Hot-Wire Deposition of Hydrogenated Nanocrystalline SiGe Films for Thin-Film Si Based Solar Cells

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ABSTRACT

Hydrogenated nanocrystalline silicon germanium (nc-SiGe:H) is an interesting alternative material to replace hydrogenated nanocrystalline silicon (nc-Si:H) as the narrow bandgap absorber in an a-Si/a-SiGe/nc-SiGe(nc-Si) triple-junction solar cell due to its higher optical absorption in the wavelength range of interest. In this paper, we present results of optical and structural investigations of nc-SiGe:H thin films made by hot-wire chemical vapor deposition (HWCVD) with a coil-shaped tungsten filament and with a disilane/germane/hydrogen gas mixture. The optical band gaps of a-SiGe:H and nc-SiGe:H thin-films, which are deposited with a same disilane/germane /hydrogen gas mixture ratio of 3.4/1.7/7, are about 1.58 eV and 2.1 eV, respectively. The nc-SiGe:H thin-film exhibits a larger optical absorption coefficient by about a factor of 2 ~ 4 in the 600-900nm range than nc-Si:H thin-film. Therefore, a thinner nc-SiGe:H layer, ~ 500nm thick, may be sufficient for the narrow bandgap absorber in an a-Si based multiple-junction solar cell.

1. INTRODUCTION

Narrow bandgap amorphous SiGe (a-SiGe:H) alloys have been used as the bottom-cell i-layers in the tandem and triple-junction amorphous silicon based solar cells [1-3]. As an attractive alternative material for a-SiGe:H, hydrogenated nanocrystalline silicon (nc-Si:H), which has stronger absorption than a-SiGe at λ>850nm and is stable under prolonged light exposure, has been successfully used in a multiple-junction solar cell and nc-Si:H based solar cells with efficiencies exceeding 9% have been obtained by several groups [4-6]. However, the absorption coefficient of nc-Si:H is low and a thickness of about 2 μm is required, even with efficient light trapping, for the nc-Si:H absorber in the Si-based thin film solar cells. Furthermore, nc-Si:H is usually prepared at a much lower deposition rate as compared with a-SiGe due to the use of high hydrogen dilution. The combination of minimum thickness required and the low deposition rate translates into a long total-deposition time for the layer and subsequently into a significantly higher capital cost for a manufacturing equipment producing nc-Si:H based solar cells. Two approaches could be used to reduce the total deposition time: one is to increase nc-Si:H deposition rate with new techniques, such as HWCVD, VHF PECVD and microwave PECVD; and the other is to find a nanocrystalline material with higher optical absorption, such as nc-SiGe:H thin-film, thus only a much smaller thickness is needed for narrow bandgap intrinsic absorbing layer.

At the University of Toledo, we investigated nc-SiGe:H films deposited using HWCVD, to find suitable HW deposition conditions for nc-SiGe films as well as deposition conditions for SiGe material containing amorphous/nanocrystalline mixed phases. In this paper, we present results of optical and structural investigations of SiGe films made by HWCVD.

2. EXPERIMENTAL

The SiGe films, approximately up to 1.3 μm thick, are deposited on quartz glass, crystalline silicon (c-Si) wafer and stainless steel (SS) substrates using HWCVD technique with a coil-shaped tungsten filament. Two types of coil-shaped filament with the same filament diameter of 0.75 mm but with different filament length have been used in this study. The coil-shaped filament Type L is typically 100cm long of 0.75 mm diameter tungsten wire wound in a coil approximately 7 mm in diameter, while the coil-shaped filament Type S is only 30 cm long of 0.75 mm diameter tungsten wire wound in a coil approximately 8 mm in diameter. Detailed description of this HWCVD system is given in a previous paper [7].

Gas mixtures with germane/disilane/hydrogen gas mixture ratios R of 3.4/1.7/7, 2.4/1.7/7 and 0/1.7/7 are used for depositing SiGe films. Currently, the ratio R of 3.4/1.7/100 is used for the deposition of a-SiGe:H intrinsic absorbing layer for bottom component cell of a triple-junction a-Si:H based solar cell. The filament temperature T_{fil} is set in the range of 1700 – 2000 °C, while the substrate temperature T_{sub} in the range of 150 – 400 °C. The deposition rates of >28 Å/s for a-SiGe:H film growth and of >8 Å/s for nc-SiGe:H can be easily obtained with this HWCVD system.

