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Growth of Amorphous Silicon Germanium (a-SiGe:H) Alloys Thin Film by PECVD

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Abstract

Hydrogenated amorphous silicon-germanium (a-SiGe:H) alloys thin films had been grown by Plasma Enhanced Chemical Vapor Deposition (PECVD) method. The films were grown on corning glass # 7059 from a gas mixture of silane (SiH_4) and germane (GeH_4) 10% diluted in hydrogen (H_2). UV-VIS-NIR spectra analysis of a-SiGe:H alloys thin films showed that the sub-bandgap absorption $\alpha(h\nu)$ spectra of a-SiGe:H alloys shift to lower photon energy with increasing in GeH_4 flow rate. The optical bandgap of a-SiGe:H alloy decreased non linearly from 0.94 eV – 0.75 eV with increasing in GeH_4 flow rate from 2.5 sccm – 25 sccm. The photo-sensitivity (σ_{ph}/σ_d) of a-SiGe:H thin films were improved as the optical bandgap (E_{opt}) increased.

Keywords: *a-SiGe:H, optical bandgap, PECVD, photo-sensitivity.*

1. Introduction

During the last twenty years, hydrogenated amorphous silicon germanium (a-SiGe:H) alloys had been intensively investigated and were still a promising candidate for photovoltaic application, especially as the bottom optical absorber for double and triple junction solar cells(1). The reason for this was its possibility to control the optical gap in silicon germanium alloys to lower energy by adding Ge to the alloys composition. The best double junction cell that combines United Solar best a-Si:H top cell and the optimized a-SiGe:H bottom cell exhibits initial 11.7 % and stable 9.6% of efficiency(2).

Numerous studies relating the characteristics of a-SiGe:H alloys to germanium content (C_{Ge}) had been performed. For example, the optical bandgap (E_{opt}) of a-SiGe:H was previously reported by Folsch *et.al.*(3), have a negative linear dependence on Ge content (C_{Ge}). Smith *et.al.*(4), however, found that this relation did not agree with the experimental resulted in the film deposited at different substrate temperature. In our previous study, we obtained that the optical bandgap of a-SiGe:H does not have a linear relation to Ge content, because of the difference in incorporation of Si, Ge, and H into the film(5).

Development of high photosensitive with a dense network structure of narrow bandgap material is one of the important issues in the actualization of high conversion efficiency amorphous silicon based solar cells (6). A network structure of a thin film is principally determined by the energy relaxation process of adsorbed radicals on the growing surface of the film (7). There are two main factors, which cause the low-density network of a-SiGe:H film(6). Firstly, Ge-related adsorbed radicals have smaller surface diffusion coefficient than Si-related adsorbed radicals on the growing surface. Secondly, H-Ge bonding is thermally evolved at lower temperatures compared to H-Si bonding. In other words, the opto-electronic properties of a-SiGe:H are strongly depend on the [Ge]/[Si] atomic ratio. Beside that, the deposition parameters are also essential in determining films properties.

Several groups have tried to prepared hydrogenated amorphous silicon germanium (a-SiGe:H) alloys from a SiH_4/GeH_4 starting gas mixture(1,5,8). The quality of such prepared alloys, however, relatively poor in comparison with a-Si:H film, since a high density of Ge dangling bonds ($>10^{17}$ cm^{-3}) due to the preferential attachment of H to Si(9).

Thin film silicon based materials are obtained from a large variety of deposition techniques, which produce material from amorphous to polycrystalline. The most common technique for preparing a-Si related material and a-SiGe:H is Plasma Chemical Vapor Deposition (Plasma-CVD), and a-SiGe:H has been deposited from a gas mixture of SiH_4 / GeH_4 with H_2 dilution(10).

In this paper, we report our study on the opto-electronic properties of hydrogenated amorphous silicon-germanium (a-SiGe:H) alloys with different in GeH_4 flow rate grown by Plasma Enhanced Chemical Vapor Deposition (PECVD) method at low substrate temperature.

2. Experiment

The hydrogenated amorphous silicon-germanium (a-SiGe:H) samples were prepared by a PECVD reactor from a gas mixture of silane (SiH_4) and germane (GeH_4) diluted 10% in hydrogen (H_2) as source gasses. Decomposition of source gasses was achieved by a 13.56 MHz radio frequency (RF) generator, which produces plasma between RF electrode and substrate electrode. The samples were deposited on Corning glass #7059. Substrate temperature was kept at 200 ^{0}C, as measured by a thermocouple attached to substrate holder. The typical deposition conditions are shown in Table 1.

