MICROSTRUCTURE RELATED CHARACTERIZATION OF a-Si:H THIN FILMS PECVD DEPOSITED UNDER VARIED HYDROGEN DILUTION

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Summary We report on the structure and optical properties of hydrogenated silicon thin films deposited by plasma - enhanced chemical vapor deposition (PECVD) from silane diluted with hydrogen in a wide dilution range. The samples deposited with dilutions below 30 were detected as amorphous hydrogenated silicon (a-Si:H) with crystalline grains of several nanometers in size which represent the medium-range order of a-Si:H. The optical characterization confirmed increasing ordering with the increasing dilution. The optical band gap was observed to be increasing function of the dilution.

1. INTRODUCTION

Hydrogenated silicon (Si:H) often enters low-cost and large-area optoelectronics and microelectronics. However, amorphous Si:H (a-Si:H) and microcrystalline Si:H (μc-Si:H) suffer from some bonding disorder at atomic level in comparison to crystalline Si. Main differences originate from Si-H bonds. Many studies demonstrate the decisive role of hydrogen in the formation of a-Si:H and μc-Si:H network. It has been proved that a-Si thin films prepared from silane diluted with hydrogen in PECVD (a-Si:H) exhibit lower degradation during light exposure, the so-called Staebler-Wronski effect [1, 2]. The increase of hydrogen dilution or the film thickness assists the evolution from the amorphous to microcrystalline material. At the boundary between amorphous and microcrystalline silicon, the so-called protocrystalline material is obtained that includes amorphous phase with the medium-range order. The protocrystalline silicon was found to be more stable against light degradation [2]; however, its growth strongly depends on the specific deposition condition, especially hydrogen dilution and the film thickness. Therefore deposition conditions play a key role in obtaining suitable solar cell material. Therefore, a thorough characterization of Si:H thin films for solar applications is of vital importance.

This work reports on experimental studies of the of a-Si:H and μc-Si:H thin films deposited by PECVD from hydrogen diluted silane. The influence of dilution on structural and optical properties was investigated. It was found out that at dilutions between 30 and 33 the phase transition from amorphous to microcrystalline silicon occurs. Just below the dilution of 33 we expect the deposition of the protocrystalline Si. Infrared (IR) absorbance analysis offered knowledge about the microstructure, namely about the bonding of hydrogen in the Si:H network of Si:H.

2. EXPERIMENTAL

A series of 9 undoped a-Si:H films (Table 1) was deposited at the Delft University of Technology, the Netherlands, on clean Corning 1737 glass substrates by 13.5 MHz rf excited parallel plate PECVD industrial deposition system (rf power 13.5 W) especially for extensive studies of short- and medium-range order connected with the photodegradation studies [2, 3].

The hydrogen (H_2) to silane (SiH_4) gas flows define the dilution ratio $R = (H_2)/(SiH_4)$ that was varied from 5 to 40. A reference sample was deposited using pure silane ($R = 0$) with no additional hydrogen. To avoid the thickness-dependent deposition of Si:H, the thickness of all films was kept constant at approximately 300 nm.

XRD analysis was carried out on an automatic X-ray powder diffractometer X´pertPro with a thin film attachment. The Cu X-ray tube was used (the X-ray wavelength of 0.154 nm). The incident angle of the X-ray beam (0.5 degrees) was kept constant during the XRD measurements. The diffraction angle 2ϑ varied from 15 to 70 degrees.

The measurements of the optical properties were performed on the Specord 210 spectrophotometer in the broad UV-Vis-NIR spectral region of 190 – 1100 nm. Infrared absorbance spectra were recorded with the Nicolet 380 FTIR spectrometer in the range of 400 – 4000 cm^{-1} with the single-bounce ATR (attenuated total reflection) sampling accessory with diamond element and trapezoidal silicon crystal with a beveled edge of 45°. ATR technique offers a high sensitivity of absorbance measurements due to

special data acquisition by multipassing the investigated thin films by IR radiation.

3. RESULTS AND DISCUSSION

The X-ray diffraction data of the samples evidence the progressive formation of crystalline Si with increasing R (Fig. 1 – 4). Only the amorphous structure was detected for the samples with $R \leq 30$ (Fig. 1, 2).

