Study on the Growth of Microcrystalline Silicon Films in Atmospheric-Pressure VHF Plasma Using Porous Carbon Electrode

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Abstract. Using atmospheric pressure (AP) plasma excited by a 150-MHz very high-frequency (VHF) power, the growth process of hydrogenated microcrystalline silicon (μc-Si:H) films was studied. A porous carbon electrode, which had originally been developed for the high-quality Si epitaxy at low temperatures, was used for the plasma generation in the area of 30×100 mm². VHF power density ($P_{\text{VHF}}$) and H₂/SiH₄ ratio were varied as parameters under a fixed substrate temperature of 220 °C. It was shown that μc-Si:H films having good uniformities of thickness and crystallinity in the area of 20×80 mm² were obtained without being contaminated by dusty particles. Although increasing H₂/SiH₄ ratio led to the improvement of both deposition rate and film crystallinity, a crystallized Si film with a Raman crystalline volume fraction of ~72% was obtained with a high deposition rate of 5 nm s⁻¹ at $P_{\text{VHF}} = 24$ W cm⁻², even if hydrogen was not added to the process gas mixture (H₂/SiH₄ = 0). Numerical simulations of the gas flow revealed that the process gas mixture was uniformly injected into the narrow plasma gap region from the opposite side of the substrate surface and suggested that the gas residence time in the plasma at the central part of the plasma region was long enough (>5 ms) to sufficiently deplete the source SiH₄, promoting the crystallization of the growing film without the necessity of H₂ addition.

1. Introduction

Low-temperature hydrogenated microcrystalline silicon (μc-Si:H) is a promising material for the use in large-area electronic devices. In particular, μc-Si:H films deposited on plastic sheet substrates can realize flexible and low-cost thin film transistor-based devices and solar cells. Thus, there is a strong demand for the high-rate deposition of good-quality μc-Si:H films at low temperatures. Generally, μc-Si:H films are prepared by plasma-enhanced chemical vapor deposition (PECVD) using SiH₄ and H₂ as the source gases. In conventional radio-frequency PECVD processes, high H₂/SiH₄ ratio conditions are utilized to promote the crystallization of Si films at low temperatures. However, the depositions at substrate temperatures lower than 100 °C result in the decrease in deposition rate and the deterioration of film quality as far as conventional PECVD processes are used. This limits the practical application of those processes as the key tools for the deposition of good-quality μc-Si:H with high rates on plastic materials, such as polyethylene terephthalate and polyethylene naphthalate (PEN). Probable methods to overcome this technical issue are the use of very high-frequency (VHF) excitation of plasma and/or high working pressure [1–3].
We have been developing a thin film growth technology using atmospheric-pressure (AP) plasma excited by a 150-MHz VHF power. Note that the VHF excitation of plasma and the very high collision frequency between gas-phase species at AP lead to the trapping of charged particles in a narrow (<1 mm) gap region between electrodes and also to the small kinetic energies of ions [4]. This can avoid the ion damage of the film-growing surface, while keeping high power density in the plasma, which enables us to deposit Si films with high rate and at low temperatures [4–9].

The aim of the present study is to develop an efficient formation process of good-quality functional thin films on polymers using the AP plasma technology. By using a porous carbon electrode that has originally been developed for the high-quality Si epitaxy at low temperatures [7], the formation of \( \mu c \)-Si:H on a PEN sheet of 0.125 mm thickness has been achieved with a deposition rate of 2.5 nm s\(^{-1}\) [9].

In this paper, we discuss the growth process of \( \mu c \)-Si:H in AP-VHF plasma excited using a porous carbon electrode, focusing especially on the origin of the uniformities of thickness and crystallinity of the \( \mu c \)-Si:H films in the plasma region.

2. Experiments
The experiments were conducted in AP plasma CVD system, which is the same one as that used in our previous studies [8,9]. Figure 1 shows a schematic diagram of a porous carbon electrode used for the plasma generation. By using this type of electrode, fresh process gas mixtures can be directly supplied into the narrow plasma gap (0.5 mm) through the porous carbon plate of 3 mm thickness [7]. The size of electrode is 30×100 mm\(^2\). By supplying a 150 MHz VHF power, AP plasma was excited stably in the gap region between the electrode and a substrate as shown in Figure 1. The substrate was fixed on a TiN-coated copper susceptor of the substrate heating stage by a vacuum chuck system that ensured a sufficiently high efficiency of heat transfer across the substrate/susceptor interface.

