Contribution of ionic precursors to deposition rate of a-Si:H films fabricated by plasma CVD

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Abstract. We have studied contribution of ionic precursors to deposition rate of a-Si:H films in the downstream region of a multi-hollow discharge plasma CVD reactor using a DC bias grid and QCMs. The deposition rate decreases from 1.1 to 0.93 by applying negative bias voltage to the bias grid. The ionic precursors contribute to 7% of the total deposition rate and the dominant ionic precursors are considered to be negatively charged clusters.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) films deposited by plasma CVD have been widely used for a top cell of thin film silicon tandem solar cells[1-7]. A-Si:H films show metastability against light exposure, the Stabler-Wronski effect, which reduces significantly its initial photovoltaic conversion efficiency[8]. In SiH₄ discharge plasmas employed for a-Si:H deposition, there are three size groups of species: SiHₓ (x ≤ 3) radicals, higher order silane (HOS) molecules SiₓmHₙ (m ≤ 4), and a-Si:H particles in a size range below 10 nm (clusters)[9-13]. SiH₃ radicals are main deposition precursors, which dominate the film deposition rate. HOS molecules are generated due to polymerization reactions between SiH₂ and SiH₄. HOS radicals are generated from HOS molecules due to electron impact dissociation and they can react on surfaces as well as in gas phase. Clusters are nucleated from HOS molecules of SiₓmHₙ (n~4) and grow due to coagulation between clusters and/or deposition of SiHₓ radicals to the surface of clusters. HOS radicals and clusters are minor deposition precursors and are pointed out to lead to the light-induced degradation[14, 15].

We have previously reported that suppression of cluster incorporation into films is the key to realizing highly stable a-Si:H films[16, 17]. Based on the results, we have successfully deposited highly stable a-Si:H films of 4.7x10¹⁵ cm⁻³ in stabilized defect density by using a multi-hollow discharge plasma CVD method, by which the volume fraction of clusters in films can be reduced significantly[18]. Although ESR measurements of our 0.6 μm thick a-Si:H films show high stability, Schottky cells using such “stable a-Si:H films” still show modest light-induced degradation. We also have developed a real-time in-situ monitor of the cluster volume fraction in films by employing three quartz crystal microbalances (QCMs)[19, 20]. The real time measurements reveal that large amount of clusters deposit in the initial 60 s after turning on the discharges[20]. To reduce cluster incorporation further, we need information on minor deposition precursors in detail. Here, we report contribution of ionic precursors to the total deposition rate, obtained by using QCMs equipped with a bias grid mesh.
2. Experimental

Experiments were carried out using a multi-hollow discharge plasma CVD reactor with a DC bias grid and QCMs as shown in Fig. 1. The detail of multi-hollow discharge plasma CVD reactor is described elsewhere[17, 18]. DC bias grid of 10 cm in diameter was set at 10 mm below the lower electrode and 10 mm above the QCMs. The aperture of the DC bias grid was 1.8 × 1.8 mm², the wire was 0.8 mm, and the aperture ratio was 47 %. SiH₄ was supplied to the reactor at 30 sccm. The working pressure was 0.5 Torr. Discharge plasmas were sustained by applying 60 MHz peak to peak voltage V_pp of 34 V between the powered and grounded electrodes.

To obtain information on electron impact generation rate of radicals from SiH₄, optical emission intensities of Si* 288 nm and SiH* 414 nm were measured.

Deposition rate DR was obtained with QCMs which were set at 20 mm under the lower grounded electrode. Resonance frequency of quartz crystal decreases with increasing mass of films deposited on the crystal. Relation between mass change Δm and frequency change Δf is given by Sauerbrey equation[21],

\[
\Delta f = \frac{2 f_0^2}{A_1 (\mu_q \rho_q)^{1/2}} \Delta m 
\]

(1)

where \( f_0 \) is the initial resonance frequency of crystal, \( \mu_q \) and \( \rho_q \) is the density of crystal and the shear modulus of the quartz, \( A_1 \) is the area of crystal. From the Δm, DR was deduced by

\[
\frac{\Delta m}{\Delta t} = \rho A_2 \cdot DR 
\]

(2)

where \( \rho \) is the weight density, \( \Delta t \) is the discharge duration, and \( A_2 \) is the area of deposition. In this study, we employed \( \rho = 2.3 \) g/cm³ which is the mass density of a-Si:H.

DC bias voltage \( V_{grid} \) was applied to the grid set above QCMs to obtain information on contribution of ionic precursors to deposited films. \( V_{grid} \) was set in a range from -100 V to +100 V.

