



Characterization of HF-PECVD a-Si:H thin film solar cells by using OES studies

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ABSTRACT

Hydrogenated amorphous silicon (a-Si:H) films show considerable potential for the fabrication of thin film solar cells. In this study, the a-Si:H thin films have been deposited in a parallel-plate radio frequency (RF) plasma reactor fed with pure SiH₄. The plasma diagnostics were performed simultaneously during the a-Si:H solar cell deposition process using an optical emission spectrometer (OES) in order to study their correlations with growth rate and microstructure of the films. During the deposition, the emitting species (SiH*, Si*, H*) was analyzed. The effect of RF power on the emission intensities of excited SiH, Si and H on the film growth rate has been investigated. The OES analysis revealed a chemisorption-based deposition model of the growth mechanism. Finally, the a-Si:H thin film solar cell with an efficiency of 7.6% has been obtained.

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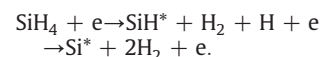
1. Introduction

Hydrogenated amorphous silicon (a-Si:H) films have been studied extensively in recent years because of their application as a photovoltaic material [1,2]. There have been many studies and conjectures regarding the gas and surface processes leading to film nucleation and growth. The Institute of Photovoltaic (IPV) realized that initial solar energy conversion efficiency is increased from 7.9% up to 8.8% by applying process control monitored by optical emission spectroscopy (OES) [3]. M. Guláš et al. indicated that OES is useful as a main experimental tool to define the concentration of the active gas phase species for carbon nanotube (CNT) growth [4]. A. Prarashar et al. had investigated the correlation between pressure, crystallinity and conductivity by using OES during a CVD process [5]. In addition, X.D. Zhang et al. used an OES to record changes in the plasma discharge, and showed that the deposition rate was correlated with film crystallinity [6]. G.S. Chen et al. used an OES to monitor the intensity of Ti emission line and then control the physical properties of TiO_x films via a flow-supply feedback loop [7].

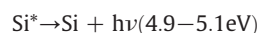
The glow-discharge deposition processes and growth mechanisms consist of deposition, bombardment and select etching of the silicon films. The deposition processes are very complicated as the physical and chemical interactions in the plasma and at the growing film surface are dependent on the RF power and frequency, the substrate temperature, the gas pressure and composition, the magnitude and the pattern of the gas flow, the electrode geometry, etc. For film deposition, the primary reactions in the gas phase are electron-impact excitation, dissociation and ionization of SiH₄ molecules. The plasma thus consists of neutral

radicals and molecules, positive as well as negative ions, and electrons. Secondary, for the ion bombardment effect: Reactive neutral species move to the substrate by diffusion, positive ions bombard the growing film. In addition, it consists of a surface reaction, such as hydrogen abstraction, radical diffusion, and chemical bonding. This step is the subsurface release of hydrogen molecules and relaxation of the silicon matrix.

A further understanding of these processes is desired to improve film quality, as well as to understand basic surface and gas chemistry. It has become widely accepted that neutral radical species are responsible for most of the a-Si:H deposition from discharges. It is well known that the electron-impact excitation processes determine light emission through the subsequent radiative decay of electronic excited species. The pioneering work of SiH₄ plasma revealed that the processes directly produce SiH* and Si* excited species [8].



Their radiative decays can be expressed by



Optical emission spectroscopy (OES) has been used to study the excited SiH, Si and H [9–11]. The equivalent SiH₃ and SiH₂ species are not detectable with this OES technique. It is important to realize the excited species and their spatial distribution of OES intensities between the grounded electrode and power electrode. In this study, we present the effect of RF power on the microstructure and efficiency

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of solar cell using RF discharge at 27.1 MHz fed with pure SiH₄ precursor. The intensity of the emitted lights as well as its spatial distribution is also measured.

