The effects of hydrogen dilution on structure of Si:H thin films deposited by PECVD

Tran Quang Trung 1, Stuchlik Jiri 2, Ha Stuchlikova 2, Le Khac Binh 1, Nguyen Nang Dinh 3, Huynh Kim Khuong 1, Phan Thi Nhu Quynh 1 and Nguyen Thi Huynh Nga 1

1 University of Natural Science HCM, 227 Nguyen Van Cu Str., 5 Distr., Ho Chi Minh City, Vietnam
2 Institute of Physics, Na Slovance 2 CZ-182 21 Prague Praha, Czech Republic
3 College of Technology, VNU, 144 Xuan Thuy, Cau Giay, Hanoi, Vietnam

E-mail: trungvclcr@yahoo.com.sg

Abstract. Si:H thin films were deposited using PECVD method at substrate temperature of 250° C with different hydrogen dilution. Structure investigations and hydrogen concentration estimation were performed using FTIR, Raman and UV-VIS spectroscopy. The IR and Raman spectra show various peak shifting when H dilution is changed. Band gaps of films were evaluated from the strong absorption regions in UV-VIS transmission spectra. The results demonstrate a transition from amorphous to nc/μc structure when hydrogen dilution increased.

Keywords: Plasma-enhanced chemical vapor deposition, hydrogen dilution, a-Si:H, nc/μc-Si:H, para-crystallines.

1. Introduction
Amorphous hydrogenated silicon (a-Si:H) is one of the famous materials for photovoltaics due to its availability in thin film, the high absorption coefficient, and the low cost of manufacturing. However, a-Si:H has some disadvantages such as low conductivity and the instability on light exposure, leading to the degradation of devices in the working environment. In recent years, microcrystalline Si:H (μc-Si:H) is considered as the ideal Si-based semiconductors which can overcome the drawbacks of a-Si:H. Both a-Si:H and μc-Si:H thin films can be deposited by PECVD method in which structures of products are depended on the experimental parameters. It is generally accepted that the crystallinity of thin films is increased with the hydrogen dilution in deposition processes. In this paper, we report our quantitative investigations of this effect. The results in this report are an advantage for preparing thin film PV devices in structures nip or pin with higher efficiency.

2. Experimental
Si:H thin films were prepared using PECVD method with the conventional 13.56 MHz RF plasma. The precursor gases silane (SiH₄) and hydrogen were used as dilution media. Two kinds of substrates (glass and two-side polished silicon) were employed in depositing: samples deposited on glass substrates were used for Raman and UV-VIS measurements whereas those on silicon substrates were for FTIR characterizations. Before depositing, the deposition chamber was desorption at 10⁻⁷ Torr and 250° C for 2 hours in order to reduce the contamination from oxygen and moisture.
To investigate the effects of hydrogen dilution on the films structure, all experimental parameters for various samples were kept constant except for the dilution ratio. The values of RF power, substrate temperature, deposition pressure, and deposition time were 10 W/cm², 250°C, 1 Torr, and 180 minutes, respectively. On the other hand, the dilution ratio R (R = flowrate of H₂ / flowrate of SiH₄) was varied from 1 to 6 in order to investigate the effects of hydrogen on the films structure. In each experiment, the films were deposited both on glass as well as silicon substrates.

Films thickness was measured using Dektak 6M Stylus Profiler. FTIR transmission spectra of films were taken by a Bruker-Equinox spectroscopy in the range 500–6000 cm⁻¹. Raman spectra were investigated using Horiba-Yvon Raman spectrophotometer. UV-VIS transmissions are characterized by a Jasco 530 UV-VIS spectroscopy. The deposition conditions and films thickness are shown in table 1 below.

### Table 1. Experimental parameters of samples.

| Sample | Dilution ratio R | Film thickness (μm) | Average growth rate (A/s) |
|--------|-----------------|---------------------|--------------------------|
| No. 1  | 1               | 3.7                 | 3.42                     |
| No. 2  | 2               | 3.3                 | 3.05                     |
| No. 3  | 3               | 1.8                 | 1.67                     |
| No. 4  | 4               | 0.98                | 0.91                     |
| No. 5  | 5               | 0.8                 | 0.7                      |

#### 3. Results and discussions

3.1. Infrared spectra and hydrogen content

The raw IR transmission data of the film is an accumulation between sinusoidal interference fringes and the strong absorption bands resulted from the vibration of Si-H or Si-O bonds. The interference fringes were eliminated from the spectra by normalizing the transmittances to the absorption-free region (6000-2500 cm⁻¹) and absorption spectra was then calculated from the normalized transmittances using the procedure described in Ref. [1]. Figure 1 represents the calculated absorption spectra of films. In all samples, there are absorption bands at 600-660 cm⁻¹, 800-890 cm⁻¹ and 2000-2200 cm⁻¹ which resulted from dipole vibrations of various SiHₓ groups as well as different vibrational modes for every group [1-4]. The strong bands around 1000 cm⁻¹ were assigned to Si-O vibrations from oxygen contaminations in our films.

