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EFFECTS OF THE SUBSTRATE POTENTIAL ON THE INCORPORATION MANNER OF HYDROGEN AND IMPURITY IN a-Si:H FILMS

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Abstract.- Effects of the bias voltage applied to the substrate on the film properties of a-Si:H have been investigated by employing the cross field plasma deposition method. A clear and continuous interchange in the infrared absorption peaks from 2090 cm⁻¹ to 2000 cm⁻¹ has been observed by changing polarity and magnitude of the bias voltage. Moreover, drastic change in the impurity doping efficiency and optimum bias voltage related with rf power have been found. By means of the optical emission spectroscopy (OES), it was confirmed that the substrate potential is as much effective in determining the film properties as the kind of decomposed species in the positive column.

Introduction.- In hydrogenated amorphous Si films prepared by plasma deposition from monosilane, there are too many parameters in determining the incorporation manner of hydrogen and impurity atoms and thereby structural and electronic properties[1,2,3,4]. While, as demonstrated by FRITZSCHE[4], KNIGHT[5], TSAI[6] and OKAMOTO[7], surface potential at the substrate also has a significant influence on the overall properties of a-Si:H films as well as other conventional deposition parameters; substrate temperature, gas pressure, gas flow rate, rf power and so forth. For a further detailed recognition of surface potential effects, we have conducted a systematic investigations by employing the cross field plasma deposition method[7] which makes it possible to control the substrate potential separately from other deposition parameters.

This paper presents a series of experimental data on the hydrogen and boron incorporation, the electrical, optical and optoelectronic properties of undoped and impurity doped a-Si:H films deposited under the externally biased condition. Besides, since optical-emission-spectroscopy (OES) of a silane glow discharge is, in the general consensus, expected to be a useful tool for understanding the plasma chemistry[8], we also discuss the results of OES during the plasma decomposition with biased condition in conjunction with the film properties.

Cross field plasma deposition system.- Figure 1 shows a schematic illustration of the deposition system employed in the work. The plasma was excited by 13.56 MHz rf oscillator through the symmetric coupling electrodes A and B settled outside the reaction tunnel chamber of 14 cm in diameter, 25 cm in height. An additional dc electric field was superimposed perpendicularly to rf electric field by using two parallel electrodes C and D separated by 14 cm. Substrate materials were held on the rotating electrode D of 10 cm in diameter. One of the noticeable merits of

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this deposition system is that the substrate potential with respect to the plasma can be controlled independently from the energy density of the plasma excited by rf electric field[9]. The distance between the center of the rf coupling electrodes and substrate was fixed to be 11 cm throughout the present work. A dc bias voltage \( V_b \) applied between the electrodes C and D, that is \( V_p-V_c \), was varied from -150 to +150V.

Figure 2 shows the \( I_b-V_b \) characteristics. As the electrode C is located deep in the positive column, the ion current into the electrode C could cancel out the saturation electron current into the electrode D. Therefore, the bias voltage \( V_b \) is fairly identical with the substrate potential \( V_p \). Regarding this characteristics as that of LANGMUIR plasma diagnostic probe[10], the voltage \( V_p \) at \( V_b = 0 \) in Fig.2 indicates the floating potential \( V_f \) at which equal number of electrons and ions arrive at a surface. The characteristic voltage \( V_f \) so called the plasma potential, above which a current \( I_b \) (mainly electron current to the electrode D) saturates in the first quadrant in Fig.2 is the space potential in the plasma. In the case of a flat bed system tried, for example, by KNIGHTS et al.[4,5,6], the substrate potential is essentially modurated by the applied rf voltage[10] and could not be externally controlled freely[11]. On the contrary, in our system, as the electrodes C and D are electrically isolated from the rf circuit, the substrate potential can be definitely controlled stably by setting of \( V_b \).

Amorphous Si:H films were deposited onto 7059 Corning glass or high resistive crystalline Si wafer from monosilane, monosilane/phosphine or monosilane/diborane mixture diluted with hydrogen gas to 3-10 vol.% at the substrate temperature of 250°C. Total gas flow was maintained to be 60-80 sccm with a pressure of 1-2 torr and input power was 55W. Under these conditions, the deposition rates were 0.7, 1.2 and 1.1 Å/sec for P-doped, B-doped and undoped films, respectively. These deposition rates are almost independent of the polarity and magnitude of the bias voltage \( V_b \) less than 150 V. This fact means that the bias voltage applied between the electrodes D and C does not disturb the plasma decomposition process in the positive column.

Fig.3 Hydrogen content \( C_H \) and absorption coefficient \( \alpha \) as a function of bias voltage.

**Effects of the bias voltage on hydrogen incorporation.** As the first step identification of a-Si:H films produced by cross field method, ir absorption spectra measurements were made with films deposited on high purity crystalline Si wafer. Figure 3 shows the hydrogen content \( C_H \) and absorption coefficient \( \alpha \) at the stretching mode frequencies 2090 cm\(^{-1}\) (dihydride group) and 2000 cm\(^{-1}\) (isolated monohydrides) as a function of \( V_b \). As seen in the figure, a clear and continuous interchange of ir absorption peaks from 2090 to 2000 cm\(^{-1}\) is observed in correspondence with the variation of \( V_b \) from the positive to negative value, even at the substrate temperature of 250°C. The bending mode absorption peaks near 840 and 890cm\(^{-1}\)(dihydride group) have been also observed in films deposited under the bias voltage more than \( +100V \). Results of P-doped films also exhibit the same tendency with the variation of \( V_b \). These facts show that the negative and positive bias voltage promote hydrogen atoms to be incorporated mainly as monohydrides and dihydrides, respectively. In contrast to this, \( C_H \) are almost independent of the bias voltage and they are about 16, 17, 18±1 at.% for undoped, P-
We have carried out the electrical, optical and optoelectronic measurements in order to understand how these different incorporation manner of hydrogen atoms reflect on the properties of a-Si:H films. Figure 4 shows the normalized photoconductivity nu under 1.9eV illumination (3x10^{14} photons/sec/cm^2) and the dark conductivity a_d at room temperature as a function of V_b. As can be seen in the figure, there exists the optimum bias voltage V_{op} for the photoconductive property of undoped films and at this bias voltage a_d exhibits minimum. V_{op} is related with rf power as also shown in Fig.4, and the values of V_{op} are about 0 and +50 V for the power of 35W and 55W, respectively. The plasma potential V_p, as already referred in the previous section, was about +60V and +110V for 35W and 55W, respectively. It is concluded comparing with these data that the optimum substrate potential with respect to the plasma is about -60V constant for both the powers.