In a series of experiments, Corning EAGLE2000 glass plates of 0.7 mm thickness (100×100 mm\(^2\)) were used as substrates. The films were prepared with a He flow rate of 50 SLM (SLM denotes liter per minute at STP) and a SiH\(_4\) flow rate of 50 SCCM (SCCM denotes cubic centimeter per minute at STP) under a constant process pressure of 1×10\(^5\) Pa. The H\(_2\) flow rate and VHF power density (\(P_{VHF}\)) were varied as parameters. The temperature of the back surface of substrate (\(T_{sub}\)) was monitored by a Chromel-Alumel thermocouple embedded in the position 3 mm apart from the susceptor surface and kept at 220 °C during deposition.

The film thickness was measured by a step profiler. The film structure was characterized by Raman scattering spectroscopy. Raman spectra were recorded with a 514.5-nm Ar\(^+\) laser radiation in the back-scattering configuration using a Raman spectrometer, which comprised a double monochromator with a resolution of 1 cm\(^{-1}\), a standard cooled photomultiplier and a photon counting system.

To discuss the growth process of Si in AP-VHF plasma, the gas flow around the plasma region was simulated by solving coupled sets of partial differential equations governing the mass, momentum, and energy transports, where the transport parameters, such as viscosity and thermal conductivity, were derived from gas kinetic considerations. The simulation model representing the actual experimental setup and conditions was calculated using the commercially available simulator PHOENICS-CVD that allowed three-dimensional visualizations of the gas flow and temperature profiles.

![Figure 1. Schematic diagram of the experimental setup.](image-url)
3. Results and discussion

3.1. Deposition characteristics of Si films

Figure 2 shows the photographs of the Si films under a fixed H$_2$ flow rate of 100 SCCM (H$_2$/SiH$_4$ = 2) as a function of $P_{\text{VHF}}$. It is clearly observed in Figure 2 that increasing $P_{\text{VHF}}$ results in the generation of dusts at the film edges downstream of the gas flow and also appears that dusty particles are not formed in the plasma region. Indeed, the observation by a scanning electron microscope revealed that no dusts were seen on the film surface. This indicates that the film-forming precursors that do not contribute to the film growth immediately condense into Si powders after being swept out from the plasma. These are consistent with the results obtained in our previous studies on the low-temperature Si epitaxy [6,7], suggesting that the VHF excitation of AP plasma is effective for the film-forming precursors to not induce the gas-phase condensation, although the possibility of the formation of Si nano clusters must be considered. As a result, by sucking the gas flow from the electrode edge zone, sticking of dusts on the substrate surface can be avoided as demonstrated in Figure 2e, which enables us to realize dust-free and continuous depositions by scanning substrate. However, all the Si films shown in this paper have been prepared without substrate scanning.

Figure 3 shows the thickness profiles of the Si film after 4 min deposition with 100 SCCM H$_2$ at $P_{\text{VHF}} = 24$ W cm$^{-2}$. The position at 0 mm corresponds to the center of the deposition area. It has been confirmed that, in this condition, the film has extremely thin or even negligible amorphous incubation layer [8,9]. The profiles in Figure 3 indicate that the film thickness is almost uniform at around 1.5 $\mu$m in the area of 20×80 mm$^2$. The distribution of crystallinity of the same film has been also evaluated. The Raman spectra are shown in Figure 4. Since no noticeable differences are observed in the spectra, it can be noted that the film crystallinity has uniformity similar to the film thickness. These suggest the almost uniform distribution of reactive species in the area of 20×80 mm$^2$, which is discussed later.

Figure 2. Photographs of the Si films under the room light. The films were deposited with $P_{\text{VHF}} =$ (a) 6, (b) 12, (c) 18, and (d,e) 24 W cm$^{-2}$ under a fixed H$_2$ flow rate of 100 SCCM (H$_2$/SiH$_4$ = 2). The film thickness is (a) 1000, (b) 640, (c) 780, and (d,e) 770 nm. The sample (e) was prepared by sucking the gas flow from the electrode edge zone to remove the dusty particles.
3.2. $H_2/SiH_4$ ratio dependences of deposition rate and crystallinity

The Raman spectra for the $\mu$-Si:H films prepared in this study had a sharp peak at around 520 cm$^{-1}$ with a shoulder on the lower wavenumber side as shown in Figure 4, which could be deconvoluted by considering the presence of two additional Gaussian peaks in the vicinity of 510 and 480 cm$^{-1}$. Raman crystalline volume fraction, $I_{cRS}^c$, was calculated as $I_{cRS}^c = (I_{520} + I_{510}) / (I_{520} + I_{510} + I_{480})$, where $I_{520}$, $I_{510}$ and $I_{480}$ are the integrated intensities of the peaks. $\gamma$ is the ratio of the back scattering cross sections and has a value of 0.8 [8,9].

