaid technologies, and an initial efficiency of 11.2%[6] of a 40 cm x 50 cm module was achieved in 2002.

Since the crystalline Si has small absorption coefficient, and has to have the film 5 times thicker than amorphous Si, requiring 5 times faster film forming technique in order to form the film in the same time as the amorphous Si film. Further, high-speed and high-quality film forming requires the use of high pressure. However, the high pressure leads to conspicuous localization of plasma, causing uniform film forming more difficult. As a countermeasure, the electrode pitch was made smaller and the electrode sectional form was changed to ensure the film deposition rate of 1.6 nm/s for 1-m class large-area, uniform film forming. By applying this high-speed deposition technique to the 40 cm x 50 cm module, the deposition rate of 1.3 nm/s and the conversion efficiency of 11% have currently been achieved for the microcrystalline Si i-layer.

Further improvements in film quality and upgrading the light-trapping technique are planned for the future to aim at a stable efficiency of 12%, and by selecting appropriate deposition rate conditions using new electrodes for micro-crystalline Si film deposition, a low-cost, large-area, high-speed film deposition technique capable of film forming at 2.0 nm/s for 1-m class size is to be established.

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2. Nagasaki Research & Development Center, Technical Headquarters
3. Advanced Technology Research Center, Technical Headquarters
2. Development of film deposition technique for amorphous Si/micro-crystalline Si tandem modules

MHI has used the high-efficiency amorphous Si/micro-crystalline Si tandem PV module in a small-size VHF plasma CVD system for 5 cm² area substrate, with the obtained results given below.

(1) Technique for high-quality micro-crystalline i-layer through appropriate crystallinity of micro-crystalline Si

Fig. 2 shows the relation between the hydrogen dilution ratio and the crystallinity of micro-crystalline Si i-layer, while Fig. 3 and Fig. 4 respectively show the relation between crystallinity of micro-crystalline Si and open-circuit voltage Voc, crystallinity and fill factor FF.

It is clear from Fig. 2 that the crystallinity gets increased as the H₂ dilution ratio increases, while the open-circuit voltage Voc and shape factor FF increase as the crystallinity goes down. This indicates that there exists an appropriate level (value) in the crystallinity. Based on these data, the conditions were determined to get high-quality micro-crystalline i-layer to allow maximum conversion efficiency.

(2) Development of micro-crystalline SiC for micro-crystalline Si p-layer

In order to improve the open-circuit voltage Voc of the micro-crystalline Si cell, micro-crystalline SiC was developed for p-layer. It was learned through Raman scattering spectra and X-ray diffraction patterns that the newly developed micro-crystalline SiC was composed of micro-crystalline Si and amorphous SiC, with the band gap of the micro-crystalline SiC changing according to C/Si ratio as shown in Fig. 5. The band gap got narrowed at the initial stage when the C/Si ratio increased; but when further increased, the band gap got widened. On the basis of these data, the micro-crystalline SiC p-layer was optimized by controlling the C/Si ratio in order to improve the open-circuit voltage Voc of the micro-crystalline Si cell by approximately 10%, from 0.517 V to 0.573 V.

In addition to the aforesaid technologies in items (1) and (2), the optimization of rear electrode film forming process and the technology for preventing the damage to the interface between top n-layer and bottom p-layer caused by micro crystallization of the top cell n-layer were developed. As a result, the initial efficiency 13.1% of the tandem cell was achieved. The structure of the experimental tandem cell is shown in Fig. 6, and the initial power generation characteristics in Fig. 7.
3. Development of tandem module technology

The technology established for high-efficiency tandem cell by using small-area VHF plasma CVD system was applied to the VHF plasma CVD system for 40cm x 50cm substrate.

(1) Development of large-area VHF plasma uniformity technique for micro-crystalline Si

Micro-crystalline Si film forming requires several times higher deposition pressure than amorphous Si film forming. In the case of VHF plasma, the plasma gets localized when the pressure is high, making it difficult to carry out large-area film forming. Hence, a silane plasma visualization device was produced to develop the plasma uniformity technique.

Fig. 8 shows the conceptional diagram of the plasma visualization device, with the ladder-shaped electrode of size 1.2m x 0.37m and the porous metallic plate being used to make the earth electrode at the opposite side visible. The VHF cable was connected to the short side of the ladder-shaped electrode to supply power.

