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High-Rate Deposition of a-Si:H Using SiH_4

T. Hamasaki, M. Ueda, M. Hirose and Y. Osaka

Department of Electrical Engineering, Hiroshima University

Higashihiroshima 724, Japan

An extremely high deposition rate of a-Si:H has been achieved by employing a new rf discharge technique. The deposition rate has been increased to more than 50 Å/sec even at a substrate temperature of 200 °C without accompanying any appreciable degradation in electrical and optical properties as compared to those of specimens prepared at a conventional deposition rate. It is found that light-induced conductivity change is remarkably suppressed by increasing the deposition rate.

§1. Introduction

Recent developments in a-Si:H applications to photoreceptors and low-cost solar cells raised a strong demand for realizing the high-rate deposition either from the silane plasma or from the higher silane. The deposition rate is in general increased by increasing the power density and the concentration of SiH_4 feed gas as well. However, the growth rate in a SiH_4 plasma has been limited typically in the range of 1∿5 Å/sec so far, because an increase of the deposition rate results in the powder formation in the gas phase. Inert gas (He or Ne) dilution of silane was used to avoid such reactions and a deposition rate over 10 Å/sec was obtained.[1] On the other hand, the use of the higher silanes has led to a deposition rate as high as 25 Å/sec when the substrate temperature Ts was kept at 250 °C and 65 Å/sec for Ts= 350 °C, although some degradations in electrical properties were observed.[2]

In this paper, we report a new deposition technique, by which a-Si:H can be deposited from pure SiH_4 at a rate more than 50 Å/sec even for Ts= 200 °C without any degradation of material properties.

§2. Experimental

The apparatus employed in this study is schematically illustrated in Fig. 1. A grounded mesh surrounding the parallel electrodes (12 cm in diameter) was used for suppressing the diffusion of reactive species toward the chamber

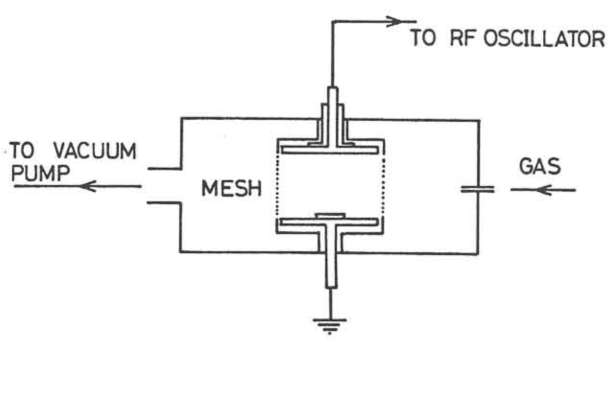

Fig.1 Experimental setup for depositing a-Si:H. RF power (9 MHz) was applied to the top electrode.

wall. As a result, the positive column, which was usually localized near the powered electrode, spreaded close to the grounded electrode. Also, it is important to note that the formation of silicon flake is eliminated by the presence of a grounded mesh. Quartz glass and c-Si substrates were placed on the grounded electrode, of which temperature was maintained at 200 °C. Total gas flow-rate and rf power (9 MHz) were respectively changed over a wide range. The film thickness was determined from the interference fringes in the wavelength range 2.5∿ 4 μm.

§3. Results and Discussion

3.1 Deposition Rate

The rate of a-Si:H growth monotonically increases with rf power and silane flow-rate, and an extremely high deposition-rate exceeding 50 Å/sec has been achieved by the rf glow discharge of pure SiH_4 (Fig. 2). Since the substrate surface is covered with the positive column by the presence of the grounded mesh, it is likely that a pronounced increase in the concentrations of reactive species near the surface results in a remarkable increase of deposition rate. In contrast to this, in the conventional rf discharge technique without mesh, the deposition rate appears to be suppressed by a poor decomposition rate of SiH_4 near the substrate surface even when the silane concentration in the gas phase is sufficient. This interpretation is compatible with our model on the growth kinetics of a-Si:H, in which the heterogeneous reactions among the reactive species such as SiH and H impinging onto the growing surface determine the deposition rate.[3] The maximum rate obtained in the present experiment (52 Å/sec) is not a ceiling value and further increase in the deposition rate could be achieved by increasing rf power more than 70 watts.