3. Results and Discussion

First, we have examined influence of \( V_{grid} \) on the discharges. Figure 2 shows \( V_{grid} \) dependence on space potential \( V_{space} \) which is deduced by
\[ V_{space} = (\omega / 2\pi)(kT_e / e) \int_0^{2\pi / \omega} \ln \left[ \frac{1 + A_e / A_a \times \exp(eV(t) / kT_e)}{1 + (A_e / A_a)} \right] dt + V_0, \tag{3} \]

where \( \omega \) is excitation frequency, \( k \) is Boltzmann coefficient, \( T_e \) is electron temperature, \( A_e \) is cathode area, \( A_a \) is anode area, \( V_0 \) is plasma potential relation to floating objects, and \( V(t) \) is the VHF voltage on the powered electrode\[22]. \( V_{space} \) tends to increase with \( V_{grid} \), in particular, it increases sharply above \( V_{grid} = 30\text{V} \), and \( V_{space} = 34\text{V} \) for \( V_{grid} = 100\text{V} \). These results suggest that the bias grid is effective to control the flux of ionic species towards QCMs.

Second, we have measured Si* 288 nm emission intensity \( I_{Si^*} \) and SiH* 414 nm emission intensity \( I_{SiH^*} \) to obtain information on influence of \( V_{grid} \) on radical generation rates. Figure 3 shows the \( V_{grid} \) dependence of \( I_{Si^*} \) and \( I_{SiH^*} \). These intensities are normalized by those for \( V_{grid} = 0\text{V} \). \( I_{Si^*} \) and \( I_{SiH^*} \) are almost constant between \( V_{grid} = -100\text{V} \) and \( V_{grid} = +30\text{V} \) then sharply increase for \( V_{grid} > +30\text{V} \). Figure 4 shows \( V_{grid} \) dependence of the ratio \( I_{Si^*}/I_{SiH^*} \) which indicates the slope of high energy tail of electron energy distribution in the plasma\[23-25\]. The results suggest the generation rate ratio of SiH2 and SiH3 is irrelevant to \( V_{grid} \) because \( I_{Si^*}/I_{SiH^*} \) is nearly constant for the whole range of \( V_{grid} = -100 - +100\text{V} \). The sharp increases in \( I_{Si^*} \) and \( I_{SiH^*} \) for \( V_{grid} > +30\text{V} \) indicate that the radical generation rates increase sharply for \( V_{grid} > +30\text{V} \), and hence it is difficult to discuss contribution of ionic precursors to deposition. Therefore, hereafter, we discuss contribution of ionic precursors for \( V_{grid} < 30\text{V} \).

Figure 5 shows dependence of \( DR \) on \( V_{grid} \). \( DR \) is normalized by that for \( V_{grid} = 0\text{V} \). \( DR \) increases slightly from 0.93 for \( V_{grid} = -100\text{V} \) to 1.09 for \( V_{grid} = 30\text{V} \). From the results in figures 3 and 4, generation rates of radicals and clusters are almost constant for \( V_{grid} < 30\text{V} \), and hence composition of precursors in the plasmas is almost the same for \( V_{grid} < 30\text{V} \). Therefore, the increase of \( DR \) in figure 5 shows that the flux of ionic precursors increases with increasing \( V_{grid} \). Effect of sputtering by positive ion was evaluated using Ar discharge, because mass of Ar+ is closed to that of SiH3+ and the sputtering rate depends on mass of positive ion\[26\]. The results show that sputtering contribute little to \( V_{grid} \) dependence of \( DR \) in figure 5. These results suggest that major ionic deposition precursors are negatively charged such as SiH3−, SiH4−, and negatively charged clusters and the contribution of them to the total deposition rate for \( V_{grid} < -40 - +20\text{V} \) is 7%. Since the electron attachment rate of clusters is much higher than that of radicals\[27-32\], the negatively charged precursors are considered to be mainly clusters. These results suggest that contribution of negatively charged clusters to films can be reduced by using electrostatic force exerted on the clusters\[33-37\].
4. Conclusions
We have studied contribution of ionic deposition precursors in deposition region of multi-hollow discharge plasma CVD using the bias grid and QCMs. The contribution of ionic precursors is 7% of the total deposition rate. The dominant ionic precursors are considered to be negatively charged clusters. These results suggest that contribution of negatively charged clusters to films can be reduced by using electrostatic force exerted on the clusters.

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