2. Experiment details

The experimental apparatus is shown in Fig. 1(a). The stainless-steel plasma chamber has an inner diameter of 40 cm and a height of 30 cm. The diameter of the parallel-plate electrodes is 25 cm and they are 0.7–3 cm apart. RF power is applied to the upper electrode through an impedance-matching network. The intensity of the emitted lights as well as its spatial distribution can be measured. Fig. 1(b) shows the experimental setup used for recording spatially resolved emission profiles. To measure the light emission intensity at different positions, slits are used and the photo collimator could be moved over a distance of 1.6 cm (power electrode D = 1.6 cm, grounded electrode D = 0 cm). The discharge parameters as nominal pressure, excitation frequency, SiH₄ gas flow and electrode gap were maintained constant at 20 Pa, 27.12 MHz, 40 sccm and 20 mm, respectively. Spatially resolved emission profiles of SiH were recorded under these conditions and results were correlated to the performance of the cells incorporating these layers. For thin film solar cell production, a conductive SnO₂ coated glass substrate (ASAHI Type-U) was used. A p-i-n construction with p-layer (10 nm), buffer-layer (10 nm), i-layer (250 nm) and n-layer (30 nm) was deposited on the ASAHI glass substrate. A 0.5 μm Ag as back contact was deposited using sputter on the cell. The solar cell (1 × 1 cm²) I–V characteristics were measured at 100 mW/cm², AM 1.5 solar simulator.

To measure the accurate values of the radical intensity by OES, it requires some analysis. Measurement errors can be split into two components: random error and systematic error. Random error often has been presented during a measurement process. It is caused by inherently unpredictable fluctuations in the readings of a measurement apparatus or in the experimenter's interpretation of the instrumental reading. To avoid errors that occurred during the experimental process, with the increase in the times of measuring, the positive and negative errors of each other are about to be compensated, then gradually tend random errors to zero. On the other hand, systematic errors are predictable, and typically constant or proportional to the true value. Systematic errors are caused by imperfect calibration of measurement instruments or imperfect methods of observation, or interference of the environment with the measurement process, and always affect the results of an experiment in a predictable direction [12]. In this study, the result of the optical emission spectroscopy measurement will be systematically found to be of the order of 0.5%.

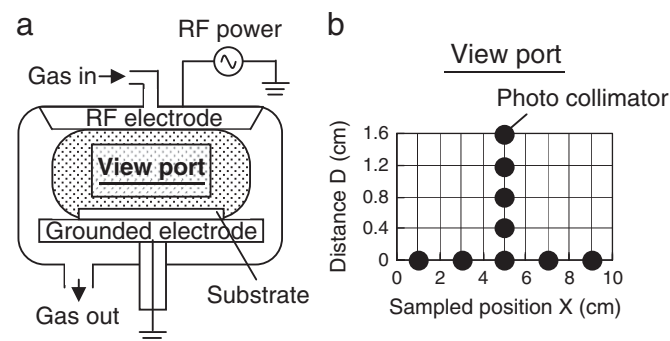


Fig. 1. Schematic diagram of the (a) deposition chamber and (b) OES photo collimator location of sampling points.

3. Results

Fig. 2 shows a series of optical emission spectra of pure SiH₄ RF glow discharges with different powers. The OES photo collimator of sampling points is located at X = 5 cm and D = 0.8 cm. The intensity of each spectrum is related to the level of the electrical signal provided for the photodiode array detector. The main features of the spectra correspond to the emission of Si (252,288 nm), SiH (414 nm) and H (656,722,772 nm) excited radicals, which directly come from dissociative excitation by electron collision processes with pure SiH₄. Spatially resolved OES measurements also have been used to record the axial concentration profiles of SiH radicals in various deposition conditions. Fig. 3(a) shows the variation of SiH intensities for five different RF powers (10 W–50 W). At the lowest RF power of 10 W, the SiH intensity does not change a lot at different horizontal X sampling positions. It can be observed that the displacement of the emission curve increased with the RF power. A higher RF power (40 W and 50 W) resulted in a larger variation of SiH emission intensities at a sampled position from X = 1 to X = 9 cm. Fig. 3(b) shows the OES intensities of SiH as a function of the distance from a grounded electrode for different RF powers. As one can observe the SiH intensity distribution is strongly affected by the RF power. For the power of 50 W, the profile shows a rather sharp maximum of intensity located at D = 0.8 cm. Similar SiH intensities at D = 0–1.6 cm were obtained for power less than 40 W.

