RAMAN AND IR STUDY OF NARROW BANDGAP A-SIGE AND μC-SIGE FILMS DEPOSITED USING DIFFERENT HYDROGEN DILUTION

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ABSTRACT

Hydrogenated amorphous silicon-germanium (a-SiGe:H) films and n-i-p solar cells near the threshold of microcrystalline formation have been prepared by plasma enhanced chemical vapor deposition (PECVD) with a fixed germane to disilane ratio of 0.72 and a wide range of hydrogen dilution R_H=(H_2 flow)/(GeH_4+Si_2H_6 flow) values of 1.7, 10, 30, 50, 120, 180 and 240. The effects of R_H on the structural properties of the films were investigated using Raman scattering and Fourier transform infrared (FTIR) absorption spectroscopy. It is found that H dilution causes the H content, especially that in SiH_2 configuration, in a-SiGe:H films to decrease and finally leads the films through amorphous to microcrystalline transition. The onset of the phase transition occurs at R_H about 180, and the crystalline formation begins first in the Si-rich region. Light soaking tests on the solar cells demonstrate that the devices with higher R_H exhibit higher stabilized efficiency after 1000 hours of 1 sun light soaking.
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1. INTRODUCTION

Narrow band gap a-SiGe:H alloy has attracted a great deal of attention for application in the tandem and triple-junction solar cells, because its optical band gap can be tailored by changing the Ge content to match longer wavelengths of the solar spectrum. However, as the Ge content increases and the bandgap decreases, the electronic and structural properties of the films tend to be inferior. Although in recent years the defect density in a-SiGe:H films has been much suppressed by e.g. H-dilution [1], cathode deposition [2], and using disilane-germane mixture without H dilution [3] in PECVD process, the further improvement in the film quality has been a challenging issue in the research and development of a-Si:H based solar cells. In the previous reports we performed a systematic investigation of the effects of Ge content [4] and H dilution [5] on the electrical and optical properties of a-SiGe:H films. In this paper we report the impact of H dilution on the structural properties of a-SiGe:H films and n-i-p solar cells near and above the threshold of crystallinity.

2. EXPERIMENTAL

The a-SiGe:H films, approximately 0.5 μm thick, were deposited on 7059 glass, crystalline silicon (c-Si) wafer and stainless steel (SS) substrates using rf (13.56 MHz) PECVD in a ultrahigh-vacuum, multi-chamber, load-locked deposition system. A gas mixture of disilane, germane and hydrogen was used with a fixed germane to disilane ratio of 0.72 and a varying hydrogen dilution ratio R_H of 1.7, 10, 30, 50, 120, 180 and 240, which is defined as the ratio of gas flows of [H_2] to [Si_2H_6] + [GeH_4]. The germane to disilane ratio is the same as what we typically use for the i-layer in the narrow-bandgap bottom cell of our standard triple-junction solar cells [6]. FTIR absorption measurements were taken for samples on c-Si substrates to obtain information on the H content and bondings. In order to analyze the structural properties, Raman scattering spectra were recorded from the films on 7059 glass and n-i-p cell devices on stainless steel, upon the excitation of an argon laser with 488nm wavelength.

Single junction n-i-p solar cells using these a-SiGe materials as the i-layers were deposited on SS substrates without the use of a back-reflector. I-V measurements were taken under a Xe-lamp solar simulator under AM1.5 spectrum. Light soaking was performed under one-sun light intensity using a metal halide lamp. The light intensity is maintained at such a level that a reference Si solar cell generates the same current as it does under a Xe-lamp simulator.

3. RESULTS AND DISCUSSIONS

3.1 FTIR ABSORPTION SPECTRA

The FTIR absorption spectra of seven a-SiGe:H samples are plotted in figures 1(a) and 1(b) with a varying H-dilution R_H = 1.7 (GD419), 10 (GD420), 30 (GD422), 50 (GD423), 120 (GD424), 180 (GD449) and 240 (GD450), respectively. The arrangement of the spectra in these figures is in the sequence from top to bottom with R_H increasing. Fig. 1(a) shows the IR spectra ranging from 400 to 800 cm^{-1}. It is seen from this figure that a prominent peak appears at about 560-640 cm^{-1} region, which is assigned to the bending vibration of Si-H and Ge-H bonds. As R_H decreases from 1.7 to 240, the peak intensity is monotonically decreased, indicating that the

hydrogen content (C_H) in the films descends with increasing H dilution, while its peak position is not obviously affected. However this peak position has a small red shift, due to the existence of Ge-H bonds in the a-SiGe:H films, in respect to the bending mode of Si-H bonds in a-Si:H at 640 cm^{-1}. This is similar to the earlier results in the literature [7], that reported the wagging or rocking modes of Si-H bonds gradually shifting from 640 cm^{-1} to 560 cm^{-1}, as the Ge relative content increased from 0 to 1.