Figure 5 shows the $H_2/SiH_4$ ratio dependences of deposition rate and $I_{cRS}^c$ of the Si films deposited at $P_{VHF} = 12$ and 24 W cm$^{-2}$. Both the deposition rate and $I_{cRS}^c$ increase with increasing $H_2/SiH_4$ ratio, indicating that the chemical reactions in gas phase and on the film-growing surface are more enhanced at the higher $H_2/SiH_4$ ratio. Increasing $P_{VHF}$ gives rise to the further enhancement of the film-forming process.

**Figure 3.** Thickness profiles of the Si films in the (a) vertical and (b) transverse directions after 4 min deposition with $P_{VHF}$ of 24 W cm$^{-2}$ and $H_2$ flow rate of 100 SCCM. The plasma width in the transverse direction is equal to the substrate size.

**Figure 4.** Raman spectra for the Si films deposited in the same condition as that in Figure 3 as a function of position in the vertical and transverse directions.
Note that crystallized films are obtained even if H\textsubscript{2} is not added to the process gas mixtures (H\textsubscript{2}/SiH\textsubscript{4} = 0). This suggests the saturation of the film-forming reactions both in gas phase and on the growing film surface and is considered to be linked to the uniformities of thickness and crystallinity of the resultant films described in the former section.

3.3. Simulations of the gas flow around the plasma region

As described above, a crystallized Si film with good uniformities of film thickness and crystallinity in the plasma region are obtained with a high rate by using a porous carbon electrode even at H\textsubscript{2}/SiH\textsubscript{4} = 0. Such a unique feature is considered to be closely related to the gas flow pattern in the plasma, because the process of both the gas-phase and surface reactions is strongly affected by the gas residence time in the plasma. Thus, we performed numerical simulations of gas flow around the plasma region. In the simulations, AP-VHF plasma was simply treated as a heat source radiating approximately 50% of the input VHF power as heat, which was determined based on the experimental data [9].

Figure 6 illustrates the contours of pressure and flow velocity on a vertical midplane through the plasma region. The flow vectors are also shown by arrows in the figure. It is observed that the pressure inside the electrode box is higher than the outside and that the pressure drop is generated in the inside of the porous carbon plate. As a result, the process gas is introduced uniformly into the plasma region from the opposite side of the substrate surface, as shown by the flow vectors. In the plasma region, the velocity in the horizontal direction is nearly zero at the center of the electrode and increases toward the electrode edge. Thus, the gas residence time in the plasma varies depending on the horizontal position. At the central part of the plasma area, the gas residence time is estimated to be longer than 5 ms.

On the basis of these results, the reaction process in the plasma can be discussed as follows. Taking into account the gas residence time (>5 ms) in the central area of the plasma region, the source SiH\textsubscript{4} molecules injected into the plasma have enough time to reach the substrate surface by diffusion. In such circumstances, atomic hydrogen generated by the decomposition of the source gas molecules can promote further decomposition of the available SiH\textsubscript{4} molecules through the repeated interactions in the plasma. As a result of such enhanced interactions between atomic hydrogen and SiH\textsubscript{4} molecules, the source SiH\textsubscript{4} might be depleted, ensuring a large flux of atomic hydrogen onto the substrate surface. By virtue of the frequent interactions of abundant atomic hydrogen with the film-growing surface together with the moderate surface heating by the plasma, the formation of crystalline Si network is greatly enhanced even at the high deposition rates. In this context, it is reasonable that the uniform supply of the source SiH\textsubscript{4} from the electrode leads to the film growth with uniform thickness and crystallinity.

4. Conclusion

We have studied the growth process of \textmu c-Si:H prepared with very high rates (>5 nm s\textsuperscript{-1}) in AP-VHF plasma excited by a porous carbon electrode of 30×100 mm\textsuperscript{2} in size at a substrate temperature of 220 °C. It is demonstrated that \textmu c-Si:H films showing good uniformities of thickness and crystallinity are obtained in the area of 20×80 mm\textsuperscript{2} and that a \textmu c-Si:H film having a crystalline volume fraction of 72% can be deposited even if hydrogen is not added to the process gas mixture (H\textsubscript{2}/SiH\textsubscript{4} = 0). We conclude
that the origin of such unique deposition characteristics result from the long gas residence time in the plasma, which greatly enhances the chemical reactions both in gas the phase and on the film-growing surface. The realization of actual thin film devices, particularly using plastic materials as substrates, awaits further empirical and theoretical investigations.

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