Growth and microstructure properties of microcrystalline silicon films deposited using jet-ICPCVD*

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Abstract: Microcrystalline silicon films were deposited at a high rate and low temperature using jet-type inductively coupled plasma chemical vapor deposition (jet-ICPCVD). An investigation into the deposition rate and microstructure properties of the deposited films showed that a high deposition rate of over 20 nm/s can be achieved while maintaining reasonable material quality. The deposition rate can be controlled by regulating the generation rate and transport of film growth precursors. The film with high crystallinity deposited at low temperature could principally result from hydrogen-induced chemical annealing.

Key words: microcrystalline silicon; jet-ICPCVD; high rate; convective transfer; crystallinity
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1. Introduction

Hydrogenated microcrystalline silicon (μc-Si:H) films have attracted intense interest in photovoltaic applications, as they potentially offer higher efficiency and stability compared to amorphous silicon (a-Si)[1−3]. For cost-effective application of μc-Si:H material in solar cells, much effort has been devoted to increasing the deposition rate while maintaining reasonable quality since films with a thickness of over 1 μm are required for sufficient light absorption, and it is already shown that device-quality μc-Si:H film could be formed at a rate above 1 nm/s[4−6]. Among various approaches for μc-Si:H film deposition, capacitively coupled plasma-enhanced chemical vapor deposition (PECVD) is undoubtedly the most conventional technique, in which growth precursors generated in plasma are predominantly transported to the growing surface by diffusion. Convective transport, which works by directly jetting growth precursors toward the growing surface, can break through the limitation of diffusion transport and greatly increase the deposition rate. In this respect, several investigations have been performed by combining gas-jet with various plasma-driven sources, such as direct current (DC)[7], microwave[8], and electron beam[9], to deposit Si-based films at a high rate. However, a large gas supply and/or high power consumption is generally needed for these types of strategy[7−9].

In this work, a technique combining very high frequency inductively coupled plasma with gas-jet (jet-ICPCVD) was used to deposit μc-Si:H films at low temperature. The influence of deposition parameters on deposition rate and microstructure properties of μc-Si:H films was systematically investigated. It is demonstrated that both high deposition rate and high crystallinity can be obtained by controlling the deposition parameters. Furthermore, mechanisms concerning these features are discussed in detail.

2. Experimental details

The experimental setup consists of a jet nozzle and a 27.12 MHz power supply (see Fig. 1). The jet nozzle, consisting of two coaxial quartz tubes, is fixed hermetically to the reactor chamber with the outer tube carrying the H_2 and the inner one carrying SiH_4 (diluted in H_2). An inductance coil circling the outer tube is used to excite the plasma. During the deposition process, growth precursors are generated in the plasma inside the nozzle and jetted toward the substrate surface to contribute to film growth.

Intrinsic silicon thin films were deposited on glass or SiO_2 substrates using the jet-ICPCVD system. The distance of the inductive coil to the substrate was kept constant at 3.5 cm throughout the present work, unless mentioned otherwise. The H_2 flow rate was varied from 14 to 148 sccm (standard cubic centimeter per minute at STP) with a SiH_4 flow rate typically at 8 sccm (20% diluted in H_2). The chamber pressure was regulated from 25 to 400 Pa and power from 60 to 180 W. All depositions were performed without intentional substrate heating. A time-dependent substrate temperature monitor showed that the substrate temperature was not more than 100 ℃ during deposition. The deposition rates were acquired from deposition duration and film thicknesses, which were measured from scanning electron microscopy (SEM, JOEL JSM-7000F) cross sectional images. Raman spectra were measured by Raman spectroscopy (Jobin Yvon HR800 UV) using the 514 nm line of Ar^+ laser as the exciting source. The crystalline fraction (X_C) was deduced from the formula $X_C = (I_{505} + I_{520}) / (I_{480} + I_{505} + I_{520})$ by the decovolution of the Raman TO phonon band[10], where

