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PROPERTIES OF MICROCRYSTALLINE P-DOPED GLOW DISCHARGE SI:H FILMS

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Abstract.- Phosphorous doped Si:H films were prepared by glow discharge decomposition of 0.01 PH$_3$-SiH$_4$ mixture gas diluted in H$_2$ gas under various deposition conditions. The conductivity of the films increases from 2x10$^{-4}$ (ohm cm)$^{-1}$ to 8 (ohm cm)$^{-1}$ with increasing discharging power for the deposition. Microcrystallization is observed through X-ray diffraction in the films exhibiting conductivity of 5x10$^{-2}$ (ohm cm)$^{-1}$ or higher. The film structure changes from amorphous phase to near perfect crystalline phase with increasing conductivity. This change is caused by the increase of the number of crystallites with nearly constant average size of about 60 Å. Microcrystallization occurs even in a very thin (~100 Å) P-doped Si:H film. The microcrystallized P-doped film has been tentatively applied to a window side layer of an ITO/n-i-p/stainless-steel type solar cell. The low absorption coefficient of this film results in the increase of photocurrent of this cell in the short wavelength region.

Introduction.- In 1975, Spear et al. showed that electronic properties of the hydrogenated amorphous Si (a-Si:H) prepared by glow discharge decomposition of silane could be controlled by substitutional impurity doping in the gas-phase. Their work opened up new possibilities for applications of this material, especially to solar cells. Recently, it has been found that the conductivity of the doped film could be improved by a high power glow discharge deposition and this improvement was caused by a partial crystallization of the film.

This fact has gathered a great interest of researchers in the fields of both the material science and the device technology. However, systematic experiments on the deposition conditions of the microcrystalline P-doped film have not been published so far. Moreover, the electronic and structural properties of the film have not yet been clarified enough.

In this paper, we present deposition conditions for the P-doped microcrystalline films and some structural properties of the films. A study on a very thin (~100 Å) P-doped microcrystalline film and its application to a solar cell are also presented and discussed.

Experimental.- The phosphorous doped Si:H films were prepared by the RF glow discharge decomposition of SiH$_4$-PH$_3$-H$_2$ mixture gas in a capacitive coupled reactor. Deposition conditions are listed in Table I.

The Si:H film was deposited on a Corning 7059 glass substrate for conductivity measurement. The structural studies of the films were performed by means of X-ray diffraction, infrared absorption and electron diffraction. X-ray diffraction measurements were performed for 0.5-1 μm thick films on stainless-steel substrates and Si(100) wafers. Cu-Kα radiation was used at the condition of 40 kV and 160 mA, and a graphite monocho-

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### Table I. Deposition conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate Temperature</td>
<td>260°C</td>
</tr>
<tr>
<td>Electrode Spacing</td>
<td>4 cm</td>
</tr>
<tr>
<td>Diameter of Electrodes</td>
<td>32 cm</td>
</tr>
<tr>
<td>PH$_3$/SiH$_4$</td>
<td>0.01</td>
</tr>
<tr>
<td>SiH$_4$/H$_2$</td>
<td>1/20-1/300</td>
</tr>
<tr>
<td>Gas Pressure</td>
<td>1-3 torr</td>
</tr>
<tr>
<td>RF Power of Discharge</td>
<td>10-200 W</td>
</tr>
</tbody>
</table>
The meter was set up in front of the detector to reduce the background.

The structures of very thin films were examined through reflection electron diffraction using an electron microscope at an acceleration voltage of 50 kV.

Results and discussions.- Figure 1 shows the dark conductivity at 25°C as a function of discharging power for the film deposition, along with the activation energy of the conductivity. With increasing discharging power, the conductivity decreases at first and then increases drastically from $10^{-4} \text{ (ohm cm)}^{-1}$ to 8 (ohm cm)$^{-1}$, and the activation energy changes from 0.2 eV to 0.02 eV, correspondingly. There are distinguishable regions: a low power and a high power region. As will be mentioned later, P-doped films prepared in the low power region consist of amorphous phase, and the films prepared in the high power region are partially crystallized. The discharging power critical for initiating crystallization shifts to lower side, when the flow rate of SiH$_4$ and/or the SiH$_4$/H$_2$ ratio are decreased.

Figure 2 shows the optical absorption spectra of the films deposited with various discharging power. The absorption spectrum of the film deposited with a discharging power of 20 W coincides with that of a non-doped a-Si:H film. The absorption coefficient decreases with increasing discharging power, and finally approaches to that of a crystalline Si.

