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# High Quality Hydrogenated Amorphous-Germanium Films Prepared by Photochemical Vapor Deposition

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A-SiGe:H films were prepared by photo-CVD using Si<sub>2</sub>H<sub>6</sub>-GeH<sub>4</sub>-H<sub>2</sub> and SiH<sub>4</sub>-GeH<sub>4</sub>-H<sub>2</sub> gas mixture. It was confirmed from the photo-electrical properties and infrared absorption spectra that hydrogen radicals played an important role in reducing the defect density of a-SiGe:H films. A-SiGe:H films having optical bandgap of about 1.45 eV with good photoconductivities of about 3-4 in magnitude were obtained. These results suggested that films prepared by photo-CVD might be suitable material for tandem type solar cell. The application of these films to solar cells was also described.

### 1. Introduction

Recently, the conversion efficiency of the a-Si:H p-i-n solar cells fabricated by a glow discharge GD) process have been improved to a level of more than 11%.<sup>1)</sup> For achieving higher efficiency, tandem type solar cells with a-Si:H and a-SiGe:H which has high collection efficiency in long wavelength region of visible light have been considered. However, the actual efficiency of the tandem type solar cells developed so far was limited to low value because of poor photoelectrical properties of a-SiGe:H films .

Although, in a GD process these properties can be improved under high power conditions <sup>2)</sup>, the application to solar cells was difficult due to much radiation-induced damages from high- energy charged particles and the contamination of residual impurities.

On the other hand, photochemical vapor deposition (photo-CVD) was recently considered as a promising method for a preparation of high performance a-Si:H solar cells due to its ion-damage-free nature .<sup>3,4,5</sup>) Furthermore, the effect of particular radicals such as hydrogen radicals can be studied independently in photo-CVD method.

In this paper we report the preparation of a-SiGe:H films by a photo-CVD process from  $Si_2H_6-GeH_4-H_2$  and  $SiH_4-GeH_4-H_2$  gas mixture. The

role of hydrogen radicals in the growth of the films were investigated and clarified for the first time by evaluating the optical and electrical properties and infrared (IR) absorption spectra which was utilized to estimate the content of H bonded to Ge and Si atoms. Furthermore, the application to solar cell was also described.

### 2) Experimental

Figure 1 shows our photo-CVD system used in this study which have already been reported. <sup>3)</sup> A low pressure mercury lamp was employed as a light source which irradiates intense  $1849^{\circ}A$  and  $2537^{\circ}A$ resonance line ( 30 mW/cm<sup>2</sup> at 3-cm distance and



Fig.1 Schematic of our photo-CVD system







Fig.4 Variation of photo and dark conductivities with the dilution ratio of H<sub>2</sub>/ Si<sub>2</sub>H<sub>6</sub> for a-SiGe:H films with E<sub>opt</sub> of 1.45 eV

the intensity ratio of 1849 Å to 2537 Å is 1/6). The reactant gases of  $Si_2H_6$ , 10 %  $Si_2H_6$  diluted with helium,  $SiH_4$ ,  $GeH_4$  and hydrogen were premixed with a very little fraction of mercury vapor in a thermally controlled mercury vaporizer before being introduced into the reactor.

A syntheses quartz-glass window (10 cm in diameter and 6 mm in thickness), which transmits 1849 Å resonance line, was coated with low vapor pressure oil and was placed between the light





source and a substrate.

The substrate was held at 200-350°C. The temperature of the mercury vaporizer was kept at 50 °C. The total gas pressure was about 2 Torr. Films were deposited on Corning 7059 glass substrate for optical and electrical measurements and on crystalline Si substrate for the IR measurements. The photoconductivity was measured under the AM1, 100mW/cm<sup>2</sup> insolation . Furthermore, the optical bandgap was determined by extrapolation from a plot of hv vs $\sqrt{\alpha hv}$ .

## 3. Results and discussion

# 3.1 Characterization of a-SiGe:H films prepared without hydrogen

First, we prepared undoped a-SiGe:H films from  $\text{Si}_2\text{H}_6$  -GeH<sub>4</sub> and  $\text{SiH}_4$ -GeH<sub>4</sub> without hydrogen. In Fig.2 the optical bandgap (E<sub>opt</sub>) is illustrated as a function of the gaseous ratio of GeH<sub>4</sub> to the sum of hydrides. As can be seen in this figure, E<sub>opt</sub> decreased to 1.4 eV by increasing the gaseous ratio of GeH<sub>4</sub>. A conspicuous change in E<sub>opt</sub> was found in SiH<sub>4</sub>-GeH<sub>4</sub> system due to the fact that the reaction probability of GeH<sub>4</sub> ( $\sigma_Q^2$ : quenching cross section=140) <sup>6</sup>) is higher than that of SiH<sub>4</sub> ( $\sigma_Q^2$  = 26). In Si<sub>2</sub>H<sub>6</sub>-GeH<sub>4</sub> system, the change in E<sub>opt</sub> was also different when 10 % Si<sub>2</sub>H<sub>6</sub> diluted in helium was used. In this paper, the films prepared from Si<sub>2</sub>H<sub>6</sub>(10%) -GeH<sub>4</sub> and SiH<sub>4</sub>(100%)-GeH<sub>4</sub> gas mixture





Eopt

were mainly described.