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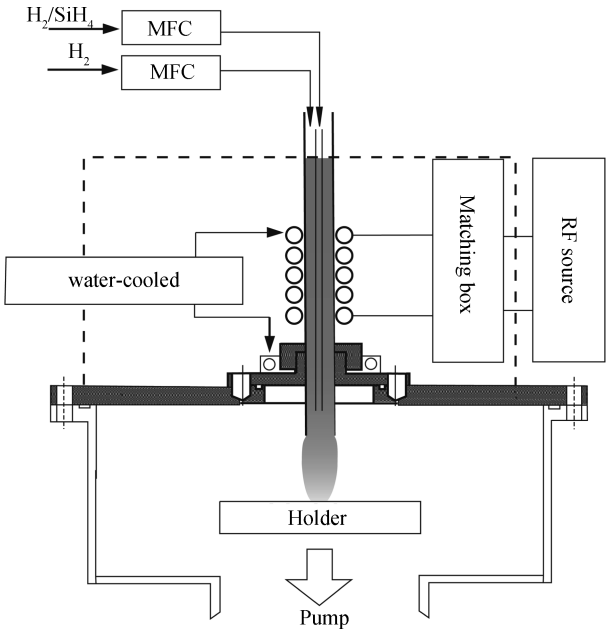

Fig. 1. Schematic diagram of the experimental setup.

I_{480}, I_{505}, and I_{520} are the integrated intensities of the Raman lines corresponding to amorphous, intermediate and crystalline phases, respectively. X-ray diffraction (XRD, Rigaku D/Max-RA) was acquired using CuKα radiation (λ = 1.54056 Å) with 2θ ranging from 20° to 60°. Structural characterization of the deposited films was also carried out using transmission electron microscopy (TEM, JEOL 4000EX). Electron spin resonance (ESR, Bruker A300-10/12) was performed to assess defect density, and UV-visible spectroscopy (LAMBDA 900UV) was used to evaluate the optical band gap.

3. Results and discussions

3.1. Growth rate

Figure 2 shows the deposition rate of the films deposited at a constant power of 100 W as functions of the deposition parameters, including gas flow rate, chamber pressure, and distance from the activation zone to the substrate (i.e., the transport distance of precursors). As seen from Fig. 2(a), increasing the H_2 flow rate from 14 to 148 sccm while keeping a fixed SiH_4 flow rate of 8 sccm results in a rapid increase in deposition rate from 2 to 22 nm/s. The deposition rate increases with the decrease in chamber pressure and a high deposition rate of 30 nm/s is obtained at a pressure as low as 40 Pa (Fig. 2(b)). By shortening the distance from the activation zone to the substrate, the deposition rate is obviously increased (Fig. 2(c)). Furthermore, the deposition rate reaches 34 nm/s at a SiH_4 flow rate of 27 sccm and a distance of 3.5 cm, a value much higher than the one when the SiH_4 flow rate is 8 sccm at the same distance. Even a deposition rate above 100 nm/s can be achieved by further increasing the SiH_4 flow rate, two orders of magnitude higher than that of a 13.56 MHz PECVD μc-Si:H.

In a jet-ICPCVD system, growth precursors are jetted directly toward the growing surface. The increase in deposition rate could be attributed to the reduced transit time t_{tran} (defined as the time during which the precursors travel from activation