The optical and structural properties of as-deposited films are investigated by Vis-NIR transmission

spectroscopy, Raman scattering spectroscopy, X-ray diffraction (XRD) and Fourier transform infrared (FTIR) absorption spectroscopy.

3. RESULTS and DISCUSSIONS

3.1 Optical absorption coefficient of nc-SiGe:H

The optical gaps and absorption coefficients of SiGe films are evaluated from their Vis-NIR transmission data [8]. The optical band gap of nc-SiGe:H made by HWCVD at a disilane/germane/hydrogen gas mixture ratio R of 3.4/1.7/7 is about 2.1 eV. Figure 1 shows the optical absorption coefficient of this nc-SiGe:H film in comparison with the optical absorption coefficients of nc-Si:H film by VHF PECVD and a-Si:H film by RF PECVD. An absorption coefficient of bulk c-Si wafer from the literature [9] is also plotted for comparison. Compared to nc-Si:H thin-film, the nc-SiGe:H film exhibits a higher optical absorption coefficient by about a factor of 2 ~ 4 in the long wavelength range with light energies between 1.1 and 2.4 eV.

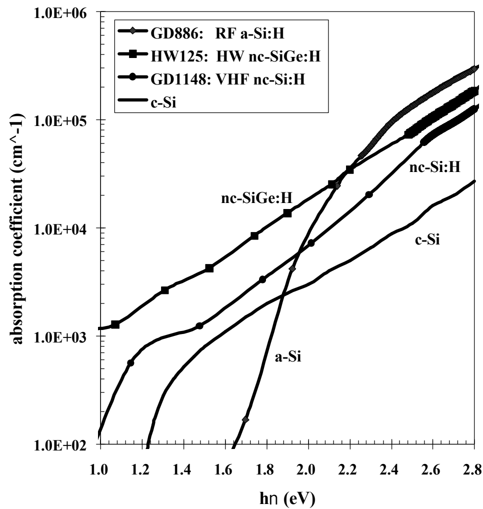

Fig.1. Optical absorption coefficient of nc-SiGe:H film deposited by HWCVD, nc-Si:H film by VHF PECVD, a-Si:H film by RF PECVD and bulk c-Si wafer.

Thus, in stead of nc-Si:H absorbing layer with a thickness of about 2μm, a thin nc-SiGe:H intrinsic layer of a thickness of only about 0.5 μm may be sufficient for generating current. With a deposition rate of 8 Å/s for nc-SiGe:H made in the HWCVD system, a deposition time of about 10 minutes is needed for a nc-SiGe:H layer of 0.5 μm thick. That is an acceptable deposition time for PV mass production.

3.2 Dependence of film crystallinity on different T_{fil}, T_{sub} and gas mixtures

Raman measurements are done on a series of SiGe films. From the Raman spectra as shown in Fig. 2, the Raman characteristic vibrations of dominant nanocrystalline phases could be observed clearly. Crystalline Si-Si TO band near 500 cm^{-1}, crystalline Si-Ge TO band near 400 cm^{-1} and crystalline Ge-Ge TO band near 300 cm^{-1} appear in the Raman spectra. It can be seen that the positions and intensities of the Si-Si, Si-Ge and Ge-Ge Raman peaks are obviously shifted and changed with the disilane/germane/ hydrogen gas mixture ratio R. By comparing the height of the 282 cm^{-1} and 400 cm^{-1} peaks in Fig. 2, it is also observed that the Ge atoms, in the SiGe films with a disilane/germane/hydrogen gas mixture ratio of 3.4/1.7/7, are mostly bonded to Si in the SiGe phase. Only a small fraction of Ge is in a nc-Ge:H clustered phase.

