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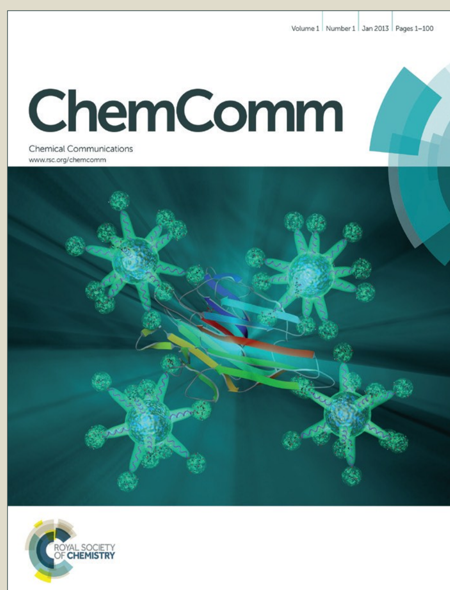

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Fabrication of High-QualityAmorphous Silicon Film from Cyclopentasilane Vapor Deposition between Two Parallel Substrates

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Cyclopentasilane converts into amorphous silicon film between two parallel substrates under atmospheric pressure by thermal decomposition at 350−400 ℃, which combines the advantages of high throughput with cost reduction and high quality film formation.

The Amorphous silicon is the main material for the manufacture of various devices such as solar cells and thin-film transistors. Currently, within the industry, the two most popular processes for preparing amorphous silicon are: (i) low pressure CVD (LPCVD) at high temperature and (ii) plasma enhanced CVD (PECVD) under vacuum. LPCVD can achieve mass production by using a simple deposition chamber but high processing temperature is necessary, which generates a large number of dangling bonds in the films and results in poor electronic properties. On the other hand, PECVD provides high quality thin film at low temperature. However, high production cost and low throughput hinder its widespread use. The fabrication of high quality amorphous silicon film at low cost remains a great challenge.

The principle of fabricating devices by a solution process has sparked intensive research from the viewpoint of reducing processing cost[1-5]. We first proposed a concept for fabricating silicon film from silicon ink by ink jetting and spin coating[1]. By using this process, the fabrication cost was significantly reduced because of the high throughput coupled with the use of a simple instrument. Recently, we fabricated an amorphous silicon solar cell by whole-solution processes with a conversion efficiency of 0.51%[5]. In this year, Bronger and coworkers achieved an efficiency of 3.5 % for an amorphous silicon solar cell when they used polymerized neopentasilane as start material by coating process[6]. However, the film from solution process exhibited low repeatability because it greatly depends on the purity of liquid source, contamination during the polymerization and coating processes, and oxygen content in glove box. Theoretically, there are two difficulties when attempting to obtain high quality film using solution process. First is the oxidization of silicon ink during the polymerization and coating process even under nitrogen atmosphere with oxygen content less than 1 ppm. Second is the thermal decomposition of polysilane introduces porous structure of amorphous silicon film with a low density of 1.9~2.0 g/cm^3 (2.2 g/cm^3 for standard *a*-Si:H by PECVD). Si-Si and Si-H bond break and rearrange into *a*-Si:H film, simultaneously generates a large volume of silane and hydrogen gas. When the gases escape from the film, they pass through the top layer, leaving numerous voids and traces inside the film (Fig. 1a). This phenomenon is much more obvious for thick films. . High angle annular dark field (HAADF) STEM image analysis (unpublished result) indicated the top film shows lower density than the bottom layer. Although the use of a liquid silicon source is good means to reduce the processing cost, another solution is required to overcome the current problems.