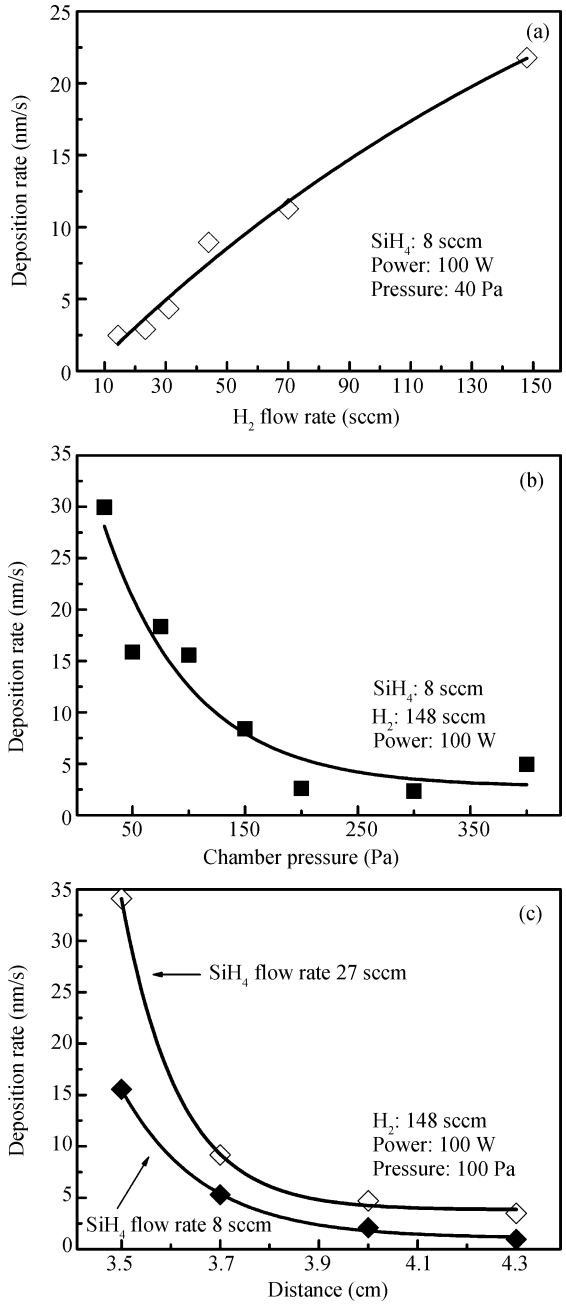

Fig. 2. Deposition rate of the films as a function of (a) H_2 flow rate, (b) chamber pressure, and (c) distance from activation zone to substrate. The deposition duration for all films was 3 min.

zone to growing surface), which can be expressed as[11]

$$t_{tran} \propto p_{cham} d / f_{total}, \quad (1)$$

where f_{total} is the total gas flow rate (combined flow rate of SiH_4 and H_2), d is the transport distance of growth precursors, and p_{cham} is the chamber pressure. According to this model, increasing the flow rate of H_2 (and thus the total gas flow rate f_{total}), or decreasing the chamber pressure p_{cham}, or shortening the distance d, a reduced transit time (and thus a high deposition rate) can be achieved in the present jet-type CVD system, which is consistent with our experimental results (see Fig. 2). In addition, collisions between precursors are decreased and the mean free pass of precursors is increased with decreased

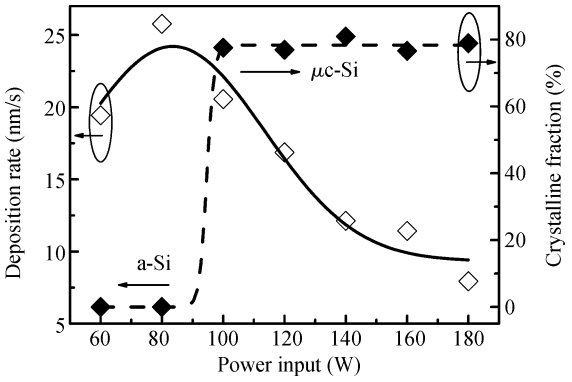

Fig. 3. Deposition rate and crystalline fraction of the films as a function of power input. The deposition pressure, duration, and flow rates of SiH_4 and H_2 were 40 Pa, 3 min, 8 sccm and 148 sccm, respectively.

chamber pressure, which increases the orderliness of precursor transportation and thus the amount to of precursors reaching the substrate surface, resulting in the increase in the deposition rate. Meanwhile, a reduced polymerization reaction in plasma due to a decreased transit time also contributes to the high deposition rate.

