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Substrate Temperature Control of Narrow Band Gap Hydrogenated Amorphous Silicon Germanium for Solar Cells

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Abstract: The effect of substrate temperature control on the characteristics of hydrogenated amorphous silicon germanium (a-SiGe:H) alloys grown by radio frequency Plasma Enhanced Chemical Vapor Deposition (rf-PECVD) method have been investigated. The a-SiGe:H alloy thin films were grown on Corning #7059 glass by using 10% dilution of silane (SiH_4) and germane (GeH_4) in hydrogen (H_2) as source gases. The substrate temperature was varied from 150 to 250^{o}C. The SiH_4 flow rate was fixed at 70 sccm, while the GeH4 flow rate was 1 sccm. The result shows that the optical band gap (E_{opt}) of a-SiGe:H thin film does not have a linear relation to substrate temperature. The highest photo-conductivity of ~10^{-5} S/cm was achieved at substrate temperature of 200°C with the deposition rate of 1 Å/s. It has a correlation with a wider E_{opt}. By applying this film to the a-SiGe:H single-junction p-i-n solar cell, the initial conversion efficiency of 6.8% was obtained under 34mW/cm^2 light illumination.

Introduction

Recently, narrow band gap hydrogenated amorphous silicon germanium (a-SiGe:H) alloy has attracted a great deal of attention and still a promising candidate for solar cell application. The interest comes from the potential of using narrow band gap a-SiGe:H as the bottom cell for double and triple junction solar cells, because its optical band gap can be tailored by changing its composition to match the wavelength of the solar spectrum.

The development of highly photosensitive narrow band gap a-SiGe:H is one of the important issues in obtaining high conversion efficiency amorphous silicon (a-Si) based multi-junction solar cells. Several groups have tried to prepare a-SiGe:H alloys from a SiH_4/GeH_4 starting gas mixture [1,2]. The quality of such prepared alloys however is relatively poor in comparison with a-Si:H film, since there is a high density of Ge dangling bonds ($>10^{17}$ cm^{-3}) due to the preferential attachment of H to Si [3].

To achieve a high efficiency with a-Si:H tandem cell structure, the narrow band gap material should have an optical band gap of less than 1.5 eV [4]. This band gap value is chosen on the basis of good photo electronic properties for narrow band gap material, in most cases an a-SiGe:H alloy. However, the electronic properties deteriorate as the optical band gap is reduced with an increase in Ge content [5]. Although, it is known that the optoelectronic properties of a-SiGe:H is strongly dependent on the [Ge]/[Si] atomic ratio and H content, the deposition parameters such as substrate temperature and the deposition rate are also essential in determining H content and film properties [6]. Ge incorporation in the film is effected by substrate temperature (T_S). This may be attributed to the variation of sticking coefficient of GeH_3 radicals with T_s [7].

A network structure of a thin film is principally determined by the energy relaxation process of adsorbed precursors on the growing surface of the film [3,8,9]. Therefore, in the film formation process for obtaining highly photosensitive material with a dense network structure, the distance over which precursors can diffuse on the growing surface should be long. A longer surface diffusion distance (l) of radicals can be achieved either by its larger surface diffusion coefficient (D_s) or a longer staying time (τ_S) on the surface. This relation is expressed by

$$l = \sqrt{2D_s \tau_s} \qquad (1)$$

with $D_s = \nu a_0^2 \exp(-E_s / kT)$ (2)

where ν is the vibration frequency of radicals, a_0 the jump distance, and E_s the activation energy for the site jumping [3,8].

In this paper, the effect of substrate temperature on the characteristics of the a-SiGe:H thin films deposited by radio frequency Plasma Enhanced Chemical Vapor Deposition (rf-PECVD) method are presented.

Experimental

The a-SiGe:H thin films were grown on Corning #7059 glass by an rf-PECVD reactor from a gas mixture of silane (SiH_4) and germane (GeH_4) 10% diluted in hydrogen (H_2). The schematic diagram of our rf-PECVD reactor is shown in Figure 1. Decomposition of source gasses was achieved by an rf-generator, which produces plasma between the rf electrode and substrate electrode. The substrate temperature was varied from 150 to 250°C, as measured by a thermocouple attached to the substrate holder. The typical deposition conditions are shown in Table 1.

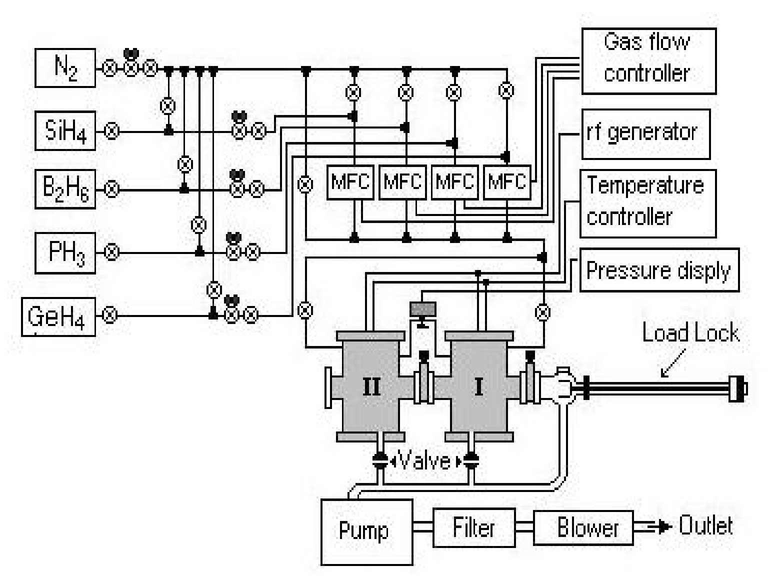

Figure 1. The schematic diagram of the rf-PECVD reactor.