The main absorption bands of Si-H bonds show evident alternations with increasing H dilution. The 640 and 880 cm⁻¹ bands tend to low energy side whereas the 2000 cm⁻¹ one shows peak shifting and raising of new peaks in the high energy side when the ratio R is increased. These features of IR spectra are the signs of amorphous – crystalline transition in high dilution depositing conditions [2, 3].

Figure 1b clarifies the alternations of the absorption bands around 2000 cm⁻¹ with increasing H dilution. At R = 1, the main absorption peak appears around 2000 cm⁻¹, which is often assigned to the vibration of Si-H bond in the amorphous matrix. The shoulder which occurred around 2100 cm⁻¹ (when R = 2 and at high H dilution) becomes a peak and a new peak arises at about 2250 cm⁻¹. For higher dilution the peak at 2100 cm⁻¹ is lower while the peak at 2250 cm⁻¹ becomes more pronounced. The peak at 2100 cm⁻¹ is explained as vibration mode of hydrogen bonded to the surface of crystalline phase, i.e. the hydrogen in the grain boundary voids in μc-Si:H [3].
The absorption spectra of the samples on Si substrates. R is the dilution ratio. The peak shifts are emphasized by vertical dashed lines. The alternations of absorption bands around 2100 cm$^{-1}$.

In Ref. [11] the 2125 and 2245 cm$^{-1}$ peaks are assigned to the stretching mode of SiH$_2$ group with one, two or three backbone oxygen atoms. Therefore, at high H dilution, the effects of oxygen contamination are larger. According to our opinion, the peak shifting and raising at the region of 2100 cm$^{-1}$ represents the sum of both oxygen impurity and amorphous – microcrystalline transition.

The hydrogen content of the samples is estimated by using the following formula [2, 3]

$$C_{H,i}(at) = \frac{A_i}{N_{Si} \nu_i} \int \alpha(v) d\nu ,$$

where $\alpha(v)$ is the film absorption coefficient at the wave number $\nu$ and $\nu_i$ stands for the wave number region of vibration, $N_{Si}$ is the atomic density of silicon. For different absorption bands, the proportionality constant $A_i$ takes different values. In many references, the rocking-wagging vibrations of all kinds SiH$_x$ group result in the absorption band around 660 cm$^{-1}$ [1, 3, 5]. In addition, the proportionality constant for 660 cm$^{-1}$ band is independent of the preparation conditions and H content [3]. Therefore, this band was employed to estimate hydrogen content evaluation in our samples. The constant was chosen at 1.6 x 10$^{-19}$ cm$^2$ and the atomic density of Si was taken at the value of the crystalline Si: 5 x 10$^{22}$ cm$^{-3}$ [3]. The evaluated values of H content are shown in figure 2. Due to various reasons, the H content estimated from this method may have an error larger than 15% [3, 4].

**Figure 1.** The absorption spectra of the samples on Si substrates. R is the dilution ratio. The peak shifts are emphasized by vertical dashed lines. The alternations of absorption bands around 2100 cm$^{-1}$.

**Figure 1.** Hydrogen content in the samples as a function of H dilution.
The hydrogen content at first increases with H dilution in the low and medium dilution (R=1-3) and has its maximum at R = 3. From figure 1b it can be observed that when R = 1 or 2, there are only weak shoulders around 2250 cm\(^{-1}\) together with the increasing of the H content. As this shoulder becomes peaks and these peaks get stronger (R > 3), the H dilution also decreases. The maximum at R = 3 can be explained as the “transition region” between \(\mu\)-c-Si:H regime and a-Si:H regime of deposition [3]. When the dilution is higher the H content decreases together with the growth of crystalline phase in the films.

3.2. Raman spectra

In figure 3a, Raman spectra of the samples are shown in comparison with the amorphous lines taken from our other work [9]. The features of Raman scattering lines show that the films are mixtures between amorphous, paracrystalline and crystalline phase of various volume fractions. With increasing H dilution, the main peak shifts gradually to 520 cm\(^{-1}\), demonstrating the transition from amorphous regime to microcrystalline regime.