Fig. 4 shows the temporal evolution of the SiH emission intensity during the deposition of the p-i-n solar cell. One can see that the consequence of increasing the power in silane plasma resulted in the enhancement of the SiH intensity. In addition, it showed that the fluctuation of the SiH emission intensities increased with the RF power.

The effects of the RF power on (a) the SiH emission intensity, (b) the deposition rate of the absorber i-layer and (c) the efficiency of the p-i-n thin film solar cell are shown in Fig. 5. Fig. 5(a) revealed a linear increase of the SiH emission intensity, and hence, of the total electron density, as a function of power. Fig. 5(b) shows the deposition rate of the i-layer as a function of power. The deposition rate increases with the RF power and SiH intensity. It is consistent with the increase in the concentration of various active species in the plasma. Fig. 5(c) shows the initial efficiency of the solar cells deposited on the SnO₂ coated glass substrate. It showed that the efficiency of thin film solar cells decreases with increasing power and i-layer deposition rate. The lowest RF power (10 W) results in an increase of the efficiency up to nearly 7.6%. In addition, uniform deposition rate and homogeneity thickness of the i-layer can be obtained at a lower RF power (10 W–20 W).

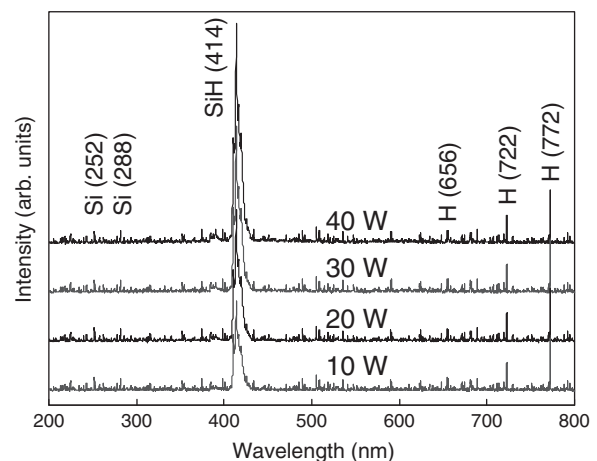


Fig. 2. Optical emission spectra of pure silane plasma with different RF power. The OES photo collimator positioned at X = 5 cm and D = 0.8 cm.