Table 1. Deposition conditions of a-SiGe:H film

Item	Conditions
Substrate temperature	200 ^{0}C
Reaction pressure	400 mTorr
RF power	50 Watt
RF frequency	13.56 MHz
Gas flow rate:	
SiH_4	70 sccm
GeH_4	2.5 – 25 sccm

The optical properties of the films were found by UV-VIS-NIR measurement. The absorption coefficient (α) was calculated from transmittance spectra obtained by UV-VIS-NIR measurement using relation,

$$\alpha = -\frac{1}{d}\ln T(\lambda) \qquad (1)$$

where d and T(λ) denote the thickness of the film and transmittance as a function of photon wavelength, respectively. The optical bandgap (E_{opt}) was determined using Tauc's plot method from hν versus $(\alpha h\nu)^{1/2}$, where hν denote the photon energy. Dektak IIA was used to measure the thickness of the films. The electrical properties (dark- and photo-conductivity, σ_d and σ_{ph}) were then obtained by current-voltage (I-V) measurement using two points (coplanar) method.

3. Results and Discussion

One of the attractive features of a-SiGe:H alloys is due to the possibility of changing in the optical properties of these material with composition to match the absorption to the solar spectra. Figures 1 (a-d) show the absorption spectra for a series of a-SiGe:H thin films of different GeH_4 flow rate obtained by UV-VIS-NIR measurement.

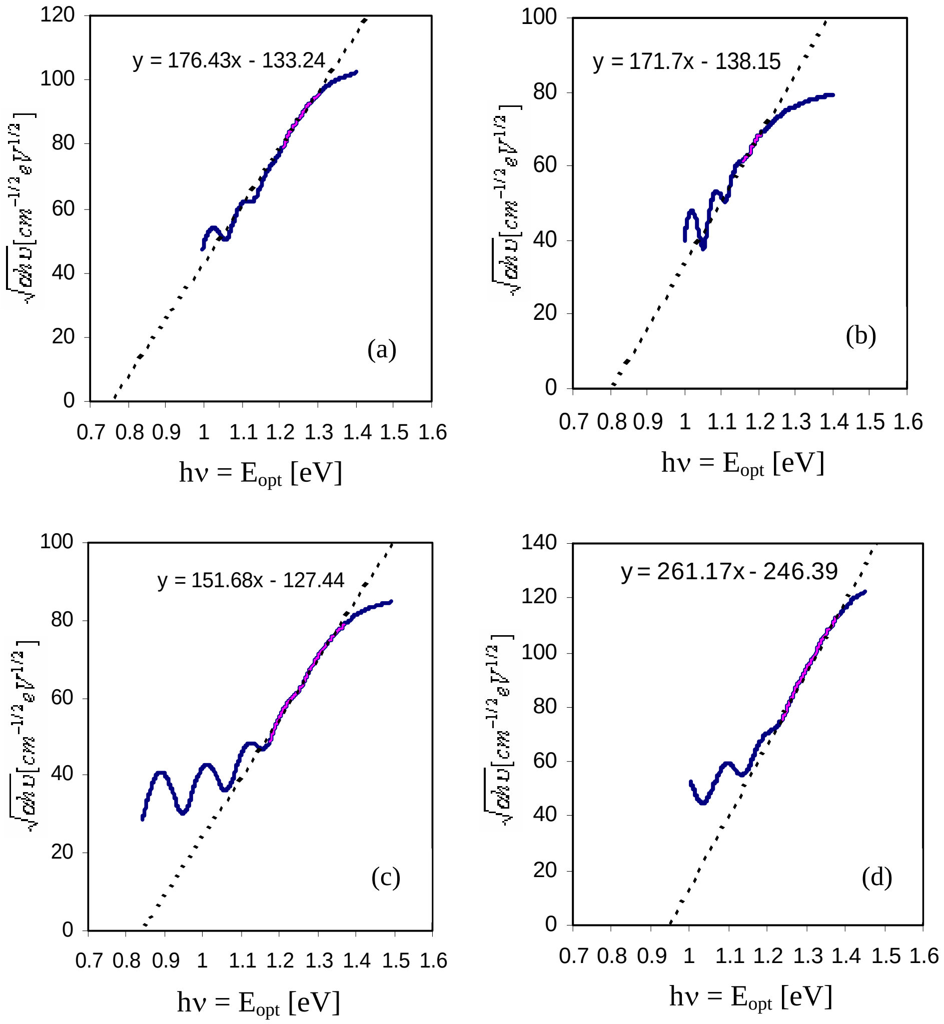


Figure 1. Absorption spectra and determination of the optical bandgap of a-SiGe:H films. (a) Q_{GeH4} = 25 sccm, (b) Q_{GeH4} = 20 sccm, (c) Q_{GeH4} = 12.5 sccm, and (d) Q_{GeH4} = 2.5 sccm