Table 1. Deposition conditions of the a-SiGe:H films.

Item	Conditions
Substrate temperature	150 - 250 ^{0}C
Reaction pressure	500 mTorr
rf power	30 Watt
rf frequency	13.56 MHz
Gas flow rate:	
SiH_4	70 sccm
GeH_4	1 sccm

The optical absorption coefficient (α) were calculated from transmittance spectra obtained by UV-VIS-NIR measurement and the optical band gap (E_{opt}) was determined using Tauc's plot method from hν versus $(\alpha h\nu)^{1/2}$, where α and hν denote the optical absorption coefficient and photon energy, respectively. Dektak IIA was used to measure the thickness of the films. The photo-conductivities of these films were found by using two point probe (coplanar) method.

Results and Discussion

Figure 2 shows the absorption spectra for a series of the a-SiGe:H thin films deposited at different substrate temperature. The absorption edges of the a-SiGe:H thin films are observed to shift smoothly to higher photon energy and the sub band gap absorption decreases with an increase in substrate temperature from 150°C to 200°C. For the films deposited at the substrate temperature from 200°C to 250°C, the absorption edges shift smoothly to lower photon energy and the sub band gap absorption increases. Optical interference effects in thin films cause some oscillations raised in the absorption spectra. From the absorption coefficient as shown in Figure 1 it might be concluded that the a-SiGe:H alloy thin films still have amorphous structure.

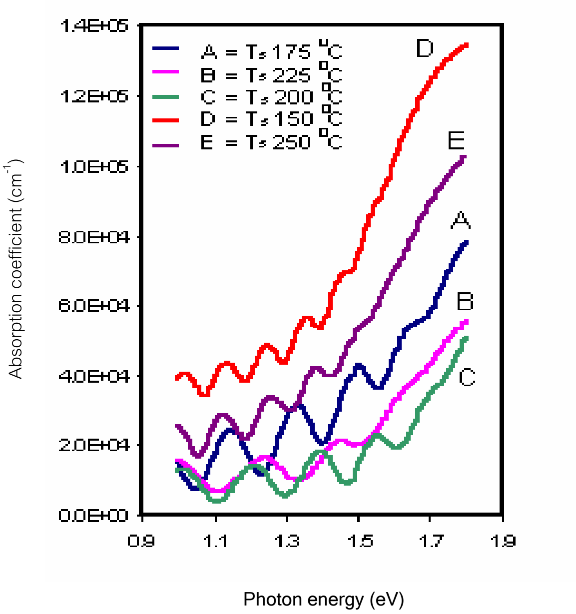

Figure 2. The absorption coefficient curve for a series of the a-SiGe:H films deposited at various substrate temperature.

The optical band gap (E_{opt}) of the a-SiGe:H thin films increased from 1.20 eV to 1.39 eV with an increasing in substrate temperature from 150°C to 200°C and decrease to 1.26 eV at the substrate temperature of 250°C as shown in Figure 3. On the other hand, the E_{opt} of a-SiGe:H thin films does not have a linear relation to substrate temperature, because of the difference in incorporation of Si, Ge, and H atoms into the films. The increase in the E_{opt} at substrate temperature of 200°C is probably due to decreasing Ge content or increasing H content.

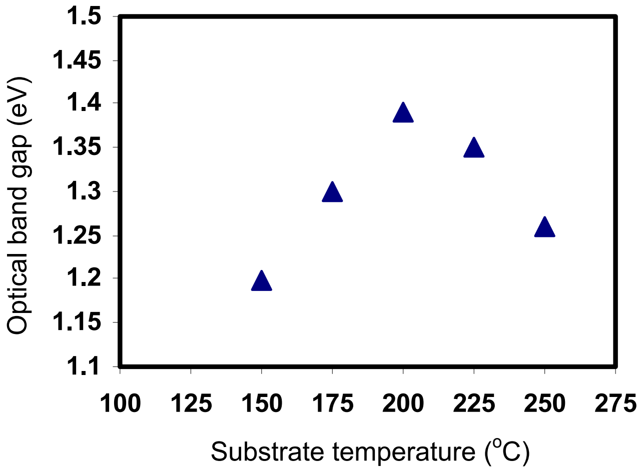

Figure 3. The optical band gap of the a-SiGe:H thin films as a function of the substrate temperature.