3.2 Electrical and Optical Properties

Figure 3 represents the conductivity σ in dark and under AM-1 (100 mW/cm^2) illumination for various a-Si:H films. Both dark- and photo-conductivity are basically independent of deposition rate when it exceeds 15 Å/sec, while in the conventional glow discahrge either of SiH_4 or of

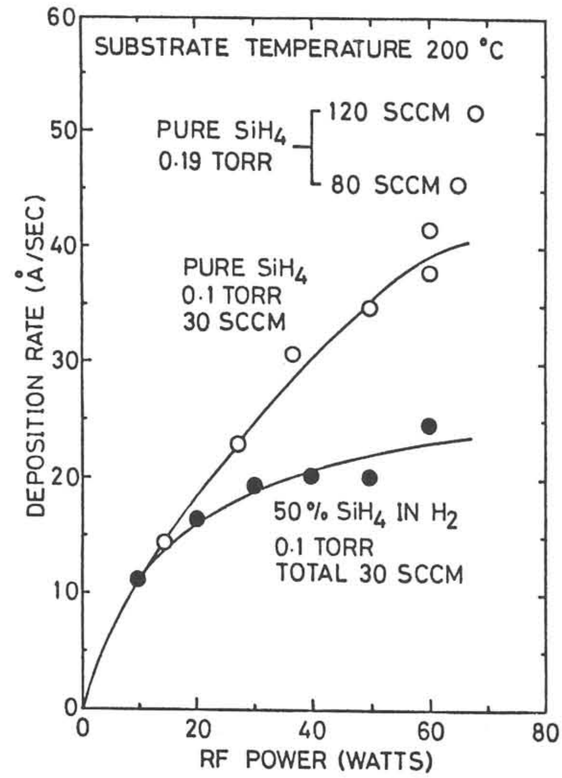

Fig. 2 Deposition rate of a-Si:H as a function of rf power.

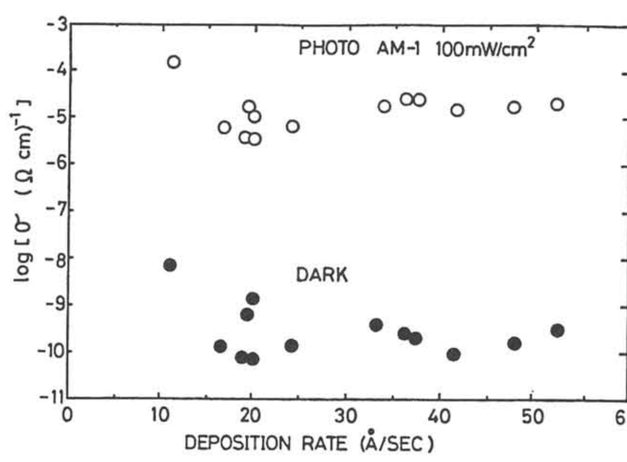

Fig. 3 Dark- and photo-conductivity of a-Si:H as a function of deposition rate.

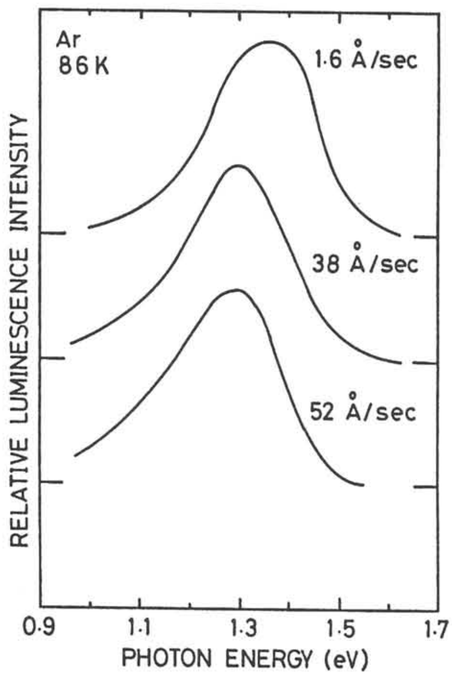

Fig. 4 Luminescence spectra for a-Si:H samples prepared at various deposition rate. Top curve refers to a specimen obtained by conventional discharge technique without mesh.

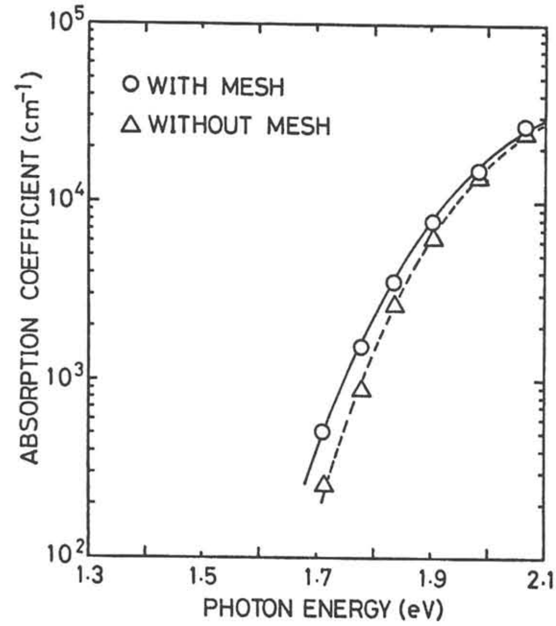

Fig. 5 Absorption coefficient as a function of photon energy for a-Si:H films obtained by various discharge apparatus.

