Plasma Chemical Vapor Deposition and Characterization of Hydrogenated Amorphous Silicon from Silane and Dichlorosilane Mixtures

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Abstract

We introduce plasma chemical vapor deposition of hydrogenated and chlorinated amorphous silicon (a-Si:H(Cl)) films from silane (SiH_4) and dichlorosilane (SiH_2Cl_2) mixtures [1], and employ optical emission spectroscopy (OES) [2-5] to discuss how a high deposition rate (r_d) is achieved with the technique. The results from characterization of the a-Si:H films deposited are also presented.

Introduction

Low temperature deposition of large area hydrogenated amorphous silicon (a-Si:H) [6] for flat panel displays [7] and for solar cells [8] is one of the most successful applications of plasma chemistry. However, two major problems still remain to be solved. They are (1) limitation in production throughput, and (2) light-induced metastability of optoelectronic properties [9]. We have recently reported deposition of a-Si:H(Cl) from SiH_4 and SiH_2Cl_2 gas mixtures[1]. The material had comparable optoelectronic properties as a-Si:H, was deposited at higher r_d, which would lead to a higher production throughput, and showed improved stability against illumination. In this paper, we present results from OES experiments on radio-frequency (rf) glow-discharge plasmas of SiH_4 and SiH_2Cl_2 gas mixtures for deposition of a-Si:H(Cl) to discuss the mechanism leading to the higher r_d. Optoelectronic properties of a-Si:H(Cl) are also discussed.

Experimental Conditions

A-Si:H(Cl) films were deposited by a 13.56 MHz rf glow discharge plasma [10] of SiH_4 and SiH_2Cl_2. The rf power density was 30 mW cm^{-2}. The total flow rate was maintained constant at 5 sccm, while the flow ratio (X_{Cl}) of SiH_2Cl_2 to

the total flow was varied between 0 and 60 %. The gas pressure was kept at 4 Pa. Corning 7059 glass and polished high-resistivity crystalline silicon (c-Si) substrates were placed on the anode of a diode-type parallel plate plasma chamber and maintained at 250 °C during deposition. The spacing between the substrates and the powered electrode was 4 cm.

For OES measurements [5], plasma emission was collected through a quartz window with quartz optics and lead through a quartz optical fiber into a 25-cm grating polychromator attached with an intensified diode-array detector. OES signal was obtained by subtracting the detector background signal from the detected plasma emission spectrum in a personal computer. X_{Cl} was kept at 10 %, and the intensity of the OES signal ([SiH*]) from electronically excited SiH at 414 nm was measured as a function of the total flow rate in the range of 2 - 10 sccm, and of the discharge power density of 13 - 130 mW cm^{-2}. To obtain information about the surface reaction, a-Si:H(Cl) was deposited at X_{Cl} = 20 % on a c-Si wafer with a trench structure of 1 μm width and 3 μm depth, and the step coverage observed by a scanning electron microscope (SEM) [11,12].

Optical transmission/reflection and Fourier transform infrared transmission spectra were measured with the samples deposited on the glass and c-Si substrates, respectively. Coplanar aluminum electrodes were evaporated onto a 3 x 20 mm^2 piece of sample on the glass substrate. The gap width and length of the electrode spacing was 0.2 and 3 mm, respectively. The sample with electrodes was used for room temperature dark and photo (AM1 100 mW cm^{-2}) conductivity and constant photocurrent measurements (CPM) [13].

Light-soaking was done for two hours at room temperature with a tunable pulsed dye laser [14,15]. Pulse width, repetition rate were 10 ns and 10 pulse per second, respectively. Sample temperature during light-soaking is estimated to be 30 °C [15]. Wavelength and pulse energy were 640 nm and 5 mJ / pulse, respectively.

Results and Discussion

Figure 1 shows the dependencies of r_d and CPM defect density (N^{CPM}) in as-grown samples on X_{Cl}. There is a three-fold increase in r_d with X_{Cl} from 0 to 20 %, while r_d stays almost constant in the range X_{Cl} > 20 %. The range of 0 % < X_{Cl} < 10 % is particularly important because N^{CPM} does not increase while r_d more than doubles.