Furthermore, it was reported that an increase in deposition rate with increasing SiH_4 flow rate is associated with the generation rate of the precursors ($\mathrm{d}[X]/\mathrm{d}t$), which is proportional to the product of electron density (n_e) and number density of the SiH_4 molecules [SiH_4] expressed as follows[12],

$$\mathrm{d}[X]/\mathrm{d}t \propto n_e \times [\mathrm{SiH_4}]. \quad (2)$$

A high electron density n_e beyond 10^{12} cm^{-3} exists in the jet-ICPCVD system as measured by the Langmuir probe due to excitation by very high frequency inductively coupled plasma and confinement within a small space. A higher deposition rate can be achieved at high SiH_4 partial pressure (see Fig. 2(c)) or at high power (see Fig. 3), which generates a higher electron density. In fact, the increase in precursors reaches a plateau due to SiH_4 depletion at a higher power. In contrast, enhancement of the etching effect of atomic hydrogen on the growing surface under higher power results in a decrease in the growth rate[5].

3.2. Microstructures

It is important to note from Fig. 3 that there exists a threshold power around 90 W, below which the deposited silicon film has an amorphous structure. The crystalline fraction remains roughly unchanged at a high level as the power increases to above 100 W, implying that the ion bombardment effect is not evident under higher power in this plasma system.

Although a high deposition rate could be achieved under the conditions of high H_2 flow rate, low chamber pressure and short transport distance, crystalline characteristics of the films may degenerate. Hence, microstructure properties of the films deposited under a constant power of 100 W were investigated. The total flow rate was kept constant at 156 sccm while the SiH_4 concentration (SC) was varied from 1% to 5% by increasing the SiH_4 flow rate from 8 to 40 sccm. This allowed for a high deposition rate of over 20 nm/s to be obtained (see Fig. 2). The measured Raman and XRD spectra of the films are shown in Figs. 4(a) and 4(b), respectively. Based on the evolution of

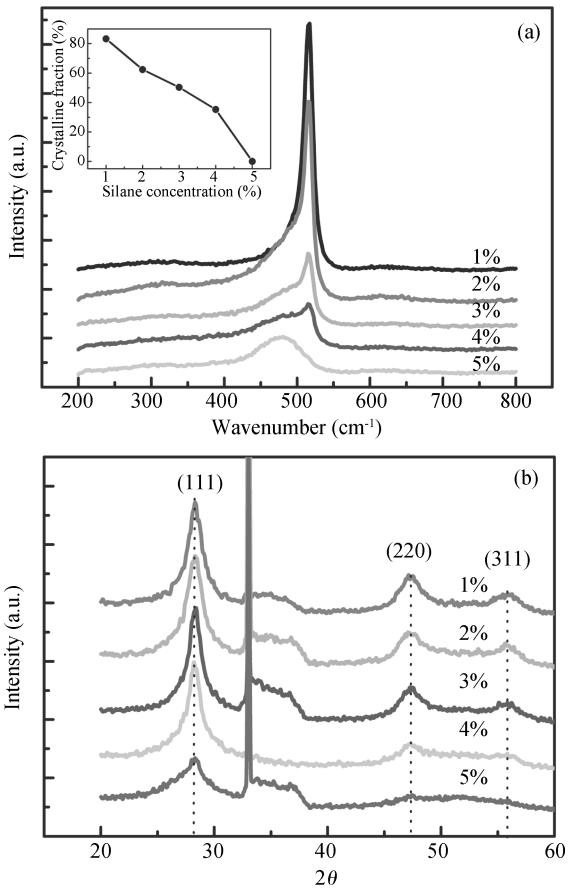

Fig. 4. (a) Raman spectra and (b) X-ray diffraction patterns of the silicon films deposited at varying SiH_4 concentrations. The deposition power, pressure and duration were 100 W, 100 Pa, and 5 min, respectively. The inset in (a) shows the crystalline fraction of the films as a function of SiH_4 concentration.