Figure 3 shows the conductivities of a-SiGe:H films prepared without introducing hydrogen, plotted as a function of  $E_{opt}$ . The photoconductivities decreased rapidly with increasing Ge content. This reduction in the photoconductivity is similar to that of GD films prepared under a low RF power condition, which is strongly related to an increase in the number of Ge dangling bonds due to the weakness of Ge-H bonds. 2,7)

# 3.2 Characterization of a-SiGe:H films prepared with hydrogen

In order to reduce the densities of dangling bonds and to obtain highly photoconductive films, the effect of hydrogen radicals on optical and electrical properties was examined. Figure 4 shows the variation of conductivities with  $H_2/Si_2H_6$ ( $E_{opt} = 1.45 \text{ eV}$ ). Photo and dark conductivities enhanced with increasing  $H_2$  flow rate, and high photoconductivities were obtained with a high substrate temperature. This fact may suggest that hydrogen radicals played an important role in reducing the defect density of a-SiGe:H films.

Figure 5 shows the conductivities of high quality films prepared from  $Si_2H_6-GeH_4-H_2$  and  $SiH_4$  -GeH\_4-H<sub>2</sub> with a high dilution ratio of hydrogen ( = 10), as a function of  $E_{opt}$ . Although, photoconductivities decreased slightly



with decreasing in the  $E_{\rm opt}$ , the change in conductivities were relatively small. These results were different from the films prepared by a GD process at a high power. <sup>2)</sup>

Figure 6 shows the relationship between deposition rate and  $E_{\rm opt}$  in a-Si:H and a-SiGe:H films having various photoconductivies and  $H_2/Si_2H_6$  and  $H_2/SiH_4$ . Circles represent the films with high photoconductivies of more than  $10^{-5}$  S/cm. High quality a-SiGe:H films having smaller  $E_{\rm opt}(<1.7 \ {\rm eV})$  could be prepared at a lower deposition rate. In order to reduce the dangling bonds which was increased by increasing the Ge content, it was necessary to suppress the deposition rate for much incorparate of hydrogen into the films.

To clarify the role of the hydrogen radical clearly, IR measuremetns were done . Figure 7 shows the contents of H bonded to Ge[Ge-H] and that of H bonded to Si[Si-H] and their sum determined from the wagging mode vibration , as a function of  $\rm H_2/Si_2H_6$ . The change in Ge-H with dilution ratio was unclear, but Si-H and the total bonded H increased with dilution ratio. This implies that the density of dangling bonds in these films can be easily reduced in photo-CVD by introducing hydrogen gas .

Furthermore, the contents of Ge-H, Si-H and their sum as a function of the Ge content x, calculated from  $E_{opt}$ , are shown in Fig.8. The contents of Ge-H and total bonded H did not decrease even though Ge content was varied from O to 0.5. These contents of total bonded H were



Fig.7 Contents of H bonded to Ge[Ge-H] and that of H bonded to Si[Si-H] and their sum as a function of the dilution ratio of hydrogen

quite different from those of GD films which decreased with an increase of the Ge content.7)

### 4. The application to solar cells

The a-SiGe:H films described above have been applied to the i-layers of p-i-n type solar cells . At the present stage of the optimization, a conversion efficiency of 2.3 % (Voc = 0.661 V, Isc = 10.3 mA/cm<sup>2</sup>, FF = 0.336) using i-layer with  $E_{opt}$  of 1.45 eV was obtained under AM1, 100 mW/cm<sup>2</sup> illumination. The Voc was higher than that ( Voc = 0.59) reported by Mitsubishi Electric <sup>8)</sup>, using i-layer with  $E_{opt}$  of 1.55 eV. This high Voc might be useful for the application to tandem type solar cells.

#### 5. Conclusion

We have shown that high quality a-SiGe:H films can be easily obtained by photo-CVD using  $Si_2H_6$  -GeH<sub>4</sub> -H<sub>2</sub> or SiH<sub>4</sub> -GeH<sub>4</sub> -H<sub>2</sub> gas mixture with a high dilution ratio of hydrogen. It was found that hydrogen radicals played an important role in reducing the defect density of a-SiGe:H films. A-SiGe:H films having good photoconductivies (>10<sup>-5</sup> S/cm) at E<sub>opt</sub> wider than 1.45 eV and a large ratio of photoconductivities to dark conductivities of about 3-4 in magnitude were obtained. At the present stage, cell efficiency of 2.3 % with i-layer having E<sub>opt</sub> of about 1.45 eV, was obtained.





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