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High-rate deposition of hydrogenated amorphous silicon films by Cat-CVD with high stability for light soaking

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Introduction

Plasma enhanced chemical vapor deposition (PECVD) has been recognized in the semiconductor industry as one of the most useful technologies to obtain thin films at low substrate temperatures. However, hydrogen (H) atoms around 10 at.% are usually included in hydrogenated amorphous silicon (a-Si:H) films prepared by PECVD although H content should be reduced below a few at.% in order to increase the stability for light soaking.

Catalytic chemical vapor deposition (Cat-CVD) is one of the promising low-temperature deposition techniques. In Cat-CVD method, deposition gases are decomposed by catalytic cracking reactions on a heated catalyzer placed near substrates. The films are deposited at substrate temperatures around 300 °C without using plasma. Large-area deposition is also possible only by enlarging the expanding area of the catalyzer. H content can be reduced around 3 at.%. These are all the advantages of Cat-CVD method in comparison with PECVD. Using Cat-CVD, it is expected to deposit a-Si:H films at high deposition rates with low H content, and so that, improve the stability for light soaking in solar-cell applications.

In the previous studies, a-Si:H films with the initial dangling bond (DB) density of the first half of 10^{16} cm^{-3} , the deposition rate of 3 nm/s and the H content of 6 at.% were obtained.

In this study, Cat-CVD a-Si:H films prepared with various conditions are examined to realize both high deposition rate and high stability for light soaking. It is demonstrated that the catalyzer-surface area is one of the key parameters to determine the DB density. The feasibility of Cat-CVD a-Si:H films is investigated by fabricating solar cells. Catalytic plate is proposed in order to decrease the heat radiation from the catalyzer with keeping the same catalyzer-surface area.

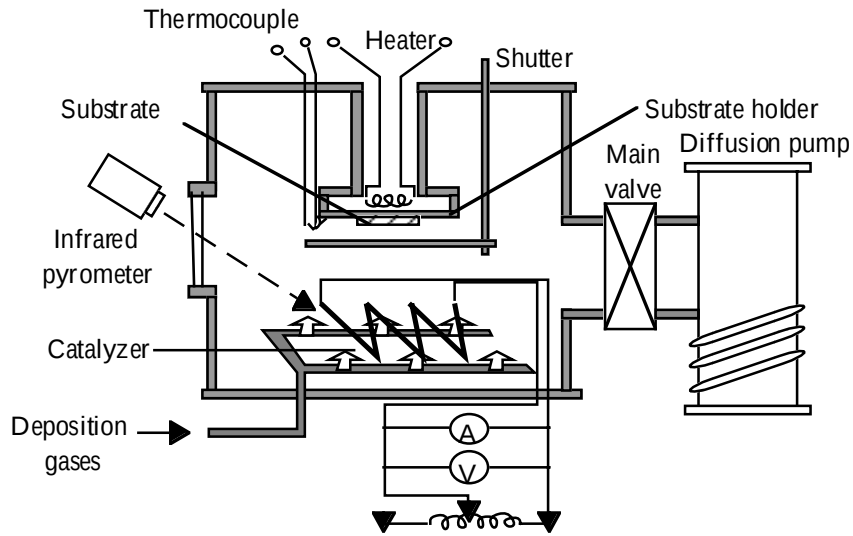


Fig. 1. Schematic diagram of Cat-CVD apparatus.

Experimental

Cat-CVD apparatus used in this study is schematically shown in Fig. 1. a-Si:H films were prepared by Cat-CVD using a gaseous mixture of SiH_4 and H_2 . Flow rate of SiH_4 was changed between 22.5 sccm and 30 sccm and that of H_2 was fixed at 13 sccm. Gas pressure during deposition was changed between 0.63 Pa and 0.80 Pa. The catalyzer made of W was set under the substrate with a distance of 60 mm. The temperature of catalyzer was changed between 1600 and 2000 and monitored using an infrared pyrometer through a quartz window. Catalyzer was made of tungsten wire of the diameter of 0.5 mm or tungsten plate of the thickness of 0.05 mm and of the width of 25 mm or 30 mm. The temperature of substrate holder ranged between 100 and 400. Substrate-surface temperature was monitored by a thermocouple attached on the substrate surface with ceramic paste. Substrates used were singlecrystalline Si for estimating the H content and fused quartz for other measurements.

Film thickness was measured by a stylus profilometer using the step formed by the mask during deposition. H content in a-Si:H films was estimated by the Si-H wagging-mode signal intensity in Fourier-transform infrared (FTIR) spectroscopy using a value of $2.1 \times 10^{19} \text{ cm}^{-2}$. DB density in a-Si:H films was also evaluated by X-band electron spin resonance (ESR) at room temperature. Optical band gap of a-Si:H films was estimated by the well-known Tauc plot.