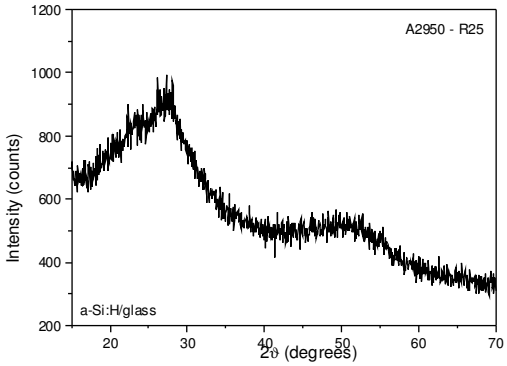

Fig. 1. The XRD scan of the sample prepared at the dilution = 25. The broad peaks belong to the amorphous Si and to the glass substrate.

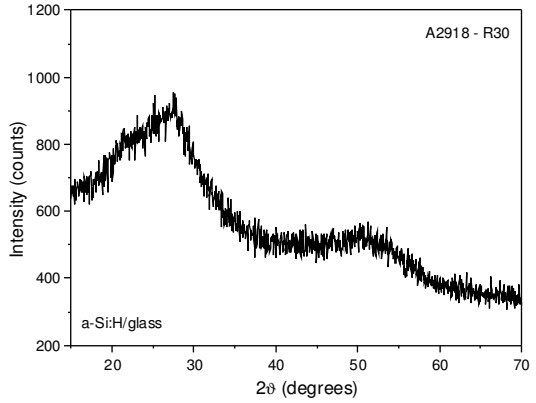

Fig. 2. The XRD scan of the sample prepared at the dilution = 30.The broad peaks belong to the amorphous Si and to the glass substrate.

The diffraction patterns in Fig. 3, 4 for the samples deposited at dilutions 30 and 33 demonstrate differences in the structure. The samples become polycrystalline. At the dilutions between R = 30 and R = 33, the transition between amorphous and microcrystalline silicon occurs. In this narrow range of dilutions, the deposition of protocrystalline silicon is expected. The three sharp peaks of the diffraction lines belonging to the crystalline Si were detected. As the medium-range order (crystalline sites of the dimensions of about 2-3 nm) was proved in a-Si:H films of the same thickness deposited on single-crystalline silicon under the same deposition conditions [2], we expect similar properties of a-Si:H samples deposited on glass just below the protocrystalline regime.

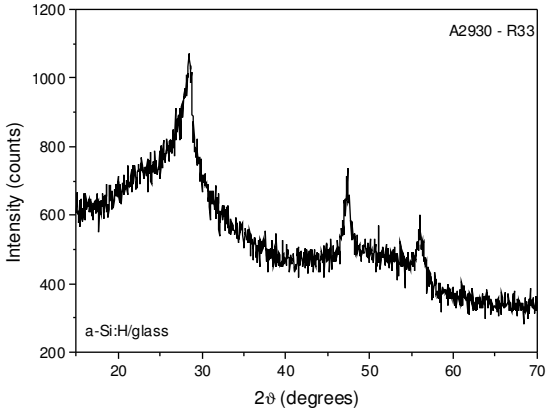

Fig.3. The XRD scan of the sample prepared at the dilution = 33. Three sharp diffraction lines evidence the presence of crystalline phase.

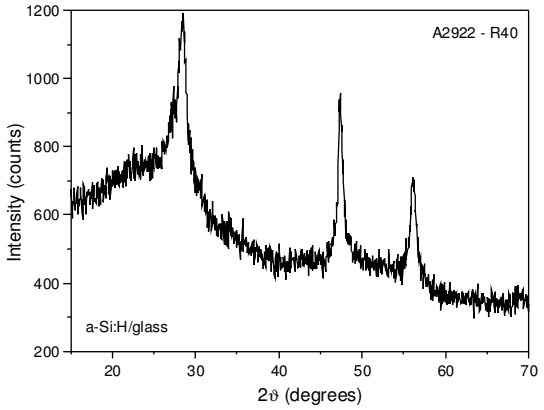

Fig. 4. The XRD scan of the sample prepared at the dilution = 40. Three sharp diffraction lines evidence the presence of crystalline phase.