Figure 3 shows the grazing incidence diffraction (GID) X-ray pattern of the as-deposited SiGe film (HW129, see Fig. 2 for deposition conditions) with a film thickness of d = 141 nm. In the GID X-ray spectrum, diffraction at the SiGe planes (111) centered at $2q$ = 28.30°, (220) centered at $2q$ = 46.96° and (311) centered at $2q$ = 55.66° can be seen clearly.

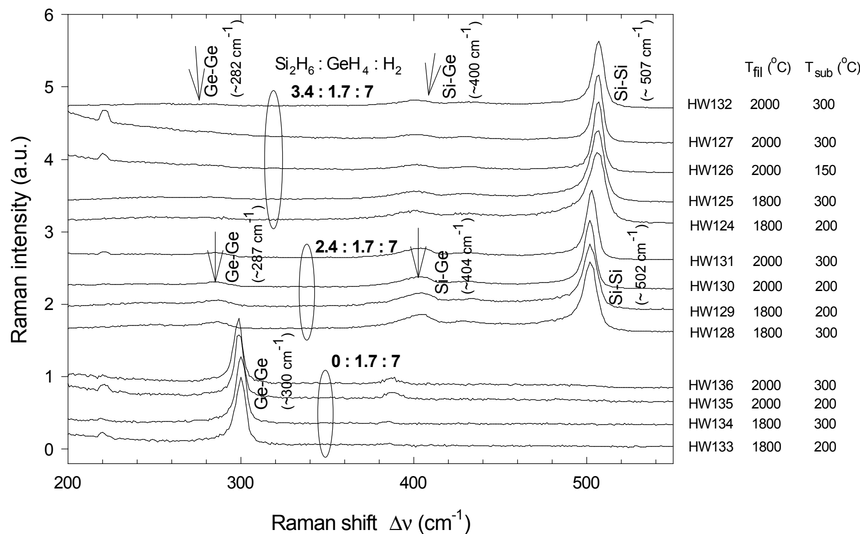

Fig. 2. Raman spectra of SiGe and Ge films deposited with different T_{fil}, T_{sub} and gas mixtures.

By comparing the relative peak heights of (220) and (311) peaks to (111) peak, it can be determined that the crystallites of this SiGe film are randomly distributed. From the X-ray diffraction patterns, the crystallite size $d_{x\text{-}ray}$ can be calculated from the Debye-Scherrer equation [10]. The crystallite size of this SiGe film calculated from the peak (111) is $d_{x\text{-}ray}$ = 17 nm.

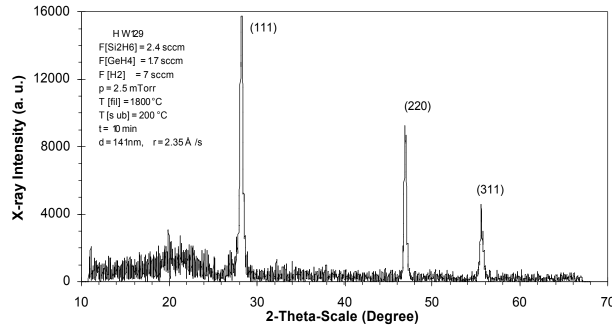

Fig. 3. The GID X-ray spectrum of the nc-SiGe:H film.

3.3 Influence of filament length

The above introduced SiGe and Ge films all have been deposited using the coil-shaped filament Type L with a typically filament length of 100cm. The Raman results show that all these films are of dominant microcrystalline phases with the crystalline volume fraction X_c > 60 % even thought the filament temperature is T_{fil} ~ 1800 °C and the substrate temperature as low as T_{sub} ~150 °C. The FTIR results show that the hot-wire nc-SiGe films have very small hydrogen contents of < 2%.

If the filament is replaced with the coil-shaped filament Type S with a typically filament length of 30 cm, the film structures and deposition rates are greatly changed although the other deposition parameters are maintained at same values. Using filament Type S instead of Type L, one four-depositions run is done at F_{Si2H6} = 3.4 sccm, F_{GeH4} = 1.7 sccm, F_{H2} = 7.0 sccm, t = 15 min and p = 3.1 mTorr by setting T_{sub} = 200 °C and 300 °C, T_{fil} = 1800°C and 2000°C, respectively. The four depositions have a nearly same deposition rate of about 5.7 Å/s. These films have optical band gaps of about 1.58 eV evaluated from Tauc-plot. Raman results show that the four samples are characteristic of nearly 100% amorphous SiGe phase.