the peak at 520 cm^{-1} in the Raman spectra and the diffraction peaks in the XRD spectra, the deposited films appear to cover the phase transition from amorphous to microcrystalline silicon. The crystalline fraction (X_C) as a function of SiH_4 concentration is also shown in the inset of Fig. 4(a). This shows that the crystalline fraction increases with decreasing SC (i.e., the increase in H_2 concentration), revealing the positive effect of H atoms on the structural improvement of deposited films.

In Fig. 4(b), three diffraction peaks can be seen at 2θ = 28.3, 47.3, and 55.8°, which were assigned to (111), (220), and (311) crystalline planes, respectively. The XRD spectra also show that the intensity of the diffraction peaks increases with a decrease in SC, indicating improvement in the structural orderliness of the deposited films. The average grain size calculated according to the Debye–Scherrer formula is 10–20 nm, which increases with decreasing SiH_4 concentration.

High crystallinity of the μc-Si:H film deposited at a high rate was also directly observable using TEM. Concentric circles seen in selected area electron diffraction (SAED) patterns (inset in Fig. 5(a)) indicate the typical microcrystalline features of silicon. From the cross-sectional TEM image shown in Fig. 5(a), crystallites can be seen growing directly on the SiO_2 layer. The high-resolution TEM image (Fig. 5(b)) shows very dense micrograins embedded in the texture of the film with a

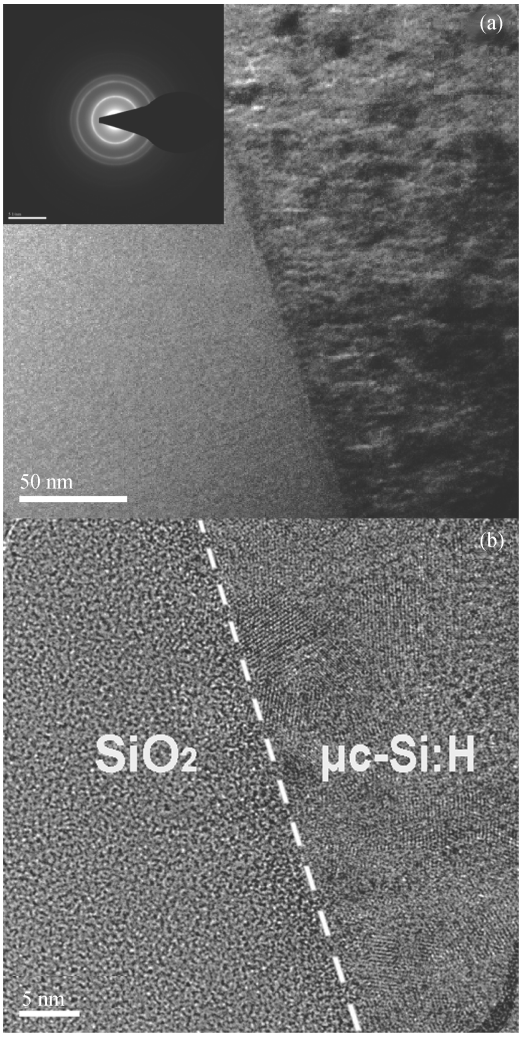

Fig. 5. TEM images of a μc-Si film deposited on SiO_2. (a) Cross-sectional TEM view and (b) high resolution TEM view of the film/SiO_2 interface. The inset in (a) shows the transmission electron diffraction in a selected area mode.