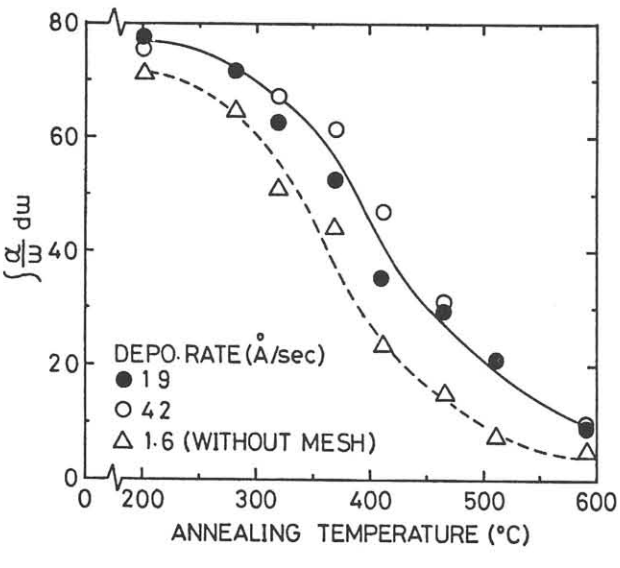

Fig. 6 Integrated intensities of the SiH stretching absorption as a function of annealing temperature.

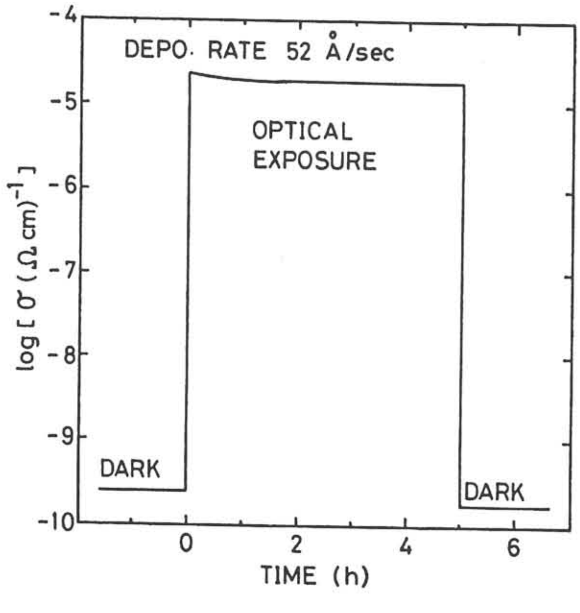

Fig. 7 Conductivity as a function of time before, during, and after exposure to 200 mW/cm^2 AM-1 illumination.

Table I Annealing effect on dark- and photo- conductivity of samples prepared at high deposition rates.

DEPOSITION RATE (Å/sec)	ANNEALING TEMPERATURE (°C)	DARK CONDUCTIVITY $(\Omega\ cm)^{-1}$	PHOTOCONDUCTIVITY $(\Omega\ cm)^{-1}$
38	as depo.	2.1×10^{-10}	1.3×10^{-5}
	370	7.6×10^{-11}	1.4×10^{-5}
	465	5.2×10^{-11}	1.1×10^{-5}
52	as depo.	4.5×10^{-10}	2.0×10^{-5}
	370	3.9×10^{-11}	2.0×10^{-5}
	465	2.4×10^{-11}	7.3×10^{-6}

Si_2H_6, dark- and photo-conductivity decrease with an increase of deposition rate.[2)]

For the optical characterization of specimens prepared at high deposition rates, the luminescence and optical absorption spectra were taken. The luminescence peak exhibits a small red-shift by increasing the deposition rate, although the intensity and shape of the spectra for high-deposition-rate sample are almost unchanged (Fig. 4). The peak energy shift from 1.37 to 1.3 eV could be associated with a change in the optical bandgap, because the optical bandgap obtained from the optical absorption spectrum (Fig. 5) varies from 1.75 to 1.65 eV.

3.3 Stability

Thermal stability of the deposited samples is examined by observing annealing effect on the integrated intensities of the SiH stretching absorption (Fig. 6). Samples were kept at each annealing temperature for about 20 minutes in the vacuum (10^{-4} Torr). Hydrogen evolution rate is not increased by high-rate deposition. Also, the dark- and photo-conductivity of high-rate samples is less sensitive to annealing even at 465 °C (Table I). As for light-induced change in conductivity, the photoconductivity is decreased only by $\sim$20 % after 5 h exposure to 200 mW/cm^2 illumination and the corresponding change in the dark conductivity is less than one order of magnitude (Fig. 7), and the sample returned to the virgin state by annealing at 120 °C for one hour.

Considering the results of annealing effect and light-induced conductivity change, microstructure of a-Si:H prepared at high deposition rates might be different from that of conventionally obtained a-Si:H. Further detail in this respect will be reported elsewhere.

§4. Conclusions

Conclusions are summarized as follows:

1) The high-deposition-rate more than 50 Å/sec is achievable using the glow discharge of pure SiH_4 without accompanying any deteriorations of material properties.

2) Light-induced degradation is considerably suppressed by increasing the deposition rate.

Acknowledgement

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References

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