In this research, formation of high quality *a*-Si:H was realized using a simpler deposition system than the coating process known as atmospheric pressure CVD (APCVD) that uses cyclopentasilane (CPS, bp. 195 ℃) vapor as the silicon source. Liquid silicon is convenient for storage and transportation, and it is safer to handle than monosilane gas. Several research groups have investigated the possibility of using higher order liquid silane for the CVD deposition by experiment and computer simulation[7, 8]. However no satisfactory *a*-Si:H has been achieved. Our method differs from the traditional APCVD or LPCVD, whose hot plates were set face-to-face as shown in Fig. 1b&1c. In this system two CPS supply units attached on the side wall of main chamber (Fig. 1c) were used to replace traditional carry gas, for the purpose of creating a simple instrument, obtaining a high raw material conversion rate, and reducing precursor loss. Further, deactivation of unreacted CPS in the chamber after deposition was not an issue since all CPS was exhausted during the deposition. This CPS supply system resembles a distillation system. Even if the CPS source is partially oxidized, much less amount can transport into the chamber because of the high boiling point and low vapor pressure. This is a simplified version of a horizontal multi-wafer chemical vapor deposition reactor, where two substrates can deposit simultaneously. When the CPS molecules are introduced into main chamber, it decomposes on one hot substrate. CPS has low decomposition enthalpy when compared with monosilane (SiH_4) because of the Si-Si with a binding energy of 2.35 eV but 3.3 eV for Si-H. In addition, CPS has a ring structure with five SiH_2 units. During the decomposition on one hot substrate, one part converts to *a*-Si:H on the substrate while the remaining Si_nH_m radicals escape from the deposition site,

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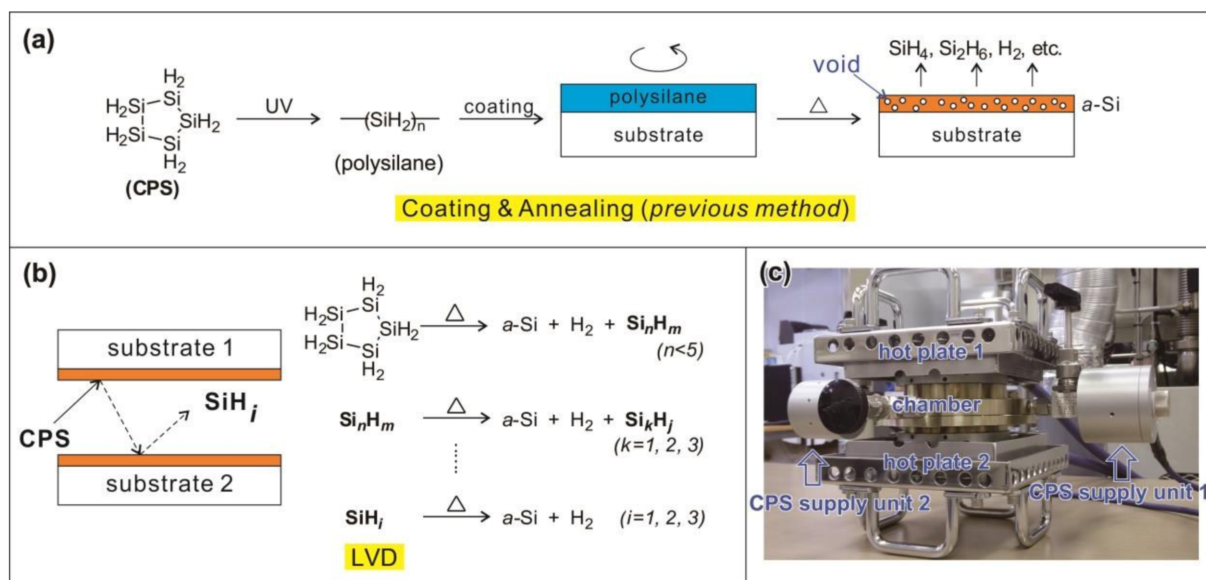

Fig. 1 Comparison of fabrication path from cyclopentasilane to amorphous silicon film, (a) previous method by solution process; (b) current method of LVD. (c) the experimental instrument of LVD, where two hot plates sandwich a main chamber, and two CPS supply units attached on side wall of main chamber.

