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Species responsible for Si–H_2 bond formation in a-Si:H films deposited using silane high frequency discharges

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Abstract

Species responsible for Si–H_2 bond formation in a-Si:H films have been studied by using a cluster-suppressed plasma CVD reactor of a diode configuration. The concentration of Si–H_2 bonds in a-Si:H films linearly decreases with decreasing the volume fraction V_f of clusters incorporated into the films, while the density of higher-order silane such as Si_2H_5 and Si_3H_7 correlates little with the bond concentration. The experimental results obtained using the diode configuration motivate us to employ a reactor of triode configuration in order to reduce the V_f value. The a-Si:H Schottky solar cell prepared with this configuration has the high initial fill factor FF = 0.60 and high stabilized value after light soaking FF = 0.56.

Keywords: a-Si:H; SiH_2; Cluster; Plasma CVD

1. Introduction

Suppression of light-induced degradation of hydrogenated amorphous silicon (a-Si:H) films has been an important issue for a-Si:H solar cells [1,2]. a-Si:H films with a low Si–H_2 bond density C_{SiH_2} have been found to show less light-induced degradation (or high stability) [3], while the mechanism leading to their correlation has not been revealed yet. This suggests that the C_{SiH_2} should be reduced to obtain higher stability of the films, and also species responsible for the Si–H_2 bond formation should be identified. Fig. 1 is the reaction model in silane (SiH_4) discharges, which has been depicted based on our experimental results for the particle growth kinetics in a particle size range from sub-nanometer to micrometer in SiH_4 high-frequency discharges employed for depositing a-Si:H films [4–6]. There coexist higher-order silane (HOS) Si_mH_n ($m \lesssim 4$, $n \leq 2m+2$) in a size range below about 0.5 nm and particles in a size range about 0.5–10 nm (clusters) in SiH_4 discharges [5]. The HOSs and clusters have possible to be incorporated into the films during the deposition. Concerning the Si–H_2 bond formation, Matsuda and co-workers have proposed the contribution of HOSs [3,7]. On the other hand, we have recently proposed that the clusters are mainly responsible for its formation. In order to obtain the detailed information on clusters, we have already developed photon-counting laser-light scattering (PCLLS) and down-stream-cluster-collection (DCC) method realizing their highly sensitive detection [8]. Information of the HOSs can be obtained with a quadrupole mass spectrometer (QMS) [9]. In order to identify which of HOSs and clusters mainly contribute to the SiH_2 formation, we have to carry out such measurements using the same reactor as and under the same experimental conditions as those for the film deposition experiments.

In this article, we report such recent experimental results and, based on the results, we discuss the important species responsible for the Si–H_2 bond formation in a-Si:H films. Moreover, we report some preliminary results of a-Si:H film deposition obtained using the reactor of the triode configuration.

2. Experimental

Experiments were carried out using a capacitively-coupled high-frequency discharge reactor of a diode or

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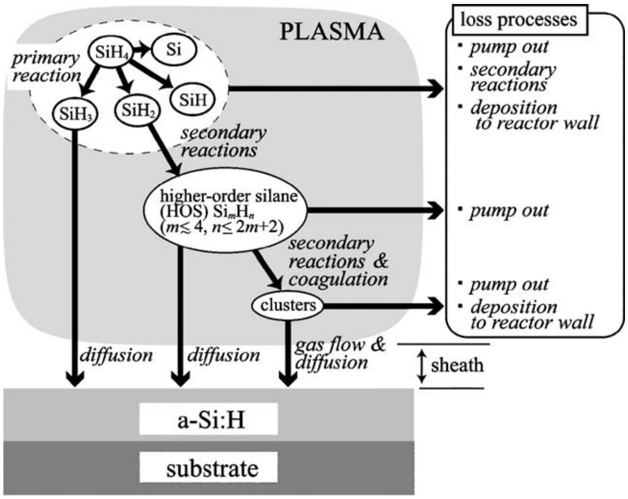

Fig. 1. Model of HOS and cluster formed and their deposition in silane plasma.

