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Effects of H_2 and Ar flow rates on the deposition of hydrogenated silicon thin films by an inductive coupled plasma-chemical vapor deposition system

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ABSTRACT

Amorphous hydrogenated silicon films were deposited on quartz substrates in an inductive coupled plasma-chemical vapor deposition system with four internal low inductance antennas units. Different Ar and hydrogen flow rates were tested for their influences on the structures of deposited films. For monitoring purposes, Langmuir probe and optical emission spectrometer were installed to detect the variation of electrical field in plasma during deposition. Data from Langmuir probe and optical emission spectrometer were analyzed subsequently. After deposition, the films were examined by X-ray diffraction and Raman spectrometer for their microstructures. Results indicate that under the supply of pure Ar flow, the deposition rate can be expedited to 3.5 nm/s and amorphous films were formed on quartz substrates. With the supply of mixed hydrogen and argon (Ar 15 sccm + H_2 50 sccm + SiH_4 50 sccm), the deposition rate can reach 4.5 nm/s. Although it is well known that a high supply of H_2 helps the formation of micro-crystalline silicon, these deposited hydrogenated Si films, confirmed by X-ray diffraction patterns and Raman spectroscopy, all maintained their amorphousness under various range of Ar and H_2 flow rates.

1. Introduction

For manufacturing solar panels using plasma enhanced chemical vapor deposition (PE-CVD) process, the higher plasma density and larger, uniform plasma zone is advantageous. The first development of plasma systems to have the high plasma density is electron cyclotron resonance (ECR) plasma system developed in 1980s. The ECR utilizes helical wave-excited plasma by coiled tubes to greatly enhance the plasma density, however, with fairly limited area. It was until 1990s found that the density of inductively coupled plasma (ICP) can be high at low pressures [1]. For example, in the review article by Amorim, the plasma density was reported to reach 10^{12} cm^{-3} in a specifically designed ICP system [2]. The main advantage of ICP is that sufficient radicals flux can be created at low pressures, which helps to deposit films effectively. For silicon based thin film solar panels, improved ICP systems have been utilized extensively after late 1990s. The system we used in the current study is designed to produce large-diameter radio frequency (RF) plasmas at 13.56 MHz by an internal, fully insulated, double half-loop antenna. Such design is efficient to reduce the antenna inductance and minimize the electrostatic coupling while simultaneously attain plasma densities as high as 5×10^{11} cm^{-3} [3,4].

For the deposition of amorphous hydrogenated silicon (a-Si:H) films, dilution of the precursor gas silane (SiH_4) by argon or hydrogen in chemical vapor deposition (CVD) substantially affects the deposition, structures and optical properties of hydrogenated amorphous silicon (a-Si:H) films. For instance, the crystallinity drops as the silane concentration increases ($SiH_4/(SiH_4 + H_2) = 0.71\% \rightarrow 1.04\%$) [5]; Considerably reduced deposition rate was observed as Ar dilution ratio increased ($Ar/(Ar + SiH_4) = 60 \rightarrow 97$) with a slightly nano-size crystal growth [6]; Both the deposition rate and crystallinity were increased by the increased Ar and decreased hydrogen flow rates ($Ar/(Ar + H_2) = 0 \rightarrow 0.65$, $Ar = 0 \rightarrow 13$ sccm, $H_2 = 20 \rightarrow 7$ sccm) [7]; The deposition rate was enhanced but crystallinity obviously diminished as SiH_4/H_2 (more H_2) increased from 3% to 7.5%. Meanwhile, when $SiH_4/H_2 = 5\%$ and Ar raised from 0 to 40 sccm the crystallinity enhanced but deposition rate increased at first and then lowered down [8]; The deposition rate went down as the Ar/SiH_4 ratio increased ($Ar/SiH_4 = 100 \rightarrow 630$, $Ar = 200$ sccm, SiH_4 varied) while the crystallinity enhanced and then decreased [9]; hydrogen dilution ($H_2/SiH_4 = 0 \rightarrow 50$) usually caused higher crystallinity [10,11], and higher deposition rate ($SiH_4/(H_2 + SiH_4) = 0.02 \rightarrow 0.2$, $SiH_4 = 10$ sccm) [12]. These studies, among many others reported recently, indicate that higher SiH_4 flow rate can expedite the deposition of hydrogenated silicon films and hence the higher deposition rate, the lower crystallinity of the films.

In regarding the effect of H_2 flow, many studies attributed them to cause the decrease of deposition rate by the phenomenon of hydrogen

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etching, which is (i) excessive atomic H in plasma leading to the break of weak Si–Si on substrate surface, and (ii) more silane radicals in plasma with lower sticking coefficient during deposition [7,9–11,13–15].

As for Ar, several studies show that [7–11,16,17] both crystallinity and deposition rate can be enhanced if Ar flow was below certain rates. When Ar flow increased beyond a threshold, deposition rate went down and so did the crystallinity. One reason to drive these changes is by the fact that Ar collides with silane and hydrogen in plasma to create many radicals and then deposit on the substrate. This sets out the simultaneously improvement of deposition rate and crystallinity.