diffusing into the chamber as a new and active precursor for next deposition (Fig. 1b). We named this deposition method, where CPS vapor decomposes and deposits between two parallel substrates, as liquid-source vapor deposition (LVD, Figure 1b). The parallel substrates serve not only as the deposition site for silicon precursor (CPS or the decomposed radicals) but also as the radical generator. The Si_nH_m radical provides the opportunity to form a high quality film even at low processing temperature, similar as PECVD. That is, LVD combines the advantages of both thermal CVD for low cost mass production with high quality similar to that of PECVD. In this way, the plasma damage to the film in PECVD can be avoided. By controlling the CPS supply speed, substrate temperature, and deposition time, we can adjust the deposition rate, film quality, and thickness accurately.

The decomposition of CPS and *a*-Si:H film formation by Fourier-transform infrared spectroscopy (FTIR), transmittance and reflectance spectroscopy in the UV-Vis range (UV-Vis TR) under various processing temperature was monitored. In a nitrogen glove box with oxygen concentration less than 1 ppm, we set two substrates in the chamber for different measurement methods, for example, UV-Vis TR by quartz substrate, and FTIR by *c*-Si(100) substrate with high-resistivity (>1000 Ω cm) polished on both sides. For deposition, a 2 cc glass bottle with 20 µL CPS (*excess*) is set in the CPS supply unit. There are 3 parameters to adjust the deposition, substrate temperature (processing temperature), CPS supply speed (CPS supply unit temperature) and deposition time. Firstly, we change the processing temperature from 250 ℃ to 400 ℃, while fixing the CPS supply unit temperature at 130 ℃. After 1 hour deposition, the substrates are cooled to room temperature and measured. The FTIR-absorption spectra are shown in Figure 2. These spectra are dominated by two strong absorption bands, one around 2000 cm^{-1} and the other at 640 cm^{-1}. There are also two weak absorption peaks evident at approximately 875 cm^{-1}. When the processing temperature is less than 250 ℃, there is no absorption from FTIR spectra, indicating no film on the substrate. Increasing the processing temperature to 275 ℃, three sets of absorption bands appear at 2100, 850-900, and 650 cm^{-1} regime. The bands at 845, 890 and 2100 cm^{-1} are associated with SiH_2 group[9], demonstrating the presence of the polysilane film on the substrate. The film formed on the quartz substrate is transparent with a wide band gap of 2.5eV. When the processing temperature increased to 300 ℃, the peak near the 2100 cm^{-1} shifted to 2080 cm^{-1} and the film color changed to light brown, demonstrating the *a*-Si:H formation . The high quantitative analysis of H content was performed by Fourier transform infrared (FTIR)[10]. It has been found for *a*-Si:H material[11] that the calibration constant of the integrated strength of the rocking-wagging-rolling vibrations around 650 cm^{-1} is independent of hydrogen content and of sample preparation. The H content (C_H) in the 300 ℃ sample is approximately 36.0 at.% (atomic percent), contributing to the incomplete conversion. This situation does not change until the processing temperature reaches to 350 ℃, where the C_H decreases to 9.8%. The band gap shows the value of 1.67 eV for 350 ℃ sample, which is similar to the *a*-Si:H film by PECVD. High processing temperature (400 ℃) slightly deduced the C_H and band gap to 7.9% and 1.48, respectively.