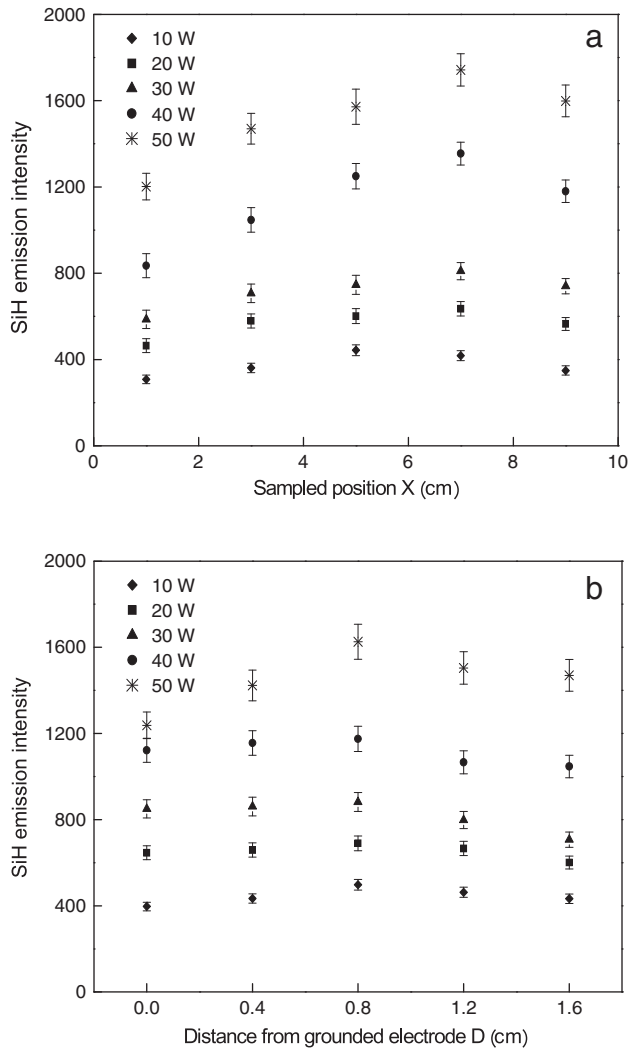


Fig. 3. Spatial distribution of SiH (414 nm) emission intensity at a different (a) sampled position X and (b) distance from grounded electrode D in pure silane plasma at power between 10 and 50 W.

4. Discussion

OES is an efficient monitor to identify amorphous growth condition. Torres et al. [13,14] mentioned that the ratio of emission intensities SiH/H can be used to determine the microstructure of the deposited film. In this study, different SiH intensities were detected by changing the RF power at a high frequency of 27.1 MHz. Spatially resolved OES measurements also have been used to record the axial concentration profiles of SiH radicals with different RF power. As shown in Fig. 3, the SiH intensity does not change a lot at different horizontal X sampling positions when the lowest RF power of 10 W was applied. A higher RF power (40 W and 50 W) resulted in a larger variation of SiH emission intensities at a sampled position from X = 1 to X = 9 cm. It implied that uniform deposition rate can be obtained at a lower RF power (10 W–30 W). A higher RF power (40 W and 50 W) showed poor uniformity of deposition rate. The deposition rate is a sensitive function of the SiH intensity. Therefore, the intensity of the SiH peak could be used to monitor the deposition rate of a-Si:H films. The real time monitoring of the SiH intensity at various positions between the RF electrode and the substrate could be applied to in-situ control of film quality during the deposition of a-Si:H in a plasma enhanced chemical vapor deposition (PECVD) system. In addition, an increase of the deposition rate is accompanied by an increase of the

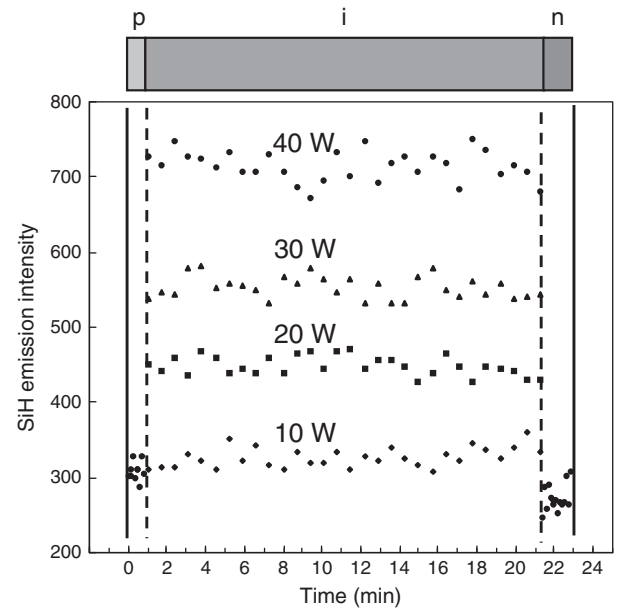


Fig. 4. Temporal evolution of the SiH emission intensity during the deposition of the p-i-n solar cell. The i-layer was deposited by using different power from 10 to 40 W.

SiH intensity, thus it could cause more defects or dangling bands within the film what affect photovoltaic conversion efficiency [13]. In that the behavior could determine the thin film surface morphology is consistent with other studies and references [15–17].