The absorption edges are observed to shift smoothly to lower photon energy and the sub bandgap absorption increase with increasing in GeH_4 flow rate or Ge content. The slope of absorption edges exhibits exponential portion, which decreases with increasing in GeH_4 flow rate. This tendency was due to enhancement of disorder in film or defect density and increasing in the width of the valence band tail. Some oscillatory behavior raised in the absorption spectra caused by optical interference effects in thin films.

The characteristics of amorphous silicon (a-Si) based solar cells are seriously affected by the optical bandgap of photovoltaic material 7). The conventional approach for determining of optical bandgap by using Tauc's plot method via Tauc's relation,

$$(\alpha h\nu)^{1/2} = B(h\nu - E_{opt}) \tag{2}$$

where the optical bandgap is obtained by extrapolating the plot of $(\alpha h\nu)^{1/2}$ to zero ordinate ($h\nu$) as shown in figures 1 (a-d).

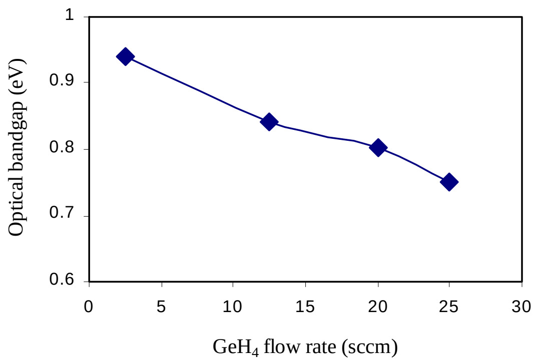


Figure 2. The optical bandgap (E_{opt}) of a-SiGe:H alloys films as a function of GeH_4 flow rate.

Figure 2 shows optical bandgap (E_{opt}) versus GeH_4 flow rate (Q_{GeH4}) for samples in which Q_{SiH4} was constant of 70 sccm. The Q_{GeH4} was varied in the range of 2.5 sccm to 25 sccm. As expected, the optical bandgap decreases from 1.27 to 1.07 eV with increasing in Q_{GeH4}. E_{opt} does not have linear relation to Q_{GeH4}, because of the difference in incorporation of Si, Ge, and H into the film. Without taking into account the existence of atomic vacancies or void, and the transition of the film rigidness caused by the difference in hydrogen content (C_H), the narrowing of E_{opt} with germanium content (C_{Ge}) due to the Ge-Ge (1.63 eV) or Si-Si (1.83 eV) bonds are weaker than Ge-H (2.99 eV) or Si-H (3.35 eV) bonds10).

The main problem of a-SiGe:H thin film is its deterioration of electronic properties as the optical bandgap reduces with increasing in Ge content. It is important to reveal the criteria in improving the quality of material. However it is more difficult than a-Si:H due to complicated microstructure of a-SiGe:H. The network of a film is determined by its surface growing process and a low defect density is obtained when radical with high surface diffusion coefficient (SiH_3 and GeH_3) are used as precursor.

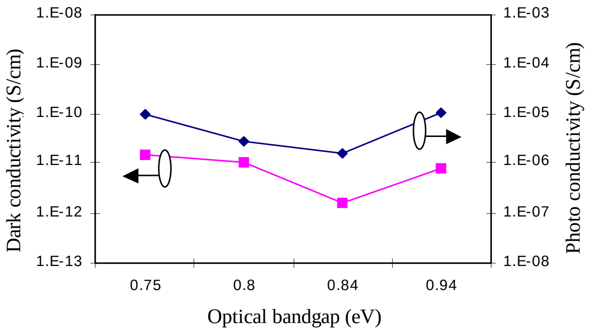


Figure 3. Dark and photo-conductivity of a-SiGe:H alloys thin films as a function of the optical bandgap.

Figure 3 shows the dark and photo-conductivity of a-SiGe:H alloys thin films as a function of the optical bandgap. It has been observed that the σ_d and σ_{ph} of the films drastically decrease in the region of E_{opt} 0.84 eV, that is probably due to the preferential attachment of H atom to Si, resulting the creation of a high density of Ge dangling bond. For optimized a-SiGe:H film having E_{opt}=0.94 eV, σ_{ph} is extremely high. This might be due to a low defect density in material.