H_2* complexes in the boundaries between microcrystallites [8].

The influences of H-dilution on the hydrogen content C_H is also illustrated in Fig.2, which was derived from the IR absorption coefficient of the Si-H bending mode in Fig. 1(a). It shows that C_H decreases as R_H increases, except one point corresponding to the phase transition region R_H=120, where an anomalous increase in C_H was found. This is similar to the observation in a-Si:H when deposited under high H-dilution to the phase transition region [9].

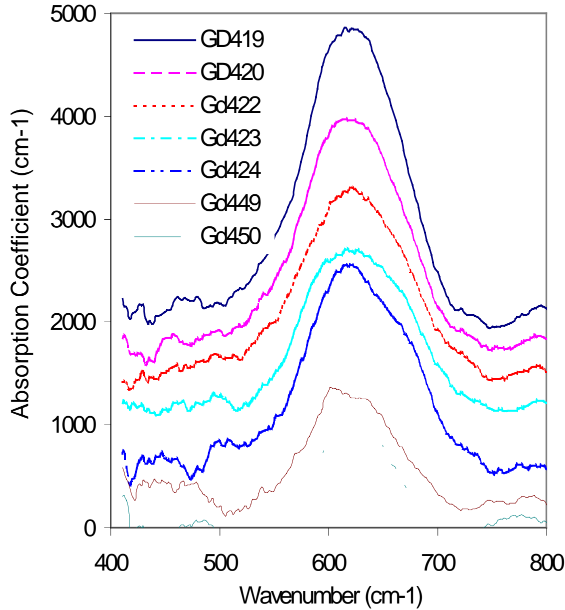

Fig. 1(a) FTIR absorption spectra of a-SiGe:H films in the range from 400 to 800 cm^{-1}. The IR spectra were taken from the samples deposited under H-dilution R_H = 1.7 (GD419), 10 (GD420), 30 (GD422), 50 (GD423), 120 (GD424), 180 (GD449) and 240 (GD450), respectively

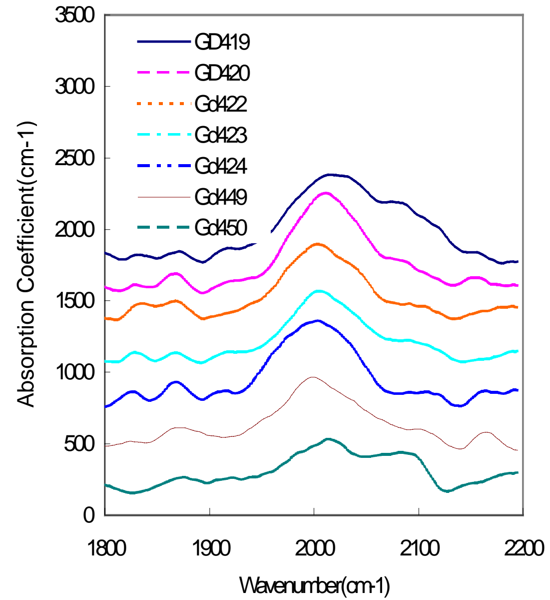

Fig. 1(b) FTIR absorption spectra of a-SiGe:H films in the range from 1800 to 2200 cm^{-1} (b). The IR spectra were taken from the same samples as in Fig. 1(a).

Figure 1(b) shows the IR spectra ranging from 1800 to 2200 cm^{-1}. It is seen that a few absorption features appear at about 2090, 2000 and 1872 cm^{-1}, which are respectively assigned to stretching vibrations of SiH_2, SiH and GeH configurations.

