Effects of Plasma Parameters on Properties of a-Si:H Related Films

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1. Introduction

Hydrogenated amorphous silicon (a-Si:H) and a-Si:H based alloys have been attracting increased attention due to its application in low-cost, large area devices. Examples of these devices include large area solar cells for power supplies and thin film transistors for flat panel displays. Since 1980, Fuji Electric has been continuing the development of the large area a-Si:H based solar cells under the Ministry of International Trade and Industry's "Sunshine Project" (currently called the "New Sunshine Program").

Plasma chemical vapor deposition (CVD) is the most commonly used method to deposit a-Si:H related films for solar cell application. An improvement in the film properties of a-Si:H is necessary to increase the efficiency of a-Si:H based solar cells. It is also important to understand the deposition mechanisms of a-Si:H films during plasma CVD for the above purpose. Because it is difficult to duplicate the experimental conditions for the measurement of the plasma parameters and for the deposition of the a-Si:H films, only a few studies have been performed that compare the plasma parameters and the deposited a-Si:H film properties.

In this report, hydrogenated amorphous silicon germanium (a-SiGe:H) is analyzed using the same plasma CVD apparatus to compare the plasma parameters and the deposited film properties. The effects of ion bombardment on the film properties of a-Si:H are also examined with the "Ion Energy Controlled Plasma CVD" (IEC Plasma CVD), which was developed to control incident ion energy on the substrate.

2. Plasma Parameters and a-SiGe:H Films

The development of high-quality, narrow-bandgap material is the key to improving the conversion efficiency of a-Si:H based solar cells. In materials having a narrow bandgap, a-SiGe:H is the most promising candidate for application. The optical bandgap (E_g) decreaases as the ratio of Ge content increases. However, the characteristics of a-SiGe:H film, such as photo-sensitivity (σ_{ph}/σ_d) and defect density (N_s) deterio-rates exponentially, as the ratio of Ge content increases. In this section, we will describe the experimental study of the plasma parameters and the film properties of a-SiGe:H.

2.1 Experiments

Figure 1 shows the schematic diagram of the plasma CVD apparatus. The reactor has a parallel-plane electrode system. The samples were deposited by capacitively coupled plasma CVD at a frequency of 13.56 MHz. The material gases were a mixture of silane (SiH_4), germane (GeH_4) and hydrogen (H_2). The E_g of a-SiGe:H is kept at 1.6eV by adjusting the gas ratio $GR = GeH_4/(GeH_4 + SiH_4)$.

Table 1 shows the deposition conditions.

Electron temperature (T_e) and electron density (N_e) of the plasma were measured by the floating double probe method.[1] Two probes were set at the same height 10mm above the grounded electrode. Deposition

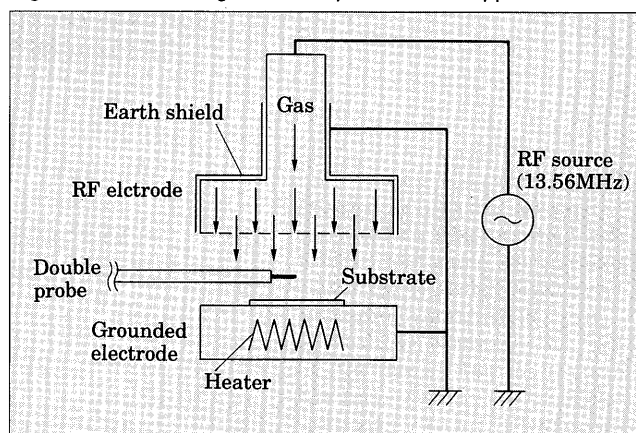Fig.1 Schematic diagram of RF plasma CVD apparatus

Table 1 The deposition conditions of a-SiGe:H

Pressure	40 Pa
Frequency	13.56 MHz
Power	127 mW/cm²
$SiH_4 + GeH_4$ flow rate	40 sccm
H flow rate	200 sccm
$GeH_4/(SiH_4 + GeH_4)$	3 to 7%

of film on the probes caused an error in the current-voltage characteristics of the probe. This error was corrected through the measurement of the characteristics in the H_2 plasma before and after $GeH_4+SiH_4+H_2$ plasma.

Photoconductivity (σ_{ph}) of a-SiGe:H film was measured under simulated sunlight (AM1.5, 100mW/cm^2). Photo-sensitivity σ_{ph}/σ_d, the ratio of σ_{ph} to dark conductivity (σ_d) was also measured.

2.2 Results and discussion

Figure 2 shows σ_{ph} and σ_{ph}/σ_d as functions of substrate temperature T_s. As T_s increases, σ_{ph} increases exponentially by three orders of magnitude and saturates at above 150°C. As T_s increases, σ_{ph}/σ_d increases by two orders of magnitude and has a maximum value of 2×10^5 at 190°C. In solar cell applications, T_s is an important parameter for the improvement in a-SiGe:H film properties. Figure 3 shows T_e and N_e as functions of T_s. As seen in Fig. 3, T_e and N_e are constant within a

measurement error.