One can observe in the spectra a broad shoulder at 480 cm\(^{-1}\), which is typically represented for amorphous phase, and the peaks around 505 to 518 cm\(^{-1}\), which can be interpreted as TO scattering form of different kinds of silicon grains. In crystalline silicon, the TO phonon scattering results a sharp peak at 520 cm\(^{-1}\). However, due to the finite grain size and internal stress in thin films, this peak has a slight shift to 518 cm\(^{-1}\) with a wider peak width [7, 10]. Besides, the peak whose position varies from 500 to 510 cm\(^{-1}\) is often assigned to different structures: paracrystalline grains (about 1 nm) [8], wurtzite phase or stacking faults on grain boundaries [7-9]. We therefore decouple the Raman spectra into two Gaussian peaks at 480 and 518 cm\(^{-1}\) and one intermediate peak at 500 - 510 cm\(^{-1}\), in order to evaluate the crystallinity volume fraction in each sample (figure 3b). The position of the intermediate peak \(I_{int}\) is calculated to minimize the error between the experimental and the fitted data.

![Figure 2](image)

**Figure 2.** a) Raman spectra of Si:H thin films (on glass) of H dilution from 1 to 5. The amorphous line is added for the ease of comparison. b) The deconvolution of Raman spectra of sample No.5 and fitted lines from three Gaussian peaks at 480, 508, and 518 cm\(^{-1}\).

The total crystallinity volume fraction is then estimated using the following formula:

\[
X_C = \frac{I_{518} + I_{int}}{I_{518} + I_{508} + I_{480}} \times 100, \tag{2}
\]

where \(I_{480}\), \(I_{int}\), and \(I_{518}\) are the integrated intensities of the corresponding peaks. The reduced integrated intensity of the peaks, the position of the intermediate peak, and the calculated crystallinity volume fractions are shown in figure 4, the volume fractions of the intermediate phase and the crystalline phase are shown together with the calculated position of intermediate peak. The volume fraction of crystalline phase and intermediate phase are estimated by comparing the corresponding peak intensity.
to the sum intensity of three peaks.

![Figure 3](image3.png)

**Figure 3.** Crystallinity volume fraction of samples. The value noted at each point of the black line is the position of the corresponding intermediate peak.

The results demonstrate a transition from amorphous phase to nanocrystalline phase when H dilution is increased through the shifting of position of the intermediate peak and the intensity of crystalline peaks. When $R \leq 4$, the amorphous and the paracrystalline phase dominate film structures but the position of the intermediate peak is shifted gradually to the high energy side. When $R > 4$, the phase transition take places and the volume fraction of the crystalline phase grows strongly, leading to the decrease of the intermediate phase volume fraction. The ambiguous thing here is that in this high dilution condition ($R = 5$), the total crystallinity volume fraction also decreases from 83 to 45%.

### 3.3. UV-VIS transmittances

![Figure 4](image4.png)

**Figure 4.** The UV-VIS transmittances of the samples with different H dilution.

The UV-VIS transmissions of the samples on glass are shown in figure 5. Similar as the case of IR transmission, the UV-VIS spectra are a superposition of the inference fringes and the true transmittances of the material. It is therefore difficult to interpret the absorption coefficients from these spectra without a good optical model which accounts for multiple interferences inside the films. In figure 5, however, the effects if H dilution on the band gap of the material is clear: a film of higher H dilution has absorption edges shifted to the high energy side, which indicates larger band gaps. We therefore perform a band gap estimation using the data in strong absorption region of the spectra (table 2). The band gap increase can be explained by two reasons: 

(i) when the H dilution is increased, the film structure transforms gradually to the crystalline phase, which has a larger band gap than the amorphous one,

(ii) in high H dilution, the oxygen contamination is important, resulting in a large
amount of SiO$_x$ phase. Therefore the band gap increased.

| Samples | Band gap (eV) |
|---------|--------------|
| 1       | 1.8          |
| 2       | 2.1          |
| 3       | 2.5          |
| 4       | 2.8          |
| 5       | 3.0          |

**Table 2.** Estimated band gap values of Si:H samples.

4. Conclusion
In this report, we have investigated the effects of hydrogen dilution on the structures of Si:H thin films. The results show an increasing in crystallinity and a transition region of H content in samples when H dilution rise, which are agreed with other references. However, the larger oxygen contamination together with higher dilution demonstrates that oxygen can attack the deposition process easier in high dilution regimes, leading to a mixture structure between Si:H and SiO$_x$ in the studied films.

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