It is interesting to note the impact of R_H on the relative intensity of the stretching mode at 2090 cm^{-1}, I_{2090}, which is defined as the ratio of its intensity to that of the peak at 2000 cm^{-1}. As R_H increasing from 1.7 to 120, the relative intensity I_{2090} becomes weaker. This suggests that the relative concentration of SiH_2 configuration in a-SiGe:H films decreases with R_H increasing. But as R_H further increasing from 120 to 240, the relative intensity I_{2090} starts to increase. The dependence of I_{2090} on R_H could be seen more clearly in Fig. 2. This enhancement of I_{2090} at higher R_H is likely correlated with the formation of the microcrystalline phase in the films. We assigned it to

3.2 RAMAN SPECTRA

To clarify the structural variation we performed Raman spectroscopy measurements on the three highest diluted samples. Fig. 3 shows the Raman spectra taken from the front surface of the a-SiGe:H samples deposited on 7059 glass under R_H=120 (GD424), 180 (GD449) and 240 (GD450), respectively. For comparison the Raman spectrum of GD450R taken from the back-side of the sample of GD450 through the glass substrate is also shown in the figure.

It is seen that for the sample of GD424 (R_H = 120) two broad envelops were observed at ~394 and ~260 cm^{-1}, which may correspond to Si-Ge and Ge-Ge vibrations in the amorphous network. In addition, a shoulder at ~476 cm^{-1} was recognized, which should correspond to the TO phonon of a-Si. These results are similar to the earlier report on Raman spectra of a-SiGe:H [7].

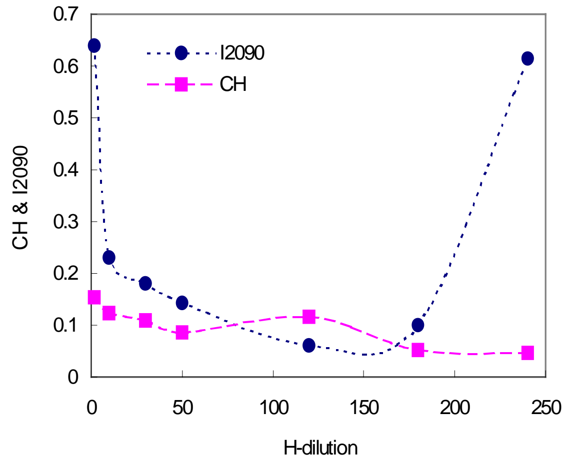

Fig. 2 The relative intensity I_{2090} and hydrogen content C_H of a-SiGe:H samples as a function of H-dilution R_H .

For the sample of GD450, it can be seen clearly that a few crystalline SiGe Raman characteristic peaks appear in the spectrum, including the Si-Si TO phonon at 496cm^{-1}, the Si-Ge vibration at 402cm^{-1} and Ge-Ge TO phonon at 284cm^{-1}. It notes that the Si-Si TO phonon has a red-shift, compared with the c-Si TO phonon. The lowered frequency could be explained in terms of the presence of the larger mass neighboring Ge atoms in the network. These observations are similar to the results reported by Jelenkovic et al [10], who obtained the similar three Raman peaks from the SiGe samples prepared by rf magnetron sputtering followed by a post-annealing crystallization at 550°C.

For Sample GD449, with a little lower H-dilution R=180 than GD450, we find that it locates near the phase transition region from amorphous to microcrystalline state. The crystalline characteristic Si-Si vibration at 498cm^{-1} is just beginning to appear in the Raman spectrum, while the Si-Ge vibration at 394 cm^{-1} keeps nearly unchanged, compared to its amorphous counterpart. The similar situation was also observed in the literature [10], where the crystalline Si-Si Raman peak first appeared in their spectra and then grew in intensity with the post-annealing time (see their Fig.4). It seems that there are phase segregation phenomena occurring in a-SiGe:H films and the crystallization is beginning first from the Si-rich region in the films.

For the Raman spectrum GD450R, taken from the back-side of GD450 through the glass substrate, only one broad peak can be found at 480cm^{-1}, indicating that the film first grown on the glass substrate is still in amorphous state, even though R_H is as high as 240. Crystallization in a-SiGe:H films is thickness-dependent as observed in a-Si:H[11].