The deposition mechanism of a-SiGe:H films can be divided into three sequential subprocesses: (1) electron impact collisions, (2) chemical reactions of the plasma, and (3) reactions on the film surface. The above result shows that T_s affects a-SiGe:H film properties but does not affect the plasma. It suggests that T_s mainly controls subprocess (3) rather than (1) or (2).

Figure 4 shows σ_{ph} and σ_{ph}/σ_d as functions of electrode gap (d) when T_s is kept at 170°C and E_g at 1.6eV. At $d=20$mm, σ_{ph} is about one-third of that at $d=30$ to 40mm. As d increases, the value of σ_{ph}/σ_d doubles. Figure 5 shows T_e and N_e as functions of d. As d increases. N_e varies slightly. At $d=20$mm, T_e is 5.9 eV. At $d=30$ to 40mm, T_e lies between 2.5 and 3.4 eV.

From these results, it was shown that when T_s was kept constant, σ_{ph} and σ_{ph}/σ_d increased as T_e decreased. There are two possible explanations for this: (1) the gas phase reactions changed as T_e decreased, and film forming precursors changed; or (2) the sheath potential

Fig.2 Photoconductivity (σ_{ph}) and photo-sensitivity (σ_{ph}/σ_d) of a-SiGe:H as functions of substrate temperature (T_s)

Fig.4 Photoconductivity (σ_{ph}) and photo-sensitivity (σ_{ph}/σ_d) of a-SiGe:H as functions of electrode gap (d)

Fig.3 Electron temperature (T_e) and electron density (N_e) as functions of substrate temperature (T_s)
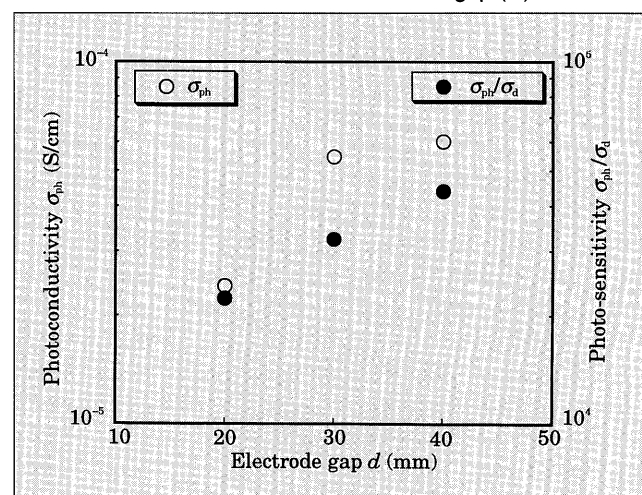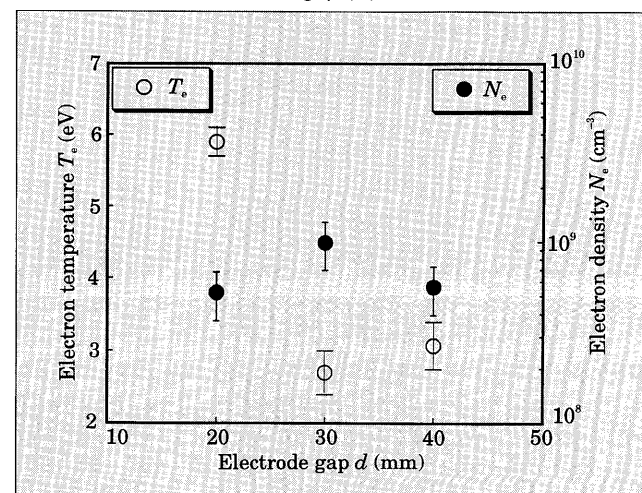

Fig.5 Electron temperature (T_e) and electron density (N_e) as functions of electrode gap (d)

near the substrate changed as T_e decreased, and incident ion energy on the film decreased.

Ion energy (V_s) is estimated, assuming that the substrate is at floating potential and collisions of ions in the sheath are negligible[2]. The estimated V_s is 23 eV at T_e=3eV and 45eV at T_e=6eV. With an increase in T_e, V_s increase to the point that ion bombardment affects the film properties, even though ion density is small. To demonstrate the effects of ion bombardment, it is necessary to keep the neutral precursors constant, that is, to control the sheath potential independent of T_e and N_e of the bulk plasma. Methods of controlling ion energy and experimental results affecting a-Si:H are described in the next section.