The microstructure factor (MSF) from FTIR spectra was calculated using 2 absorption peaks in the range from 2080 to 2000 cm^{-1}, where

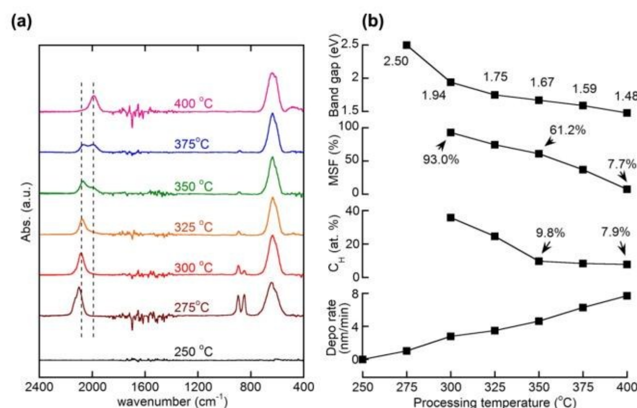

Fig. 2 Processing temperature-dependent deposition. (a) FTIR spectra on *c*-Si (100) substrate; (b) summarized data on microstructure factor, band gap, hydrogen concentration, and deposition rate.

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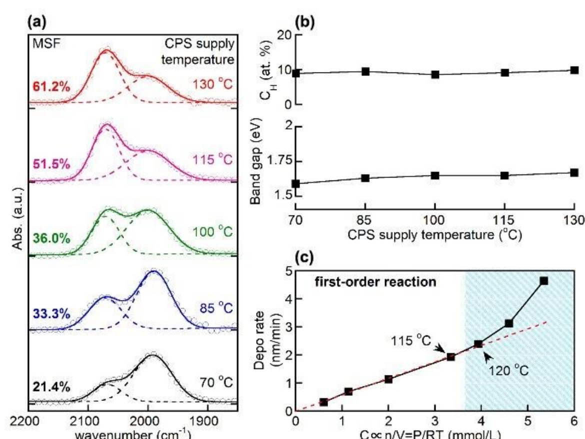

Fig. 3 (a) Peak separation for Si-H stretching of *a*-Si:H films deposited at 350 ºC with various CPS supply temperature; (b) Summarized data on band gap, hydrogen concentration. (c) Deposition rate depends on CPS concentration.

the difference is attributed to a different force constant of the Si-H oscillator when located at a void surface (2070-2090cm^{-1}) or embedded within a dielectric medium (~2000cm^{-1}) (See ref. 12 and references cited therein for an overview of early work.) That is, the MSF has been shown to increase when the concentration of micro-voids increases. Fig. 2b shows the MSF with deposition temperature from 300 to 400 ℃ under same CPS supply speed. At the processing temperature of 300 ℃, film shows a high MSF of 93.0% due to the low conversion rate from polymer to a-Si film. It decreased to 7.7% when the processing temperature was increased to 400 ℃.

In amorphous silicon solar cells, *a*-Si:H film with high band gap benefits the V_{oc}. From the discussion above, *a*-Si:H with a high band gap prepared at a low processing temperature has a worse MSF. We addressed this problem by adjusting another parameter, the CPS supply speed. In this experiment, the CPS evaporation temperature varies from 70 ℃ to 130 ℃ while fixing the substrate temperature at 350 ℃. FTIR in Figure 3a demonstrates the MSF decreases from 61.2% at 130 ℃ to 21.4% at 70 ℃, while the band gap and hydrogen atomic concentration are kept constant at approximately 1.65eV and 9.0%. Above all, by using different parameter, it is possible to obtain an *a*-Si:H film with a wide band gap and low MSF.

Figure 3c is a plot of the deposition rate depending on the CPS vapor concentration. The CPS partial pressure is not known absolutely. Suppose that CPS concentration (C) in the main chamber is associated with CPS concentration in CPS supply unit ($C=k_0C_0$). The CPS vapor concentration in the CPS supply unit (2cc glass bottle) is calculated using the Ideal gas law,