The most favourable bias voltage for photoconductive property does not agree with that minimizing the SiH2 absorption mode as can be found in Figs. 3 and 4. Namely, the following statement might not always be valid; the ratio a(2000 cm^{-1})/a(2090 cm^{-1}) is a good measure of the film quality for a solar cell material[12]. It would be imagined that a probable effect of ion damage plays a more dominant role on determining the photoconductive property than the local bonding manner of hydrogen in a-Si:H.

**Optical-emission-spectroscopy measurements.** In order to clarify the basic plasma kinetics and surface reactions encountered in biased plasma deposition, we have measured the optical-emission-spectra (OES) from the silane plasma as a function of V_b. The optical-emission intensities of the reactive species SiH, H2 and H in the positive column of plasma were not affected by V_b. On the other hand, those just above the substrate were strongly influence by V_b. Figure 5 shows the intensity ratio of radicals [SiH]/[H] and [SiH]/[H2] as a function of V_b. All the ratios [SiH]/[H], [SiH]/[H2] and [H]/[H2] have the extremes near V_b =0; increasing the absolute value of bias voltage causes the ratio of [SiH]/[H] and [SiH]/[H2] to decrease appreciably, while a small increase is noted in that of [H]/[H2]. These bias voltage dependences of the intensity ratio are similar to that of the electrical and photoconductive properties of P-doped (as can be seen in the following section) and undoped a-Si:H films. This implies that increasing the ratio of [SiH]/[H], [SiH]/[H2] and/or decreasing that of [H]/[H2] are favorable for the photoconductive and electrical properties of undoped and P-doped films. In contrast the monotonical bias dependence of the ratio a(2090cm^{-1})/a(2000cm^{-1}) is not consistent with the trend of results in OES measurements. So it can be concluded that the concept "increasing the ratio of [SiH]/[H] or decreasing that of [H]/[H2] in plasma causes high concentration of SiH2 mode in deposited films"[13] is not valid in general.

**Bias effects on impurity doping.** Since hydrogen incorporation manner was confirmed to be strongly affected by bias, it might be rather natural to

![Fig.4 Normalized photoconductivity nu and dark conductivity a_d as a function of bias voltage.](image)

![Fig.5 Ratio of optical-emission intensities of SiH, H2 and H as a function of bias voltage.](image)
consider that the incorporation manner of the impurity atoms is also correlated with $V_b$. Based on this speculation, we have carried out a series of experimental investigations on the electrical and optoelectronic properties of doped a-Si:H films deposited under the existence of $V_b$. Figure 6 demonstrates bias functional data of $\Omega_d$ and $\mu_n$ for P and B-doped a-Si:H films deposited with gaseous ratio of PH$_3$/SiH$_4$=0.5 vol.%, and B$_2$H$_6$/SiH$_4$=0.2 vol.%, respectively. As seen in the figure, $\Omega_d$ and $\mu_n$ of P-doped films have the extreme at about 0-450V biased condition which was similar trend to the results of undoped one. While, those of B-doped one exhibit monotonical change with $V_b$. Especially, the dark conductivity drastically increases with positive bias voltage above +50V. There may be three factors responsible for the enhancement of $\Omega_d$, that is, increase of boron atoms included in films, improvement of the probability that boron atoms are incorporated in an electrically active substitutional site (doping efficiency) and reduction of gap state density which allows the Fermi level to easily shift toward either extended band. In the course of the preliminary study of IMA and ESR, it has been deduced that the former two interpretations are more acceptable. These facts mean that the surface potential at the substrate has a significant influence not only on the boron including efficiency but also on the doping efficiency related to the impurity incorporation manner in a-Si:H films.

Summary. - A series of experimental investigation on the mechanism of plasma decomposition and amorphous Si deposition have been made by the cross field furnace. The result can be summarized as the following: (i) Effects of preparation condition on the film property should be devided into three separate processes of the deposition mechanism, that is, a) plasma decomposition of source gases (directly affected by gas pressure, discharge power density and kind of source gases), b) diffusion of ionized and neutral species to the vicinity of substrate, and c) deposition of species on to substrate (affected by kinetic energy and excitation energy of species very severely). The substrate potential does correlate with the processes b) and/or c). The deposition parameters such as plasma discharge power and gas pressure affect all the processes a), b) and c) through changing the substrate potential or other factors. (ii) As the experimental condition, surface potential at the substrate, distance between positive column and substrate, and substrate temperature determine the compiling manner of hydrogen and impurity atoms into the amorphous network, consequently, decide the film property. (iii) To have the controllabilities on the above three separate processes, the cross field plasma deposition method is one of the most convenient deposition technology.

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