Figure 4 shows the FTIR absorption spectra of a-SiGe:H film deposited at F_{Si2H6} = 3.4 sccm, F_{GeH4} = 1.7 sccm, F_{H2} = 7.0 sccm, p = 3.1 mTorr, T_{sub} = 200 °C and T_{fil} = 1800°C for 15 min using the filament Type S. The FTIR spectrum in 400 – 800 cm^{-1} region, as shown in Fig. 4a, has a peak centered at 640 cm^{-1} and a shoulder at 590 cm^{-1} corresponding to Si-H and Ge-H wagging modes respectively. A hydrogen content of about 7.6% is found out in this SiGe film by calculating the area under this curve in 400 – 800 cm^{-1} region. The FTIR spectrum in 1800 – 2200 cm^{-1} region, as shown in Fig. 4b, has a peak centered at 1992 cm^{-1} and a peak at 2086 cm^{-1} corresponding to SiH and SiH_2 stretching modes, respectively. A SiH_2/[SiH+ SiH_2] microstructure ratio R* is determined in this film by calculating the area under the corresponding peaks in 1800 – 2200 cm^{-1} region. FTIR result shows that a hydrogen content of about 7.6% and a R* of 0.43 are found out in these a-SiGe:H films.

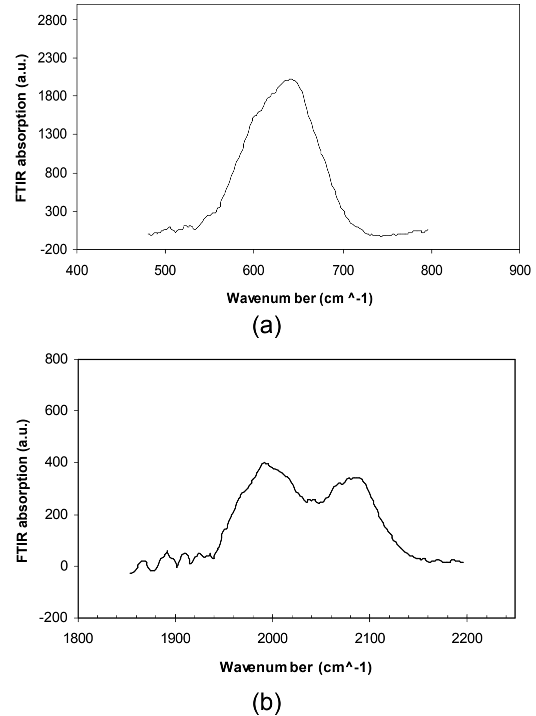

Fig. 4. FTIR spectra of a-SiGe:H film in the region of a) 400 – 800 cm^{-1} and b) 1800 – 2200 cm^{-1}.

4. CONCLUSIONS

The deposition rates of >28 Å/s for a-SiGe:H film growth and of >8 Å/s for nc-SiGe:H can be easily obtained with University of Toledo's HWCVD system. Using a filament of 100 cm long, nanocrystalline SiGe films with crystalline fractions of > 60% and low hydrogen contents of < 2% are preferentially grown in random orientation. Using a short filament with length of 30cm, amorphous films are preferred produced. The optical band gaps of a-SiGe:H and nc-SiGe:H thin-films, which are deposited with a same disilane/germane/hydrogen gas mixture ratio of 3.4/1.7/7, are about 1.58 eV and 2.1 eV, respectively. Compared to nc-Si:H thin-film, nc-SiGe:H thin-film has an lower band-gap and exhibits an greater optical absorption coefficient by about a factor of 2 ~ 4 in the long wavelength range with photon energies between 1.1 and 2.4 eV. Efforts on improving nc-SiGe:H thin-film quality and investigating the usage of nc-SiGe:H thin-film in single- and multi-junction structures are under way.

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