3. Ion Energy and a-Si:H Films

The effects of ion bombardment during plasma CVD on the film properties of a-Si:H are still controversial. Because it is difficult to control ion energy while keeping other plasma conditions constant, only a few quantitative studies have been performed. We developed the "Ion Energy Controlled Plasma CVD" (IEC Plasma CVD) to control ion energy independent of plasma parameters such as T_e and N_e. In this section, we will describe IEC Plasma CVD and the effects of ion energy on a-Si:H film properties.

3.1 IEC Plasma CVD

Figure 6 shows the schematic diagram of the IEC Plasma CVD apparatus. The reactor consists of a conventional diode system with two planar electrodes inserted into the plasma, parallel to both the RF electrode and the grounded electrode. The two electrodes can function as a floating double probe for plasma diagnostics, and one of them can also be used as a substrate holder for film deposition with an internal heater. In this configuration, incident ion energy (V_s) is controlled by a DC bias voltage (V_d) applied between the two probes. The current that flows into the probes does not exceed the ion saturation current and is much smaller than the discharge current. Thus, the effect of probe insertion on the plasma is negligibly small.

If the mean free path of ions is longer than the sheath thickness, V_s is represented as [3]

$$V_s = V_e \ln\left\{ \frac{1}{4K} \sqrt{\frac{8m_i}{\pi m_e}} \frac{1+ae^{-\frac{V_d}{V_e}}}{1+a} \right\}$$

where V_e is the electron temperature in unit eV, K is a constant of approximately 0.61, m_i, is the mass of an ion m_e is the mass of an electron, and a is the area ratio between the two probes and whose value is unity in this experiment. If V_e is constant, V_s is dependent only on V_d. The value of V_e is determined by measuring the probe current versus the V_d characteristics during plasma, using the IEC Plasma CVD apparatus as a

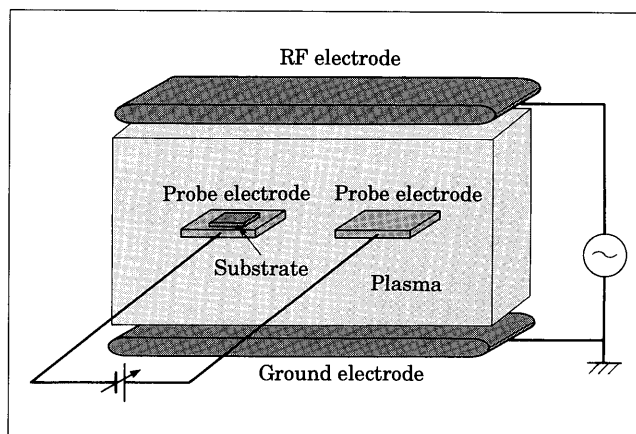Fig.6 Schematic diagram of the IEC plasma CVD apparatus

Table 2 The deposition conditions of IEC plasma CVD

Pressure	6.7 Pa
Frequency	13.56 MHz
Power	10 mW/cm^2
SiH$_4$ flow rate	20 sccm
H$_2$ flow rate	20 sccm

floating double probe. Thus, V_s is controlled by V_d.

3.2 Experiments

The probes were made from stainless steel and were 36mm by 36mm by 4mm in size. The conductive substrate was biased through the metal substrate holder and heated by a small insulated heater. The two probes had identical structures. RF voltage of 13.56 MHz was applied between the RF electrode and the grounded electrode, both having a diameter of 160mm. The distance between the RF and the grounded electrode was 80mm, and the distance between the probes and the grounded electrode was 45mm.

Table 2 shows the deposition conditions. Defect density N_s was measured by electron spin resonance (ESR) using a powder-like a-Si:H sample. Films of about 1 μm thick were deposited on Al foil. The Al foil was then melted by HCl, and the powder-like sample was obtained. Bonded hydrogen density was measured by reflection type Fourier-transformed infrared transmittance spectroscopy (FTIR), using the films deposited on Ag coated Corning 7059 glasses.

3.3 Results and discussion

Figure 7 shows N_s as a function of V_s. For T_s=55°C, N_s increases by a factor of 2, from 2.3×10^{18}cm^{-3} to 4.7×10^{18}cm^{-3} as V_s increases from 20eV to 170eV. For T_s=150°C, N_s increases by a factor of 4, from 4.5×10^{16} cm^{-3} to 1.8×10^{17} cm^{-3}.