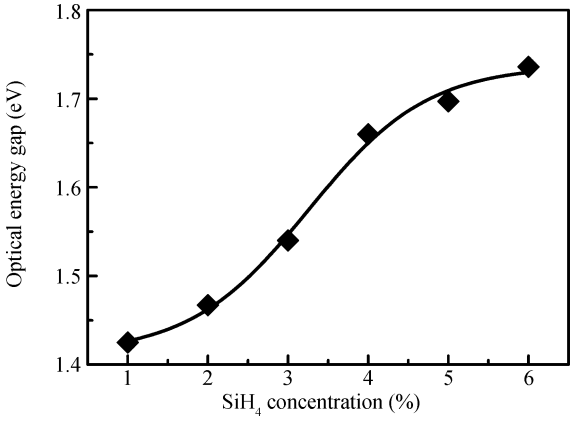

Fig. 6. Optical band gap of the films as in Fig. 4, plotted as a function of SiH_4 concentration.

small amount of amorphous silicon in the network.

Spectrophotometry covering the visible range was used to determine the absorption coefficient and optical band gap of the films. Values of the optical band gap E_{opt} were estimated from Tauc plots $(\alpha h\nu)^{1/2}$ against $h\nu$, where α is the optical absorption coefficient obtained from spectroscopy measurement. As shown in Fig. 6, the optical band gap decreases monotonically from about 1.7 to 1.4 eV as the SiH_4 concentration decreases from 6% to 1%. This indicates the transition from amorphous-dominated silicon to microcrystalline-dominated silicon with increasing H_2 partial pressure, which is in agreement with the results of the Raman and XRD measurements. Thus, the optical band gap can be easily tailored over a large range by altering the H_2 partial pressure. Defect densities estimated from the ESR signal intensity were about 1×10^{17} cm^{-3} in the present experimental conditions.

The subsurface growth model is one of the most widely accepted models used to interpret the formation of a crystallized film at low temperature[13,14]. According to this model, hydrogen-mediated chemical annealing in a growth zone below the surface promotes the rearrangement of the silicon network by breaking weak Si–Si bonds and reforming stable (crystalline) bonds[13]. Mani *et al*.[15] reported the deposition of μc-Si:H films at room temperature, and believed that hydrogen-induced chemical annealing through the rearrangement of disordered and strained a-Si bonds is responsible for the formation of crystallized films.

In fact, we found that the amorphous incubation layer near the substrate surface[16] present at the initial deposition stage gradually crystallizes during the growth process[17]. This unambiguously reveals that the hydrogen-induced chemical annealing must play a crucial role in the crystallization of microcrystalline silicon films deposited using jet-ICPCVD, considering the very low deposition temperature. In this process, abundant hydrogen atoms with sufficient energy diffused into the subsurface layer and effectively induced annealing in the subsurface zone, thus promoting the formation and growth of crystallites in the films, as shown in Fig. 4, where the crystallinity improves with increasing hydrogen concentration. In addition, it is believed that the stress in the deposited films due to the high deposition rate may further promote the crystallization process[18].

4. Conclusions

A jet-type inductively coupled plasma chemical vapor deposition (jet-ICPCVD) technique was used to deposit μc-Si:H films without intentional substrate heating. The deposition rate and microstructure properties of the deposited film could be effectively controlled by varying the gas flow rate, deposition pressure, SiH_4 concentration, input power and transport distance of the precursors. A very high deposition rate of over 20 nm/s was obtained while maintaining high crystallinity. During the jet-ICPCVD process, growth precursors were efficiently generated and rapidly transported to the growing surface, while abundant atomic hydrogen from the plasma diffused into the subsurface layer and induced the crystallization of films through hydrogen-mediated chemical annealing at low temperature.

The present method is promising for the deposition of high-quality microcrystalline silicon films at a high deposition rate. The deposition of large area, uniform microcrystalline sil-

icon film will be further realized by using a multi-jet system and/or scanning the substrate relative to the jet source. And the optoelectronic properties and behavior in solar cell devices of μc-Si:H films deposited using this technique need to be further investigated.

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