Figure 4 shows the deposition rate of the a-SiGe:H films as a function of substrate temperature. The deposition rate increase from 0.65 to 1.06 Å/s with an increase in the substrate temperature from 150°C to 250°C. The substrate temperature has a strong correlation with the reactivity of adsorbed radicals on the growing surface. At a lower substrate temperature, the SiH_3 or GeH_3 radicals contribute to the films growth through a bimolecular reaction. A higher substrate temperature makes other radicals such as SiH_2 or GeH_2 easily stick to the surface through an insertion reaction, therefore the deposition rate increases.

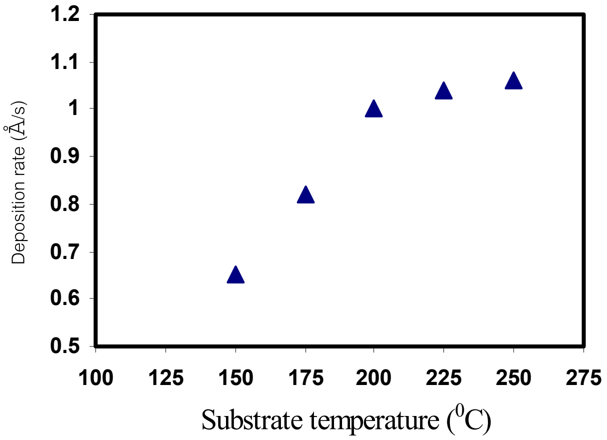

Figure 4. The deposition rate of the a-SiGe:H thin films as a function of substrate temperature.

The main problem of the a-SiGe:H thin film is its deteriorating electronic properties due to the alloy composition. It is important to reveal the criteria for improving the quality of material. However it is more difficult than for a-Si:H due to the complicated microstructure of a-SiGe:H. The network of a film is determined by its surface growing process and a low defect density obtained when radicals with high surface diffusion coefficient (SiH_3 and GeH_3) are used as precursor. From eq. (2), it is understood that a higher surface temperature results in larger surface diffusion coefficient (D_s), but the maximum temperature for producing a large D_s is limited by the H-coverage factor on the growing surface. On the other hand, the improvement of conductivity by increasing the substrate temperature is limited. In this research, the highest photo-conductivity of ~10^{-5} S/cm was achieved at substrate temperature of 200^{o}C with the E_{opt} and the deposition rate of

1.39 eV and 1 Å/s, respectively, which have a strong correlation with the lowest Ge content or a lower defect density in material as shown in Figure 5.

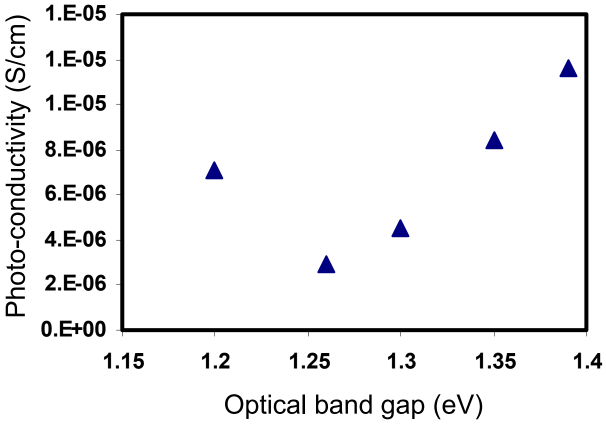

Figure 5. Photo-conductivity of the a-SiGe:H thin films as a function of the optical band gap.

The quality of a-SiGe:H alloys however was relatively poor in comparison with the a-Si:H film, since there was a high density of Ge dangling bonds (>10^{17} cm^{-3}) due to the preferential attachment of H to Si [8)]. The highest photo-conductivity was obtained at the wider E_{opt}, where the wider E_{opt} has a strong correlation with the lowest Ge content. The improvement of photo-conductivity might be due to a low defect density in the material.

The a-SiGe:H single-junction p-i-n solar cell was then deposited on a transparent conductive oxide (TCO) coated glass substrate. The cell consisted of a TCO/p(a-Si:H)/i(a-SiGe:H)/n(a-Si:H)/metal structure. The thickness of the i-layer was 3000 Å, while the thickness of p- and n-layers were 150 and

200 Å, respectively. Under 34mW/cm^2 light illumination, it had the open circuit voltage (V_{oc}) and the short circuit current (J_{sc}) of 0.615 V and 15.48 mA/cm^2, respectively. We achieved an initial conversion efficiency of 6.8%.

Conclusion

We have studied the characteristics of the a-SiGe:H films deposited by PECVD method at various substrate temperature using SiH_4 and GeH_4 gas mixture. It has been found that the E_{opt} does not have linear relation to substrate temperature. The deposition rate increased from 0.65 to 1.06 Å/s with an increase in substrate temperature from 150°C to 200°C. In this research, we successfully obtained a good quality of a-SiGe:H thin film with photo-conductivity of ~10^{-5} S/cm deposited at substrate temperature of 200°C. By applying this film to the a-SiGe:H single-junction p-i-n solar cell, we obtained the initial conversion efficiency of 6.8% under 34mW/cm^2 light illumination.

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