The above result shows that a-Si:H film properties deteriorate as ion energy increases. The ion energy applied in this experiment is 2 to 3 orders of magnitude larger than Si-Si bond strength (2.4eV) or Si-H bond strength (3.4eV).[4] This suggests that impinging ions

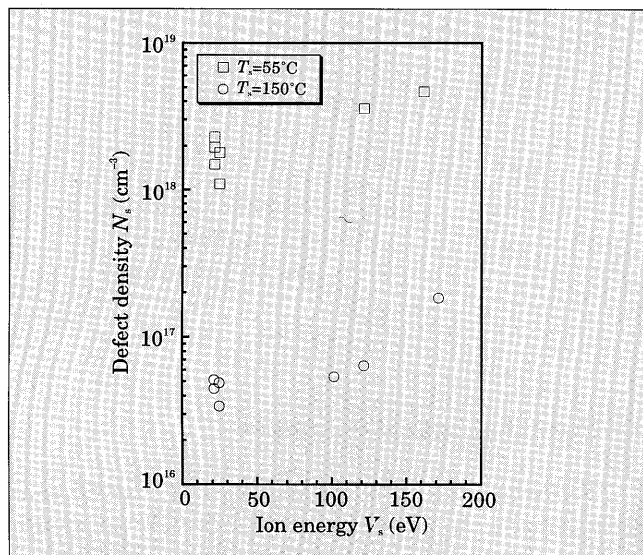Fig.7 Defect density (N_s) as a function of ion energy (V_s)

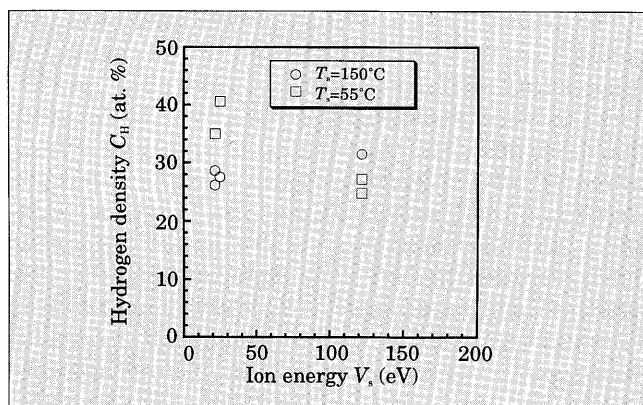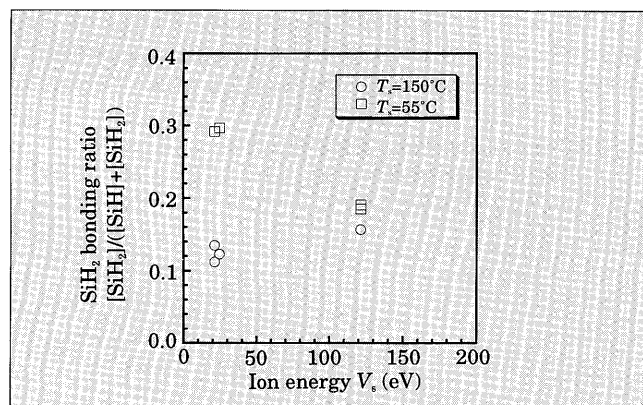Fig.8 Bonded hydrogen density (C_H) as a function of ion energy (V_s)

Fig.9 Si-H$_2$ bonding ratio ([SiH$_2$]/([SiH]+[SiH$_2$])) as a function of ion energy (V_s)

break bonds or reconstruct the a-Si:H network.

Figure 8 shows bonded hydrogen density (C_H) determined from the stretching mode spectra of Si-H and Si-H$_2$ near 2,000cm^{-1} by FTIR measurement. For T_s=55°C, C_H decreases from 40% to 25% as V_s increases from 20 eV to 120 eV. For T_s=150°C, however, C_H increases

slightly from 26% to 31%.

Figure 9 shows the Si-H$_2$ bonding ratio, [SiH$_2$]/([SiH]+[SiH$_2$]) as a function of V_s. As V_s increases from 20eV to 120eV, [SiH$_2$]/([SiH]+[SiH$_2$]) decreases from 0.29 to 0.19 at T_s=55°C. However, it increases from 0.12 to 0.16 for T_s=150°C. Normally, hydrogen density in a-Si:H decreases as substrate temperature increases.[5] The increase in C_H at T_s=150°C as V_s increases shows that the effects of ion energy are not the same as the effects of substrate heating.

The flux of ions was estimated from the probe current. It was about 10% of the film forming radicals. Thus, enough ions exist to affect the properties of a-Si:H films.

4. Conclusion

In this paper, studies on the effects of plasma on the properties of a-Si:H related films are presented. The film properties of a-SiGe:H improved when electron temperature was low. The effects of ion energy were studied by IEC Plasma CVD, which was developed to control ion energy independent of electron temperature and electron density. The defect density of a-Si:H films increases as ion energy increases. In future studies, it would be interesting to investigate the effects of ion energy on the film properties of a-SiGe:H by IEC Plasma CVD. Much higher solar cell efficiency is necessary for realization of practical and widespread use of a-Si:H based solar cells. We believe the answer will be obtained from improvement of a-Si:H related materials based on measurement and control of the plasma.

References
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