Fig. 5 shows the measured optical transmittance spectra. The shift of the onset of the sample transmittance towards increasing wavelengths is obvious with decreasing dilutions. From the transmittance spectra, wavelength-dependent absorption coefficients α were calculated. The optical band gap energies E_g were obtained from the plot of $(\alpha E)^{1/2}$ dependence on the photon energy extrapolated to zero, where E is the photon energy.

From the Table 1, the relationship between the optical band gap E_g and the dilution R can be seen. The optical band gap E_g was found to increase with the increasing dilution. For the reference a-Si:H ($R = 0$) sample E_g = 1,66 eV, for the sample with polycrystalline structure deposited at the highest dilution (R = 40) the optical band gap has been opened to E_g = 1,93 eV. This blue shift of the optical band gap is accompanied by an increase of the light

absorption and is probably due to the reduction in the crystallite size in samples deposited under increasing dilutions [4].

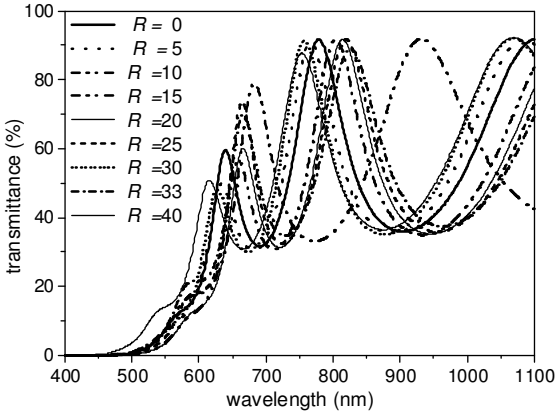

Fig. 5. Experimental transmittance spectra

Tab. 1. Growth and growth-related parameters of the samples: optical band gap E_g, vibrational modes shifts and microstructure factor μ of the samples deposited under varied dilution R

Dilution *R*	E_g [eV]	LSM position [cm^{-1}]	HSM position [cm^{-1}]	Microstucture factor μ [%]
0	1.66	1998.4	2074.7	16.28
5	1.67	1999.5	2080.9	11.05
10	1.67	2001.6	2091.1	9.14
15	1.75	2004.7	2094.2	13.23
20	1.75	2005.6	2096.4	14.42
25	1.74	2005.8	2099.4	11.36
30	1.76	2006.6	2100.7	10.78
33	1.77	2009.5	2105.1	12.66
40	1.93	2014.4	2114.0	13.96

The infrared absorbance data assist in identifying specific molecular bonds and enable to monitor the film composition and the microstructure of compounds. FTIR absorbance spectra can be seen in Fig. 6. The broad absorbance bands at ~ 2000 cm^{-1} assigned to stretching vibrational modes confirm the presence of hydrogen to silicon bonds.

The absorbance bands at ~ 2000 cm^{-1} were observed to be asymmetric for all samples under study. Absorbance peaks at ~ 2000 cm^{-1} recorded by ATR (Fig. 7) were baseline corrected and deconvoluted by least-squares fitting using two Pearson VII intensity distributions for the low stretching mode (LSM) centered at ~ 2000 cm^{-1} and the high stretching mode (HSM) at ~ 2090 cm^{-1}. The peak centered at ~ 2000 cm^{-1} belongs to vibrations of the monohydride Si-H, the peak at ~ 2090 cm^{-1} is assigned to vibrations of the dihydride Si-H_2.

From FTIR analysis, the shift of the LSM and HSM peak was observed with increasing dilution (Table 1). LSM peak position shift is a result of depolarizing field in a small cavity in which the Si-H dipole vibrates [4]. The LSM and HSM peak position shift is connected with the increasing order of the material network. Therefore, also FTIR analysis confirmed the crystalline phase evolution with increasing hydrogen dilution of silane at the Si:H deposition.

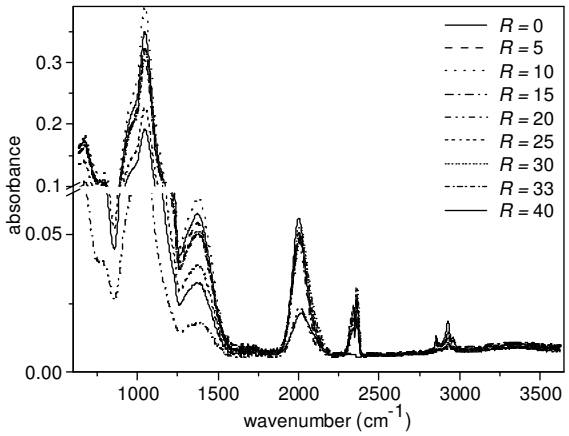

Fig. 6. Absorbance spectra (the vertical axis is broken to visualise Si-H bands at ~ 2000 cm^{-1}). The region at wavenumbers < 1500 cm^{-1} is strongly influenced by the vibrational absorbance bands of the substrate molecules.