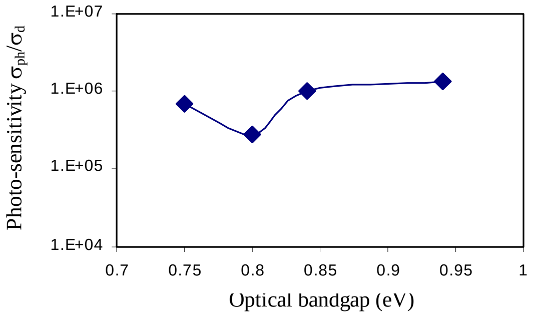


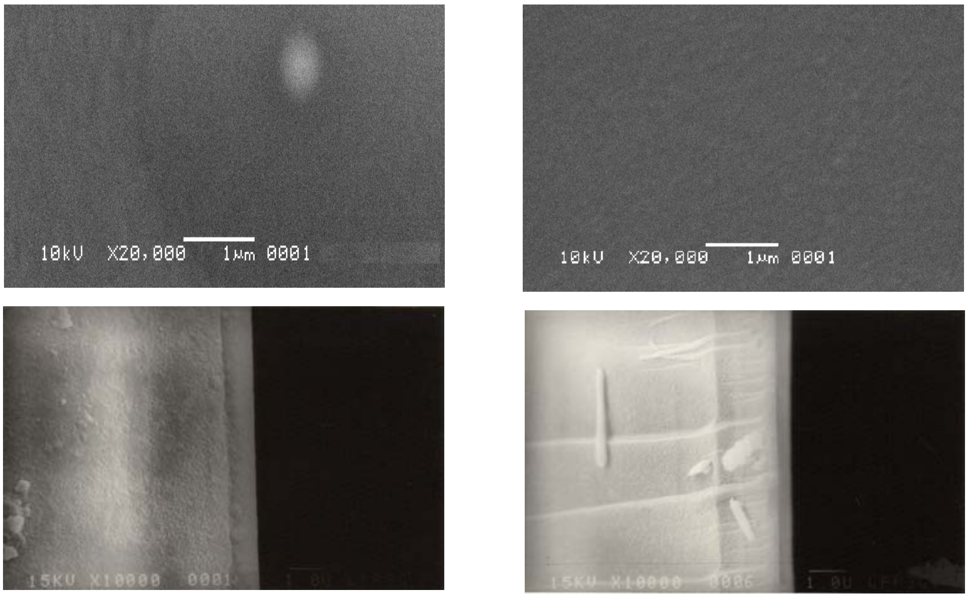
Figure 4. Photo-sensitivity of a-SiGe:H alloys thin films as a function of the optical bandgap.

Although the σ_{ph} does not have a linear relation with increasing in the optical bandgap, in this study it has been found that the photo-sensitivity (σ_{ph}/σ_d) of a-SiGe:H was improved as the optical bandgap (E_{opt}) increases as shown in figure 4. This improvement is probably considered to originate from a higher density network.

Figures 5 (a) and (b) show scanning electron microscopy (SEM) photograph of the surface and cross section of a-SiGe:H thin films deposited with Q_{GeH4} of 25 sccm and 2.5 sccm, respectively. From this photograph, it might be concluded that both a-SiGe:H films are amorphous. The thickness (deposition rate) of a-SiGe:H film increases with increasing in Q_{GeH4}, because of Ge atoms are more preferentially incorporated into the growing surface from gas mixture plasma than Si atoms.

4. Conclusion

We have studied the optical properties of a-SiGe:H film deposited by PECVD method using SiH_4 and GeH_4 gas mixture. It has been found that the optical response of a-SiGe:H films at near infrared (NIR) region. Sub-bandgap absorption $\alpha(h\nu)$ spectra of a-SiGe:H alloys



(a) (b)

Figure 5. SEM photograph of the surface and cross section of a-SiGe:H thin films. (a) $Q_{GeH4} = 25$ sccm and (b) $Q_{GeH4} = 2.5$ sccm.

shift to lower photon energy with increasing in GeH_4 flow rate, while the SiH_4 was kept constant. The optical bandgap of a-SiGe:H alloy decreases non linearly from 0.94 eV – 0.75 eV with increasing in GeH_4 flow rate from 2.5 – 25 sccm, because of the difference in incorporation of Si, Ge, and H into the film.The photosensitivity (σ_{ph}/σ_d) of a-SiGe:H was improved as the optical bandgap (E_{opt}) increases.

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