On the molecular level, in pure SiH_4 or H_2-diluted SiH_4 plasma, molecular association or dissociation are dominated by electrons' impact. For Ar-diluted SiH_4 plasma, chemical radicals are dominant in molecular reactions. M. J. Kushner recapitulated the following reactions between argon excitation (Ar^*) and silane, of which the rate constants are dominant over other reaction among different species in plasma [7,17–19]:

$$Ar^* + SiH_4 \rightarrow SiH_3 + H + Ar \quad \left(k = 1.4 \times 10^{-10}\ cm^3/s\right) \tag{1}$$

$$Ar^* + SiH_4 \rightarrow SiH_2 + 2H + Ar \quad \left(k = 2.6 \times 10^{-10}\ cm^3/s\right) \tag{2}$$

$$Ar^* + SiH_3 \rightarrow SiH_2 + H + Ar \left(k = 1.0 \times 10^{-10}\ cm^3/s\right) \tag{3}$$

$$Ar^* + SiH_2 \rightarrow SiH + H + Ar \left(k = 1.0 \times 10^{-10}\ cm^3/s\right) \tag{4}$$

$$Ar^* + SiH \rightarrow Si + H + Ar \left(k = 1.0 \times 10^{-10}\ cm^3/s\right) \tag{5}$$

So it may by quite comfortable to conclude that argon excitation (Ar^*) is a major species in Ar-diluted SiH_4 plasma.

In this study, an ICP-CVD system with four internal low inductance antennas (LIA) units were used to deposit a-Si:H films. Details of a similar system were reported in Ref. [20]. In this system, all the U-shaped LIAs were specifically designed to decrease the inductance element. The electrostatic coupling of RF voltages along the antenna conductor was minimized so that the plasma potential could be decreased. The LIA antenna was covered with an insulator in order to suppress arc discharge during high-power RF driving. LIA units were installed in the vacuum chamber at optimal positions to increase plasma uniformity over the area of 30cmx30cm. RF power with a frequency of 13.56 MHz was fed to antennas through a conventional matching box. In addition, the process chamber is equipped with a turbo molecular pump that can evacuate the chamber down to a base pressure of 1×10^{-4} Pa.

Our focus in this study is on the deposition of a-Si:H film on a quartz substrate under different H_2 and Ar flow rates. To monitor the plasma conditions, Langmuir probe and optical emission spectrometer (OES) were set up to collect data during deposition. The structures of deposited films were examined by X-ray diffraction (XRD) and Raman spectrometer to ascertain their amorphousness.

2. Experiment

Major parts in this experimental work are plasma diagnostics during deposition and film structural characterizations after deposition. Details of experimental procedure shall be discussed in the following content.

2.1. Substrate preparation

The working gas during CVD is pure H_2 (99.995%) and SiH_4 (99.999%) purchased from local suppliers. Substrates are quartz glass with dimensions of $2^{cm} \times 2^{cm} \times 1^{mm}$. Solutions for substrate cleaning are potassium hydroxide (KOH, 1 g/100 ml), acetone (100%), alcohol (95%) and de-ionized (DI) water.

The glass substrate was thoroughly cleaned by KOH solution to remove all containments and organic oils. The substrate then was further cleaned by ultrasound in DI water for 5 min to remove delicate soils. Then the substrate was cleaned several times in acetone, DI water and alcohol in turns by ultrasound. After sonication, the substrate was blown to dry using nitrogen ready for CVD process.

2.2. Film deposition

The CVD chamber with glass substrate placed inside was first vacuumed to 4.0×10^{-3} Pa and the substrate temperature was kept at 200 °C. Then Ar was pumped in at 2.66 Pa and the RF power supply (13.56 MHz, 2500 W) was turned on for 5 min. This is mainly for cleaning the volatile contaminants on the substrate. After this, H_2 was pumped in at 2.66 Pa for another 5 min to clean up the oxide on substrate surface. The deposition of a-Si:H thin film started only after all these cleaning actions. In the chamber, the distance between the antennae and substrate was about 30 cm. All process parameters are tabulated in Table 1 for readers' reference. In this study, effects on films' properties by different Ar and H_2 flow rates are the main focus. Note that the working pressure was kept at 2.66 Pa during deposition by an automatic pressure control valve to leak out gas. In addition, different dilution and gas flow ratios were summarized in Table 2 for later discussion.

2.3. Characterization

2.3.1. Plasma characterization

Langmuir probe (Espion, Hiden Analytical, UK) was used to measure the plasma potential, electron and ion density inside the chamber during deposition. The probe was inserted into chamber between the antennae and substrate with its tip positioned around the center of plasma zone. Calibration of voltage and current was carried out before measurement started. After calibrations, the range of probe voltage was set up between -50 V and 80 V with resolution of 0.2 V and maximum current of 23.776 mA. The probe was set to scan 3 times, each for about 19.53 s.

For the detection of excited species in plasma, an optical emission spectrometer (OES, Emicon HR system, Plasus, German) was employed. The probe's camera was attached to the chamber window made of quartz to minimize the optical absorption, which could lead to erroneous readings on spectrum of excited species. The resolution of OES is set to 0.2 nm.

2.4. Material characterization

- Structure
  The X-ray diffraction (XRD, Philips PW1830) uses monochromatic high intensity Cu Kα radiation ($\lambda = 1.542$ Å) to determine the crystal structures of deposited films. The scanning angle was from 20°–2θ to 70°–2θ, with a step size of 0.04° and measuring speed of 0.028° per step. The working voltage is 40 kV and current is 30 mA.
- Surface profile
  Thicknesses of deposited a-Si:H films were evaluated by surface profiler (Surfcordor ET3000, Kosaka). Before measuring, part of the deposited film was removed by adhesive tape at first. The measurement was taken along five randomly selected lines on the sample surface across the edge of deposited film. Average of these five measured data was counted as the film thickness.
- Raman spectroscopy
  To examine the amorphousness of films, Raman spectrometer (System 1000, Renishaw, UK) were used to detect the Raman shift of the deposited a-Si:H films due to the formation of crystalline Si. In the system, the