$$C \propto C_0 = \frac{n}{V} = \frac{P}{RT}$$

where P is the saturation vapor pressure of CPS[13], T is temperature (K) of CPS supply unit, R is molar gas constant. We found that the deposition can be fitted using the first-order reaction ($v=k[C]^1$) when the CPS supply temperature is less than 120 ℃. On the other hand, the deposition rate increases dramatically when T > 120 ℃. The unwanted gas-phase reaction occurs in the chamber at high CPS concentration. In principle, the deposition processes can be divided into two parts, namely the gas-phase and the surface reaction. Enlarged CPS molecule concentrations will lead to large aggregations of CPS, which is difficult to completely incorporate into an amorphous layer. It is the hydrogen-rich compound that cannot be used for photovoltaic devices. Considering the deposition rate, we obtained the optimized CPS supply temperature at 115 ℃. The amorphous silicon film with good thickness uniformity (less than 10% thickness variation on 4-inch glass wafers) can be obtained under optimized deposition condition. However the film thickness decreases dramatically on the edge of glass wafer where it is close to the chamber wall.

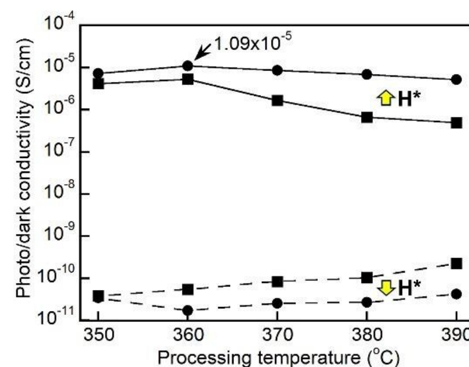

Fig. 4 Photo (solid line) and dark (dash line) conductivity of silicon film under various substrate temperatures before (square) and after (dot) hydrogen radical treatment (H*).

The electronic property of the *a*-Si:H under different processing temperature by photo/dark conductivity with a CPS supply temperature of 115 ℃ was then investigated (Fig. 4). In order to avoid the effect of the film thickness on the electronic property, *a*-Si:H films with the same thickness around 150 nm were prepared. In order to terminate the dangling bond in the *a*-Si:H, further hydrogen radical treatment (CatCVD) was employed. Fig. 4 shows the photo/dark conductivity of *a*-Si:H films before and after hydrogen radical treatment. Before hydrogen radical treatment, a low processing temperature of 350 ℃-360 ℃ yielded better performance than a higher temperature (solid line with squares). The possible reason is the higher processing temperature results in many more dangling bonds. The film has a slightly higher photo conductivity at 360 ℃ than at 350 ℃, probably because of a more thorough conversion rate at 360 ℃. Using hydrogen radicals to terminate the dangling bonds is a popular method of improving film quality. After hydrogen radical treatment, all film shows improvement, especially the film produced at higher processing temperature. The relative lack of improvement in the sample produced at the lower processing temperature (350 ℃) also indicates the as-depo films have a low dangling band (1.5×10^{17} cm^{-3} from electron spin resonance (ESR) measurement) while 400 ℃ sample had a spin density[14] of 6.2×10^{17} cm^{-3}. After hydrogen radical treatment, the spin density for all the films decreased by approximately one order of magnitude. And *a*-Si:H prepared under 360 ℃ shows the best performance with a highest photo-conductivity of 1.09×10^{-5} S/cm and lowest dark-conductivity of 1.71×10^{-11} S/cm.

Finally, we compare the oxygen contamination in *a*-Si:H film by LVD with spin coating film. According to SIMS measurement, the oxygen concentration in spin coating film is 1.0×10^{20} atoms/cm^3. LVD shows a much low concentration of 6.0×10^{18} atoms/cm^3 because it avoids the UV polymerization and coating process in our previous research. And the CPS evaporation unit also prevents the oxidized CPS entering into the main chamber. The hydrogen content measured by SIMS is 7.8%; although this is slight lower than the value of 9.0 % calculated by FTIR, the use of a different measurement method may account for the divergence. The above data demonstrate that the same quality film as prepared by PECVD can be prepared using a simple deposition chamber under atmospheric pressure.