The emission intensity of SiH is more strongly dependent upon power compared to Si and H. The study of RF power is of some

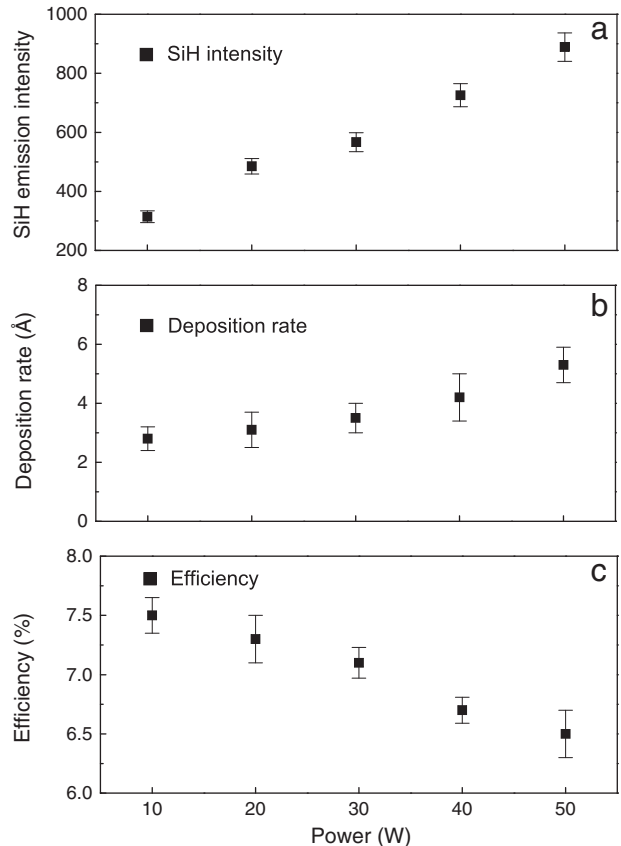


Fig. 5. Effect of the RF power on (a) the SiH emission intensity, (b) the deposition rate of the absorber i-layer and (c) the efficiency of the p-i-n thin film solar cell.

importance because its variation directly affects the total electron density. The SiH concentration appears to be determined only by the density of energetic electrons in the plasma bulk. The linear relationship of the SiH intensity with RF power has confirmed the hypothesis that these radicals originate from a one-electron collision process with silane, and not from a possible excitation of the ground-state SiH radicals.

A further increase of power resulted in a relative enhancement of the production of excited species in the bulk of the plasma, as shown in Fig. 2. The results indicate that the change of the distribution of electrons having enough energy to dissociate SiH₄ will certainly affect the film growth because it will shorten the distance between the growing film surface and the point where film precursors are initially produced. This will result in a modification of the relative flux of species reaching the surface, because of the different gas phase reactivity of each species, thus modifying their probability to participate in surface reactions.

The solar cell fabricated by the condition of the lowest RF power (10 W) had reached a conversion efficiency 7.6% for a cell thickness of 1.2 μm under standard AM1.5 illumination conditions. Within increasing of RF power, the SiH radical intensity and deposition rate are both increased which leads to worse cell performance. The higher power intensity could cause more bombardment onto the film surface resulting in rougher or sharp morphology, and we believed that it was the reason for poor cell conversion efficiency at a higher RF power [18]. The methods for analyzing the film quality such as FT-IR or PDS are only sensible to the bulk and not to the extreme thin incubation film on the samples, whereas the OES method can insight into the transient behavior and in-situ detected the closed-chamber deposition process [19]. It can be concluded that the process control by optical emission spectroscopy is a helpful tool for preparation of a high quality solar cell.

5. Conclusion

In this study, the OES technique was used to characterize the temporal behavior of pure silane plasma. The OES method has thereby proven its utility as a tool for process monitoring of the a-Si:H deposition. The a-Si:H film deposition rate depended upon the SiH emission intensity because the active species concentration increases

with increasing RF power. However, the conversion efficiency of p-i-n thin film solar cells decreases with increasing i-layer deposition rate. Finally, the amorphous silicon thin film silicon solar cell with an efficiency of 7.6% has been fabricated by using high frequency PECVD.

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