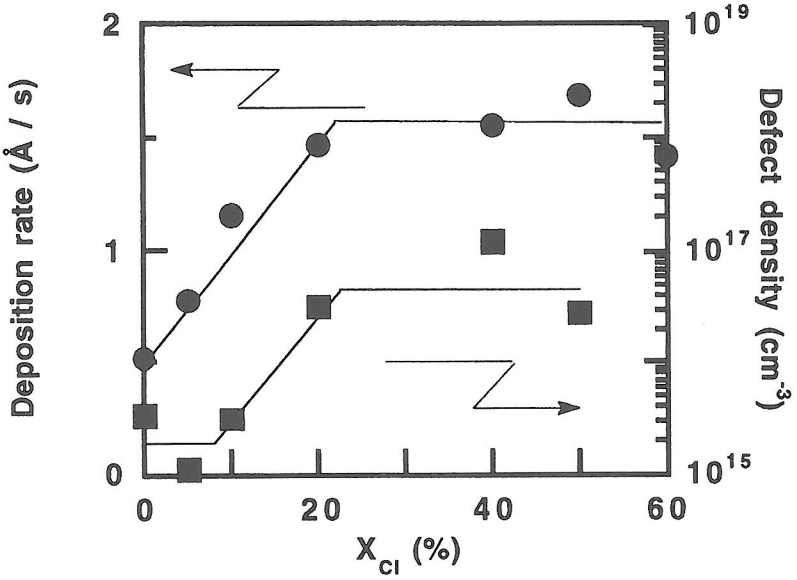

Fig. 1 Dependencies of deposition rate (●) and CPM defect density (■) on the ratio (X_{Cl}) of SiH_2Cl_2 flow rate to the total gas flow rate.

In order to clarify the mechanism which leads to the higher r_d, optical emission spectroscopy (OES) was employed as a gas-phase diagnostic technique. Figure 2 shows the dependencies of r_d (solid symbols,●,▲,■) and r_d / [SiH*] (open symbols,○,△,□) on rf power density. The circles (●,○), triangles (▲,△), and squares (■,□) represent the data for the total flow rate of 2, 5, and 10 sccm, respectively. As is seen in Fig. 2, the ratio r_d / [SiH*] stays almost constant independent of the gas flow rate and rf power density. This suggests that the increase of r_d upon introduction of SiH_2Cl_2 correlates with the increase of the generation rate of film precursors SiH_x via dissociation of source gas molecule [5]. In other words, the rate of film growth is determined by the gas-phase mechanism rather than by the surface processes.

Another feature which we learn from Fig. 2 is that r_d increases with rf power density as well as with X_{Cl}, but *decreases* with the flow rate. This is remarkable since, for

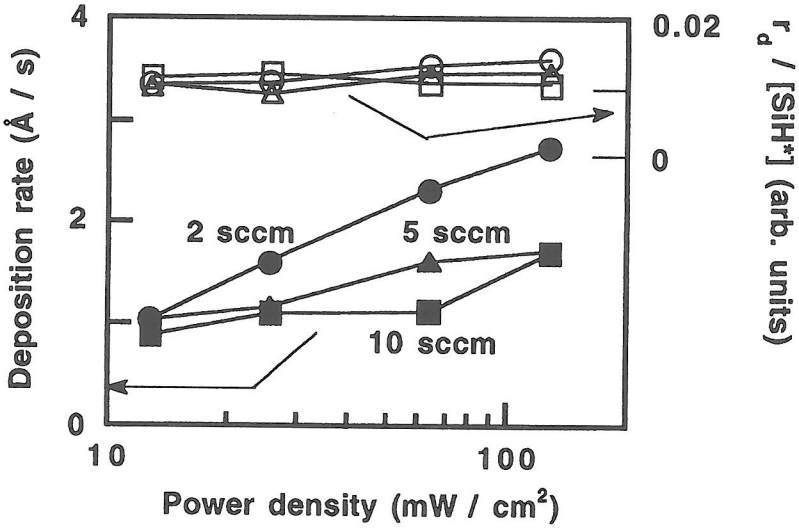

Fig. 2 Dependencies of r_d (solid symbols, ●, ▲, ■) and r_d / [SiH*] (open symbols, ○, △, □) on rf power density. The circles (●, ○), triangles (▲, △), and squares (■, □) represent the data for the total flow rate of 2, 5, and 10 sccm, respectively.

the case of a-Si:H deposition from SiH_4 plasmas, r_d increases with gas flow rate in high power and low flow rate regime and stays independent of gas flow rate otherwise.