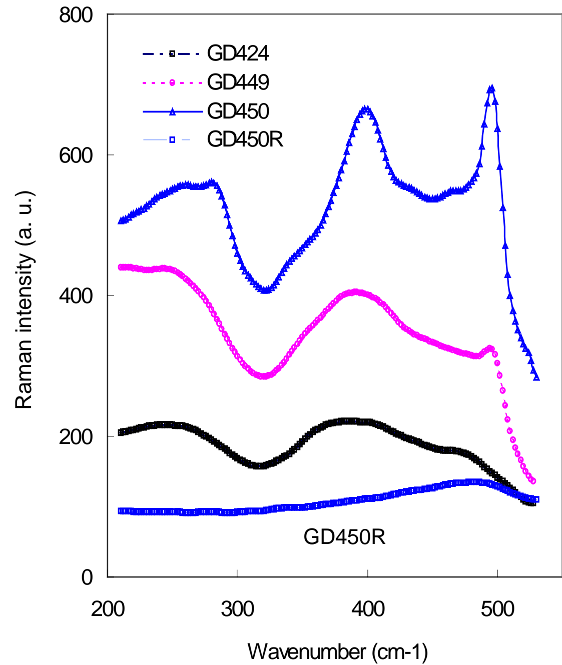

Fig. 3 Raman spectra of high H-dilution a-SiGe:H samples, with R_H=120 (GD424), 180 (GD449) and 240 (GD450), respectively. The Raman spectra were taken from the front surface of the samples, except GD450R, which was taken from the back side of sample GD450 through the glass substrate.

3.3 a-SiGe:H n-i-p solar cells

The structural variation in a-SiGe:H intrinsic layer with H-dilution should be reflected in the performances of constituent solar cells. Table 1 lists the photovoltaic parameters of a-SiGe:H n-i-p devices made with different H dilution R_H [5]. It is seen from the Table that the short circuit current density J_{sc} is roughly unchanged within the experimental error. The fill factor FF seems to increase with H-dilution, but with some fluctuation. The open circuit voltage V_{oc} increases from 0.64 V to 0.67 V with R_H up to 120, before it starts to decrease down to 0.64 V when R_H is further increased to 240. This may be correlated with the fact that small amount of microcrystalline phase is formed at R=240.

Considering the fact that the a-SiGe n-i-p solar cells are deposited on stainless steel and only about 170nm thick, we also performed Raman scattering measurements on the solar cells. For the sample GD451 with intrinsic layer deposited under R_H=180, the obtained Raman spectrum shows a main peak at ~480 cm^{-1} and a small shoulder at ~ 500cm-1, which could be respectively assigned to the Si-Si TO phonon in amorphous and crystalline network. This verifies that the sample is indeed at the beginning of the phase transition from amorphous to crystalline state.

Light soaking tests for these a-SiGe:H samples were also performed to understand the effect of R_H on the device stability. The last column of Table 1 shows the degradation under one-sun light soaking at 50 ^oC for 1000 hours. It is found that the degradation is reduced with higher R_H, down from 21% for R_H =10 to 11% for R=120.

Table 1 Performance of a SiGe:H n-i-p devices made with different H dilution R_H.

Device	H dilut	V_{oc}	J_{sc}	FF	Eff	Light Degrad.
No.	R_H	(V)	(mA/cm^2)	(%)	(%)	(%)
GD429	1.7	0.638	16.2	53.8	5.54	
GD428	10	0.64	17.7	53.1	6.02	20.9
GD425	30	0.656	17.4	59.1	6.76	21.6
Gd426	50	0.662	17.2	55	6.25	14.2
GD427	120	0.669	17	54.8	6.25	11.4
GD451	180	0.656	18.1	56	6.65	--
GD452	240	0.636	18.5	55.8	6.55	--

4. CONCLUSION

We have deposited a series single-layer films and n-i-p solar cells using narrow bandgap a-SiGe:H materials deposited via PECVD using different H-dilution ranging from R_H=1.7 to 240. Samples with higher R_H value showed lower amounts of H incorporated into the films, especially in the SiH_2 configuration, and exhibited higher light soaking stability. The onset of the phase transition from a-SiGe:H to µc-SiGe:H occurs at about R_H=180. The results from the films and devices deposited using different H-dilution suggest that high H dilution up to 120 could be used to deposit a-SiGe:H films and devices with improved light stability.

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