Figure 3 shows the X-ray diffraction profiles around the Si(ll1) diffraction peak for the films deposited with various discharging power. A film deposited with a discharging power of 20 W exhibits the diffraction pattern unique to amorphous Si, and the films formed by 150 W or higher discharging show diffraction pattern of crystalline Si. Films formed by 50 W and 100 W discharging show intermediate pattern between an amorphous Si and a crystalline Si. They seem to be partially crystallized. The mean value of the crystallite size was estimated from Sherrer's equation using the half-width of diffraction profile and this value is nearly constant at about 60 Å, as shown in Fig.4.

Annealing treatments for investigating volume fraction of the crystalline phase in the films were performed for several films formed by 150 W discharging in hydrogen atmosphere up to 800°C. Figure 5 shows typical diffraction profile before and after annealing. The crystallite size increased with annealing temperature. However, the integrated intensity of the diffraction profile was nearly constant. Therefore, the film formed by 150 W or higher discharging can be assumed to be occupied by near perfect crystalline phase in volume fraction.

The diffraction profiles of the intermediate films formed by 50 W and 100 W discharging are assumed to be the sum of the two profiles of crystalline origin and that of amorphous origin. The volume fractions of crystalline phase in the films were estimated by superimposing of the two profiles using the least square fitting, and are shown as a function of the conductivity at 25°C in Fig.4. The crystallite
size of the films, which is also shown in the figure, is almost independent of its conductivity. These results suggest that the crystallization takes place as a result of the increase in the number of the crystallites, which is associated with the increase of the conductivity.

On the other hand, by 700°C annealing of the crystallized film, the crystallite size grows up to 100 Å, but the conductivity scarcely changes. This is the evidence to support a model that the film formed by 150 W discharging consists of near crystalline phase. The dashed line in the figure indicates a conductivity change deduced from effective medium theory\(^5\) by assuming the conductivity of the crystal as 10 \((\text{ohm cm})^{-1}\) and that of amorphous as 10\(^{-4}\)(ohm cm\(^{-1}\)). The calculated conductivity of the film with crystallites in amorphous matrix as a function of crystalline phase shows fair agreement with the observed.

As shown in Fig.6, the infrared absorption coefficient around 630 cm\(^{-1}\) for various films remarkably decreases with the degree of the crystallization, accompanying the increase of conductivity. The absorption peak around 590 cm\(^{-1}\) does not show large change. According to Brodsky et al.\(^6\) the peak at 590 cm\(^{-1}\) corresponds to the rocking mode of Si-H\(_2\), and 630 cm\(^{-1}\) to the wagging mode of Si-H\(_n\) (n=1-3). From these identification and the consideration that existence of Si-H\(_2\) group is not likely, we conclude that the crystallized films contain hydrogen mainly in the form of Si-H\(_2\).

It is of interest that even the fully crystallized film contains a considerable amount of bonded hydrogen.
In a solar cell with n-i-p/stainless-steel type, very thin n-layer (100-200 Å) is required to reduce optical absorption loss. Accordingly, in an application of crystallized P-doped films, it is important whether the very thin films remain crystallized or not. This has been studied using an electron diffraction method for the films deposited by a high power deposition on a non-doped a-Si:H (1 μm thick). Electron diffraction from these films clearly shows Debye-Sherrer rings (see Fig.7) which shows that these films are crystallized even in very thin condition.

The authors fabricated two types of solar cells with n-i-p/stainless-steel structure. As the window side layer of the cell, one of these had a crystallized n-layer, and another had a 'normal' n-layer. The open circuit voltage $V_{oc}$ and the fill factor FF shows equal values for both types of cells, and the short circuit current $J_{sc}$ is improved by 13% in the cell with a crystallized n-layer. To clarify the causes of the increase of $J_{sc}$, wavelength dependence of photocurrent was measured under a constant power of incident light. As is seen in Fig.8, the photocurrent of the 'crystallized' cell is greater than that of the 'normal' cell especially in a short wavelength region. This is due to a lower absorption coefficient and a higher conductivity of the crystallized n-layer.

Summary.- The conductivity of phosphorus doped Si:H films prepared by glow discharge decomposition of 0.01 PH$_3$-SiH$_4$ mixture gas increased from $2 \times 10^{-4}$ (ohm cm)$^{-1}$ to 8 (ohm cm)$^{-1}$ with the increase of discharging power. Microcrystallization was observed in the films with conductivity of $5 \times 10^{-2}$ (ohm cm)$^{-1}$ or higher through X-ray diffraction. The film structure changes from amorphous phase to near perfect crystalline phase with increasing conductivity. This change accompanies the increase of the number of crystallites, average sizes of which are nearly constant at about 60 Å.

Microcrystallization occurred even in a very thin (~100 Å) P-doped Si:H film. This microcrystalline P-doped film has been tentatively applied to a window side layer of an ITO/n-i-p/stainless-steel solar cell. $J_{sc}$ of this cell was larger than that of normal a-Si:H solar cell.

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