The constant value of r_d / [SiH*] in Fig. 2 is comparable to that for a-Si:H deposition from SiH_4 plasma; enhancement of r_d comes together with the increase of [SiH*]. This increase in [SiH*] upon introduction of SiH_2Cl_2 into SiH_4 plasma could be interpreted as a consequence of an increase in the electron temperature caused by the loss of low energy electrons via their attachment to electro-negative chlorinated species to form negative ions [16].

The dark- and photo-conductivities, optical and infrared absorption spectra, and subgap optical absorption of the a-Si:H(Cl) films were measured. Tauc optical bandgap and bonded hydrogen content stayed almost constant while refractive index decreased with X_{Cl}. The stretching-mode

absorption peak in the infrared spectra appearing at around 2000 - 2100 cm^{-1} showed an increase in SiH_2 mode with X_{Cl}. N^{CPM} decreased with X_{Cl} up to 5 %, but increased by an order of magnitude when increased further as shown in Fig. 1. Dark- and photo-conductivities were decreased by two orders of magnitude when X_{Cl} was increased from 0 to 20 %.

As is represented by the comparable N^{CPM} for a-Si:H(Cl) of up to X_{Cl} = 10 % to that in optimized a-Si:H, addition of a small amount of SiH_2Cl_2 into SiH_4 plasma does not deteriorate film optoelectronic properties [1]. Result from a trench coverage experiment shown in Fig. 3 provides evidence for CVD-like growth of a-Si:H(Cl) which results in relaxed structure even at X_{Cl} = 20 %. This result is consistent with the excellent optoelectronic properties of a-Si:H(Cl). Deterioration of optoelectronic properties at higher X_{Cl} might be due to inclusion of chlorine into the film, which was proved by measurements of a-Si:H(Cl) on c-Si substrate with secondary ion mass spectrometry.

Upon light-soaking, photoconductivity decreased by more than three orders of magnitude at X_{Cl} = 0 %, but only less than one order of magnitude at X_{Cl} = 20 %, suggesting a higher stability of the materials with higher X_{Cl}. That looked consistent with X_{Cl} dependence of change in N^{CPM} upon light-soaking [1]. However, further experiments with thickness and wavelength dependent light-soaking as well as with electron spin resonance and photothermal deflection spectroscopy measurements revealed that the thickness of 1 μm, which is usually enough for bulk transport properties in a-Si:H to show up, is not for a-Si:H(Cl). Details will be published separately [17].

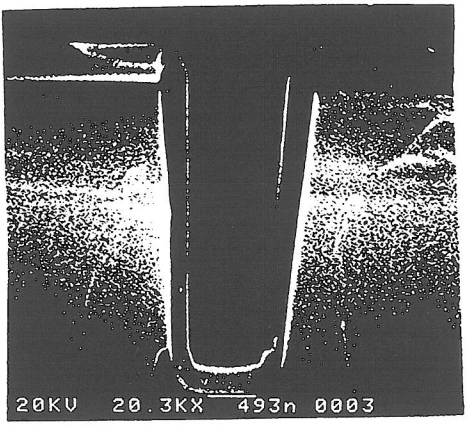

Fig. 3 Scanning electron microscope picture showing step-coverage pattern for X_{Cl} = 20 %, substrate temperature 250 °C, total gas flow rate 5 sccm, gas pressure 4 Pa, and rf power density 30 mW cm^{-2}.

Summary

In summary, deposition mechanism and optoelectronic properties of a-Si:H(Cl) from rf plasma of SiH_4 and SiH_2Cl_2 have been investigated. It has been shown that (1) addition of SiH_2Cl_2 into SiH_4 plasma increases electron temperature in the plasma so that r_d becomes higher, (2) but does not modify reactions at the film growth surface significantly. (3) Optoelectronic properties of films of $0 < X_{Cl} < 10$ % are comparable to those in optimized a-Si:H, while they are poorer for $X_{Cl} > 10$ %.

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