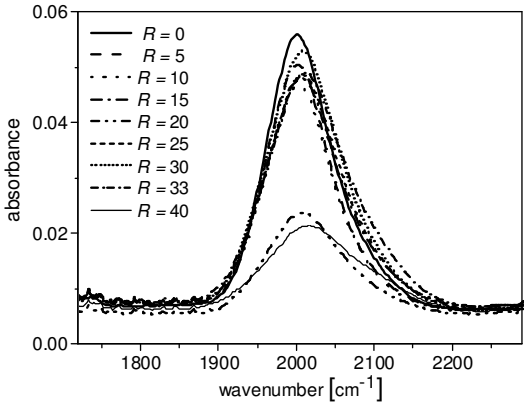

Fig. 7. The experimental IR absorbance at ~ 2000 cm^{-1} assigned to stretching Si-H vibrational modes

Integral intensities of the two deconvoluted absorption peaks are proportional to the bonded atom densities. The microstructure factor μ is the ratio of the integral intensities of LSM (belonging to Si-H) and HSM (belonging to Si-H_2) absorption bands according to the equation

$$\mu = \frac{\int A_{SiH_2}(\bar{\nu})d\bar{\nu}}{\int A_{SiH_2}(\bar{\nu})d\bar{\nu} + \int A_{SiH}(\bar{\nu})d\bar{\nu}},$$

where $\bar{\nu}$ is the wavenumber, $A_{SiH}(\bar{\nu})$ is the wavenumber-dependent absorbance of LSM,

$A_{SiH_2}(\bar{\nu})$ is the wavenumber-dependent absorbance of HSM.

The microstructure factor expresses the ratio of hydrogen bonded in the HSM to the total bonded hydrogen and is commonly considered as a figure of merit of the quality of the films when being < 10 % [6]. The values of the microstructure factor are in Table 1 and indicate that hydrogen is mainly bonded in the LSM and no special dependence on hydrogen dilution occurs. In the non-diluted sample (R = 0) the contribution of the hydrogen in the HSM bonds is the highest. With increasing dilution the contribution of the HSM bonds decreases still been in the range of ~ 9 – 14 %. Microstructure factor of ~ < 10 % according to the reference [7] indicates a material with a low void fraction. Presence of Si-H_x bonds while x > 1 is common for materials with microvoids. The microstructure factor of all samples under study is ~10 % and more which indicates that investigated Si:H samples are porous and slightly inhomogeneous.

The main expected hydride configurations are vacancies and voids. Although there is still a discussion on the origin of the LSM and HSM absorption, it is widely agreed [5] that monohydrides in vacancies contribute to the LSM and hydrides on the void surfaces to the HSM. The peak at ~ 2000 cm^{-1} is often attributed to the isolated hydrogen in monohydride bonding configuration. Hydrogen manifested in the LSMs is bonded to silicon in monohydrides in small volumes of monovacancies, divacancies or polyvacancies. The HSM peak at ~ 2090 cm^{-1} is assigned to clustered hydrogen in monohydrides, dihydrides or trihydrides at the internal surfaces of voids or at the boundaries between the crystalline grains.

4. CONCLUSION

In PECVD deposition of Si:H thin films for photovoltaic applications, remarkable changes in structure and microstructure due to the increasing hydrogen dilution were detected. From the structural analysis of the a-Si:H thin films deposited on glass substrates it was determined that the samples prepared at the dilution under 33 remain within the amorphous regime while the dilution over 33 favours the crystallization. A similar behaviour was observed by optical analysis. The optical band gap increased with increasing dilution. From FTIR data, the Si-H bonding configuration was observed. The Si-H bond representing LSM prevails over Si-H_2 in HSM. The porosity of the samples is manifested in the microstructure factor being > 10 %.

Acknowledgements

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