It became evident that by using the newly developed plasma visualization device an irregular discharge took place at the proximity of the power supply point to the ladder-shaped electrode, and the plasma emission intensity between the electrodes got weakened.

As a countermeasure, the space between electrodes was narrowed and the distance between the ladder-shaped electrode and the opposing electrode was shortened in addition to the improvement made on structural connection between VHF cable and ladder-shaped electrode.

As a result, uniform plasma could be obtained in the vertical direction of the electrode at the center of plasma electrode under a pressure of 133 Pa and plasma exciting frequency of 60 - 100 MHz as shown in Fig. 9. The plasma emission intensity at both sides of the ladder-shaped electrode was found to be weak because of the voltage distribution of a standing wave on the electrode. The phase modulation developed for large-area amorphous Si film forming was applied to get successfully a uniform distribution of plasma emission intensity over the entire ladder-shaped electrode as shown in Fig. 10.

(2) Development of 40 cm x 50 cm tandem module technique

MHI has succeeded in developing high-quality 40cm x 50cm tandem module by combining the aforesaid high-efficiency tandem cell technique and large-area VHF plasma uniformity technique for micro-crystalline Si film forming. Fig. 11 shows the initial I-V characteristic of the experimental tandem module. Thus, the initial efficiency of 11.2% could be achieved for 40cm x 50cm tandem module. Assuming from the degradation rate of the small-area tandem cell, the stable efficiency comes to be 9.8%
4. Development of high-rate, high-quality film deposition technology for micro-crystalline Si

Since the i-layer of the micro-crystalline Si cell composing the tandem PV module has low absorption coefficient, the layer has to be formed 5 times thicker than amorphous Si i-layer, requiring faster film deposition than amorphous type. High-rate film deposition under the conventional film deposition pressure caused the long wavelength sensitivity to get deteriorated, leading to drastic degradation of the PV module efficiency.

MHI’s copartner in research, National Institute of Advanced Industrial Science and Technology (AIST), has found out that high-pressure film deposition is essential for high-rate, high-quality film forming using VHF plasma CVD\(^7\). Consequently, MHI increased the pressure level several times higher than the conventional pressure at the time of film deposition, leading successfully to the development of new electrodes capable of uniform film forming. The newly developed electrodes had the space between electrodes used in a conventional ladder-shaped electrode narrowed and the electrode sectional shape improved. As a result, the film deposition rate 2.1 nm/s and the micro-crystalline Si single cell efficiency 8.0% could be obtained at 60 MHz VHF plasma as shown in Fig. 12. Further, by selecting appropriate film forming process for back electrode and intensifying the light entrapment, the conversion efficiency of 9% could be obtained.

The high-rate, high-quality film deposition technique using large-area VHF plasma enhanced CVD is currently under way. By applying the know-how obtained from small-area test to the CVD system (device) for 40cm \(\times\) 50cm substrate film forming, the initial efficiency of approximately 11% has been obtained at the film deposition rate of 1.3 nm/s for a tandem module. Further, the film deposition rate 1.6 nm/sec has been obtained for 1-m class large-area uniform film forming. MHI is determined to make further study for the development of a tandem module with conversion efficiency 12% and film forming speed 2.0 nm/s.

5. Conclusion

MHI is developing thin-film PV modules by using VHF plasma CVD, taking account of the high-rate, high-quality film deposition capability of VHF plasma CVD. As the first step to this regard, MHI has developed the VHF plasma CVD for amorphous Si film forming, aiming at high productivity, and is producing 1.1m \(\times\) 1.4m amorphous Si PV module. In order to reduce the PV module cost, high efficiency is indispensable. Hence, MHI developed amorphous Si/micro-crystalline Si tandem PV module as the second step, and has so far obtained the initial efficiency of approximately 11% using the 40cm \(\times\) 50cm tandem module with the micro-crystalline Si i-layer formed at the film deposition rate 1.3 nm/s.

As for the small-area micro-crystalline Si single cell, a high-quality film deposition technique has already been obtained, ensuring conversion efficiency of 9% or over at film deposition rate 2.0 nm/s.

In the future, MHI takes on to develop a large-area high-rate film deposition technique at 2.0 nm/s for 1 m class size, and to achieve the goal of conversion efficiency 12% by making further improvements in film quality and upgrading the light entrapment technique, contributing to the establishment of cost-down technology.

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References