triode configuration as shown in Fig. 2(a)–(c). The diode configuration was employed for detecting both clusters by the DCC method and HOSs such as Si_2H_6 and Si_3H_8 by QMS and also for depositing a-Si:H films. The triode configuration was employed only for the film deposition [8]. The reactor is of the cluster-suppressed plasma CVD type; the growth of clusters is suppressed by utilizing gas viscous and thermophoretic forces exerted on clusters together with reducing the stagnation regions of gas flow. For the triode configuration, the flux of clusters to the substrate was reduced by cutting off them with the grounded electrode mesh as well as by utilizing that the clusters diffuse slowly as compared to SiH_3 radicals being predominant deposition species. The diameter and height of the reactor made of stainless steel are 315 and 250 mm, respectively. Powered and grounded electrodes for the diode and the triode were placed 18 mm and 15 mm apart, respectively, as shown in Fig. 2(b) and (c). All the electrodes were made of stainless steel and their diameter was 120 mm. Gas of SiH_4 was supplied towards the center axis of the discharge column through 44 holes of 1 mm in diameter bored in a tube ring, as shown in Fig. 2(a), of 240 mm in diameter, which was placed at 10 mm above the grounded electrode for the diode. The flow rate and pressure were 30 sccm and 9.3 Pa, respectively. The excitation frequency and supplied power density were 60 MHz and 0.015–0.15 W/cm^3, respectively. The reactor was pumped out through both the powered electrode and four ports on the side wall of the reactor by two molecular drag pumps (pumps A and B in Fig. 2(a)). The gas flow through the powered electrode driven by the pump A contributes to reducing cluster growth in the radical generation region around the plasma/sheath boundary. When the substrate is heated up to 250 °C, the gas temperature gradient drives clusters above a few nm in size toward the powered electrode of room temperature [4]. The pump B was employed to reduce accumulation of clusters in the reactor due to the stagnation of gas flow.

To measure the density of SiH_4, [SiH_4], as well as those of Si_2H_6, [Si_2H_6], and Si_3H_8, [Si_3H_8], in the discharges, the gas passed through the powered electrodes was sampled through an orifice of 2 μm in diameter to analyze with a QMS (ANELVA M-QA100TS) as shown in Fig. 2(a). Size and density of clusters were measured by the ex situ DCC and in situ PCLLS methods [6,8]. For the DCC method, clusters were trapped on three stainless steel meshes placed parallel in series in the pumping port connected to the powered electrode as shown in Fig. 2(a). The efficiency of cluster trapping by the three meshes was estimated to be above 95%. Information on size distribution, density, shape and structure of the trapped clusters were obtained with a high-resolution transmission electron microscope (TEM; JEOL 2010). For the PCLLS method, size of clusters was deduced from their coagulation rate after turning off the discharge and, using their size value, their density was done from the absolute light intensity [6].

For deposition experiments, a-Si:H films of 1 μm in thickness were prepared on two kinds of Si wafers at a substrate temperature of 250 °C. The one is Si (111) wafers with a high resistivity (1000–5000 Ω cm) for the measurements of C_{SiH_2}, and the other is n^+Si (100) wafers for the measurements of fill factors (FF) of a n^+Si/a-Si:H/Ni Schottky solar cells. For the C_{SiH_2} measurements, an absorption intensity profile in a range of 1750–2350 cm^{-1} of spectrum measured with a Fourier-transform infrared (FT-IR) spectroscope (JASCO FT/IR-620) was

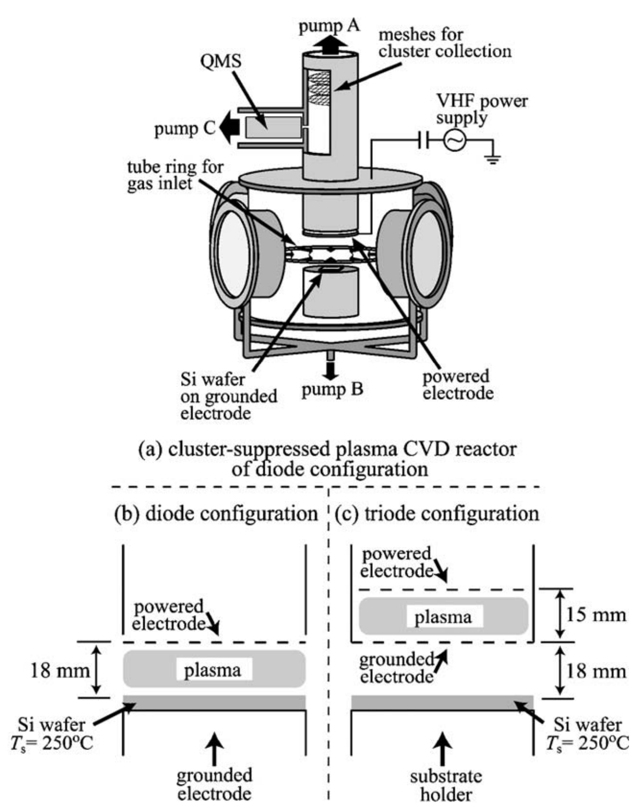

Fig. 2. Cluster suppressed plasma CVD reactor: (a) Bird's-eye view of diode; (b) cross-sectional view of diode; (c) cross-sectional view of triode.