The *a*-Si:H film was applied into an amorphous silicon solar cell as shown in Figure 5a. The cell was fabricated on a glass substrate (OA-10GF) with 400 nm zinc oxide (2% Al_2O_3 dopant) and100nm AgAu alloy reflective layer (5 atomic% Au) and 5 nm Ti adhesive layer. The

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cell was fabricated as *n-i-p* structure, with the *p*-Si layer serving as a window layer. Among the three silicon layers, *n*-Si was fabricated by solution processing with a white phosphorus (P_4) dopant (unpublished method). The intrinsic layer is deposited by using current LVD with a processing temperature of 360 ℃ and CPS supply temperature at 115 ℃ with a thickness of 150 nm, following by a post hydrogen radical treatment. After removing the oxidized surface by 1% HF solution, p-Si and top ITO electrode (1.0 mm^2) were deposited by CatCVD and sputter, respectively. The photo and dark I-V curve are displayed in Figure 5. The cell shows a 4.3% conversion rate, with a J_{sc} of 10.4 mA/cm^2, V_{oc} of 0.68V and fill factor of 0.60. The EQE of cell was calculated from the spectral response of the devices within the 300-800 nm wavelengths. It shows a maximum peak of 65%, at 500 nm (2.6 eV) of the spectrum. This result clearly demonstrates that there is no major spectrum specific loss mechanism limiting the performance of the cell prepared by LVD.

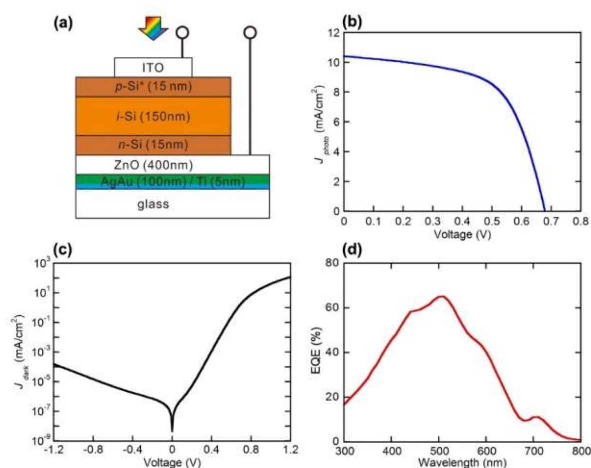

Fig. 5 (a) Schematic device design for solar cells. (b) Characteristic photo I-V curves for solar cell under AM1.5 irradiation. (c) The dark I-V curve, and (d) External quantum efficiency (EQE) of amorphous silicon solar cell.

For this system, we optimized the processing temperature and CPS supply speed. However, two other parameters were not discussed here, specifically; i) the gap between two hot plates, and ii) the hydrogen atmosphere. A detailed discussion of and potential application for the passivation layer of HIT (Heterojunction with Intrinsic Thin layer) solar cell will appear in a future research report.

Conclusions

In conclusion, the process investigated, LVD, is a simpler process than our previous spin-coating process. It works under atmospheric pressure and resolves two critical problems associated with spin-coating; the high void and the levels of oxygen concentration. By using liquid cyclopentasilane as a silicon source and two parallel substrates for film deposition, radicals were generated on the substrate at low temperatures, which yielded the formation of a high quality film on the opposite substrate. This is a completely new system that works at atmospheric pressure using a liquid silicon source, while combining the advantages of cost reduction and high quality film formation. When using this technique for an intrinsic layer preparation in solar cells, we achieved the same level as PECVD on flat substrate. Without plasma damage, it has potential applications in amorphous silicon solar cells, HIT solar cells, thin film transistors, and other devices.

Notes and references

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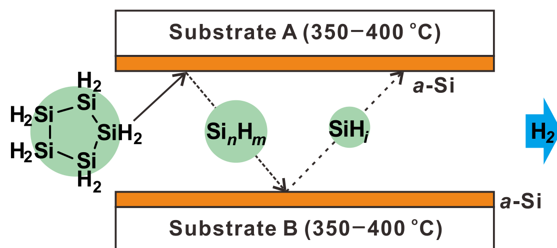

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