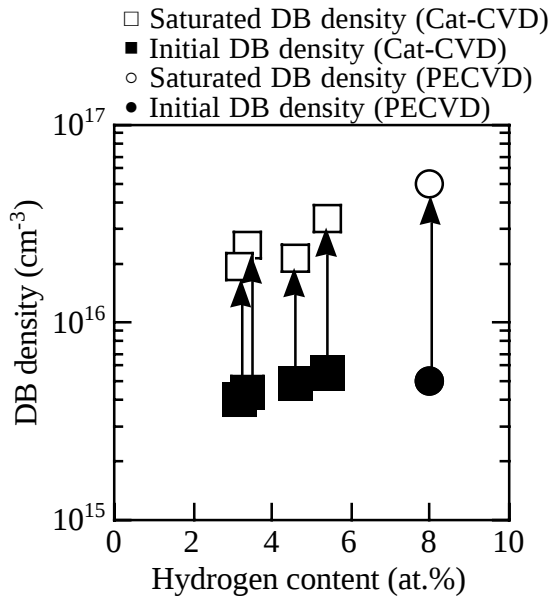


Fig. 2. Initial DB density and saturated one after light soaking as a function of the H content.

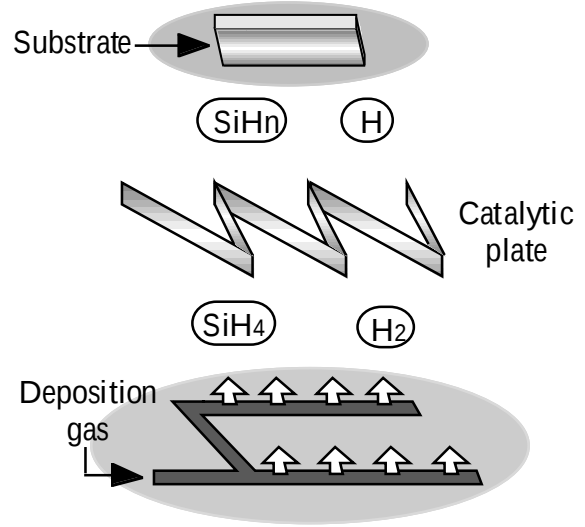


Fig. 3. Schematic of catalytic plate.

Results and discussion

Deposition rate monotonically increased with an increase in the catalyzer-surface area. DB density also increased, on the other hand, H content decreased with an increase in the catalyzer-surface area, suggesting that an increase in the heat radiation from the catalyzer due to an increase in catalyzer-surface area induces the evolution of H from the growing surface and leaves unpassivated DBs in films. Saturated substrate surface temperature monotonically increased with an increase in the catalyzer temperature. However, not only the saturated substrate surface temperature but also a behavior of an increase in the substrate temperature with an increase in the catalyzer temperature were suppressed with a reduction of the catalyzer-surface area. Therefore it was confirmed that the simple method for suppressing the thermal influence from the catalyzer on the substrate temperature and for obtaining a-Si:H films with low DB density is a reduction of the catalyzer-surface area of the catalytic wire. It was also confirmed that the cleaning of the inner wall of the chamber is very important for high reproducibility of the film quality since Si atoms sticking on the inner wall are chemically transported and included in the films on the substrate during deposition. As a result, a-Si:H films with the initial DB density of $4 \times 10^{15} \text{ cm}^{-3}$, the deposition rate above $10 \text{ } \mu\text{m/s}$ and the H content of about 3 at.% were obtained with high reproducibility by suppressing the

thermal influence from the catalyzer on the substrate and also by cleaning the chamber wall. Figure 2 shows both the initial DB density and the saturated one after light soaking as a function of the H content. Light soaking was carried out for 150 h by a Xe lamp through an IR-cut filter with 340 mW/cm². Cat-CVD a-Si:H films and PECVD ones show almost the same initial DB density. However, Cat-CVD a-Si:H films with low H content show low saturated DB density after light soaking in comparison with PECVD ones.

Cat-CVD a-Si:H films with high stability for light soaking were employed at i layer in solar cells. The solar cell using Cat-CVD a-Si:H i layer showed the initial efficiency of about 5% although both n/i and i/p interfaces were exposed to air in the fabrication process.

The deposition rate monotonically decreased with a decrease in the surface area of the catalytic wire although high-rate deposition over 15 /s should be achieved for the industrial application of the Cat-CVD method. Therefore, we proposed the “catalytic plate” for solving these trade-off problems. As shown in Fig. 3, the area for the catalytic plate facing the substrate holder drastically decreases in comparison with that for the catalytic wire with keeping the substrate-surface area if the catalytic plate is set perpendicularly to the holder. Therefore it is expected that the heat radiation from the catalyzer drastically decreased using the catalytic plate. The saturated substrate temperatures for the catalytic wire and the catalytic plate with the same surface area of 27cm² were compared as a function of the catalyzer temperature. As a result, deposition rate of 18 /s was realized with the saturated substrate temperature of 400 using the catalytic plate although the saturated substrate temperature was 470 for the same deposition rate when the catalytic wire was used.

Conclusions

It was shown that a-Si:H films with high deposition rate, low H content high stability for light soaking are obtained using the Cat-CVD, suggesting that Cat-CVD a-Si:H films are one of the promising materials for solar cells.

It is also expected that in future the catalytic plate will be widely used for the Cat-CVD system with both high deposition rate and low substrate temperature.