B－4－3 Novel Deposition Technique of a-Si:H

—— Silane Glow Discharge in Magnetic Field ——

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Introduction At present, the conversion efficiency of a-Si:H $p^+/i/n^+$ or metal/i/n^+ phtovoltaic cells is appreciably restricted by properties of the heavily doped layers, whose conductivity is at most 10^{-2} $ohm^{-1}cm^{-1}$ and the corresponding activation energy is 0.2 eV. In this paper, we report a new deposition technique of hydrogenated silicon, by which extremely large conductivity of n^+ layers and very high photoconductivity of i layers have been obtained.

Experimental Magnetic field was applied perpendicular to a substrate surface during the glow discharge depostion of a-Si:H. The amounts of reactive species SiH, H_2, and H in the plasma were monitored by the intensities of optical emission lines from the radicals. Applied magnetic field remarkably changes the emission intensities from the radicals and therefore electronic and structural properties of resulting a-Si:H films, because the electron temperature of the plasma is lowered by magnetic field.[1] An extremely high conductivity of 27 $ohm^{-1}cm^{-1}$ and a very low activation energy of 10 meV have been achieved, for the first time, in Si:H alloys prepared by the glow discharge of a SiH_4-PH_3 mixture gas in a magnetic field of 0.42 kG (Fig. 1). The substrate temperature and rf power were kept at 300°C and 20 watts, respectively. As shown in Fig. 2, high conductivity samples are reproducibly deposited when the emission lines from doubly excited singlet-states of H_2 molecules (labeled as $(2p\sigma)^2$) appearing at 377 and 392 nm are sufficiently weakened. This is possibly because preferential energy transfer from $(2p\sigma)^2$ states to PH molecules, which are reactive intermediates with a decomposition energy of 3.02 eV, considerably reduces the emission intensities of $(2p\sigma)^2$ lines. Optical absorption spectrum for the highest conductivity sample yields an optical gap of 1.6 eV, below which free carrier absorption as high as 10^3-10^4 cm^{-1} is observed. According to the Drude theory,[2] an electron mobility of 1.5 $cm^2V^{-1}sec^{-1}$ and a carrier concentration of 4.8×10^{20} cm^{-3} are obtained. The latter agrees not only with the doping ratio (5.6×10^{-3}) but also with the density of incorporated phosphorus atoms measured by Auger electron spectroscopy, being indicative of the doping efficiency close to 100 %.

X-ray diffraction data of heavily doped specimens exhibit broad and weak peaks corresponding to (111), (220), and (311) orientations. The half width of the peaks is by eight times broader than that of polycrystalline silicon with fine grains of 20 nm, so that the films contain microcrystalline phase and a large

fraction of the matrix is composed of a-Si:H network as evidenced by the optical absorption data. It is also confirmed that undoped and lightly doped specimens prepared at the same deposition conditions always show amorphous phase.

After depositing highly conductive n^+ layers, subsequent growth of i layers at a magnetic field of 0.42 kG leads to a high quality of undoped a-Si:H films (Fig. 3). Increase in the photoconductivity of undoped a-Si:H with magnetic field accompanies decrease in the number of SiH_2 bonds incorporated in the films, which is given by integrated absorption in Fig. 3, as well as decrease in the emission intensities from H radicals. This implies that the suppression of the chemical reaction $SiH + H \rightarrow SiH_2$ in the gas phase and/or on the substrate surface is important to improve the photoconductinity of i layers.

Conclusion The plasma decomposition of silane in magnetic field is a promising way to fabricate photovoltaic cells. The chemical reactions involved in the growth or doping of hydrogenated silicon are monitored by optical emission spectra from the plasma. This enables us to make a fine control of the relative amounts of the reactive species in in the silane plasma.

References (1) M. Taniguchi, M. Hirose, and Y. Osaka: J. Non-Cryst. Solids 35-36 (1980) 189. (2) Y. Mishima, M. Hirose, and Y. Osaka: J. Appl. Phys. 51 (1980)1157.

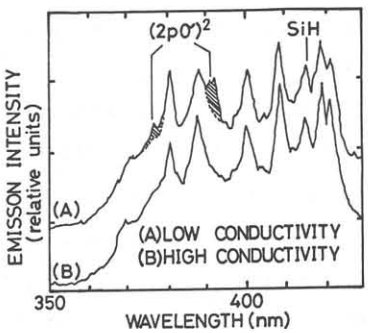

Fig. 2. Optical emission spectra during the deposition of high (27 $ohm^{-1}cm^{-1}$) and low (10^{-2} $ohm^{-1}cm^{-1}$) conductivity samples.

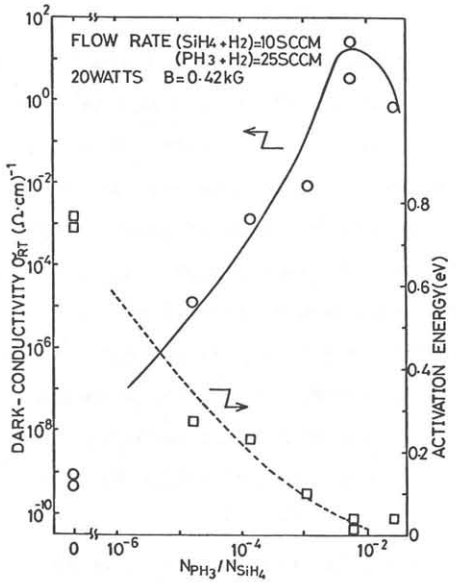

Fig. 1. Conductivity and its activation energy vs. doping ratio.

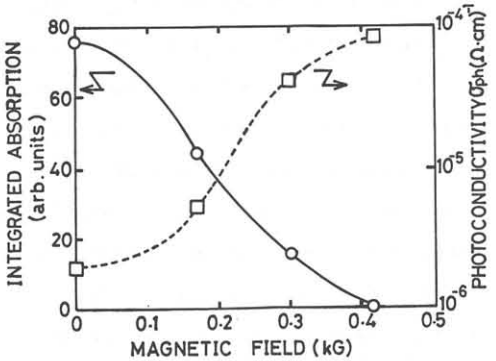

Fig. 3. Photoconductivity at a flux of 10^{15} photons/cm^2sec and integrated absorption due to SiH_2 bonds for undoped specimens produced at various magnetic field.