

ON NANOMETER ORDERING IN THIN AMORPHOUS HYDROGENATED SILICON

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Summary We investigated thin films of amorphous hydrogenated silicon (a-Si:H) deposited by PECVD under increasing dilutions of silane plasma by hydrogen. We found out that under increasing additional hydrogen at the depositions, thin films obtain less hydrogen bonded to silicon. The optical band gap energies determined from UV Vis transmittance and reflectance spectra were found to be increasing function of the dilution. We deduce that optical band gaps expand due to the decreasing dimensions of silicon nanocrystals. They were calculated to be of 2 – 4 nm which proves the medium-range order in a-Si:H.

1. INTRODUCTION

Ordering in amorphous hydrogenated silicon (a-Si:H) thin films has been recently intensively studied, especially due to microelectronics and solar applications [1-5]. Results obtained over last years demonstrate a wide range of properties of a-Si:H thin films including quantum size effect (QSE) also referred as the quantum confinement [2].

Quantum-size effect is reported to be accompanied by an increase of the light absorption and the blue-shift of the optical band-gap due to a reduction in the crystallite size. [6-7]. Material with the size-dependent band-gap is attractive for optical absorption-based applications. In a-Si:H nanocrystalline Si quantum dots surrounded by a-Si:H clusters may play the role (Fig.1) [8]. The quantum size effect is usually studied by transmission electron microscopy, Raman spectra and predominantly by photoluminescence.

In this paper, we intend to show how the results of optical UV Vis measurements can reveal the nanometer ordering in a-Si:H. Then, the influence of hydrogen content on nanometer ordering is discussed.

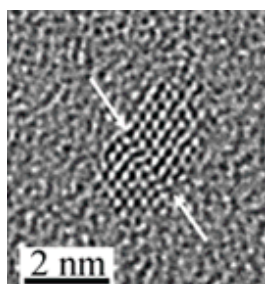


Fig.1. A nanocrystalline region in a-Si:H [8]

2. EXPERIMENTAL

The thin undoped a-Si:H samples films (Table 1, 2) were deposited at the Delft University of Technology, the Netherlands, by 13.5 MHz rf excited parallel plate PECVD industrial deposition system (rf power 13.5 W) especially for extensive photodegradation studies [9, 10]. The samples were deposited on clean Corning 1737 glass substrates (the series A) and crystalline silicon (c-Si) substrates (the series B).

The hydrogen (H₂) to silane (SiH₄) gas flows define the dilution ratio $R = (H_2)/(SiH_4)$ that was varied from 5 to 20. 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 300 nm.

XRD analysis carried out on an automatic X-ray powder diffractometer X'pertPro with a thin film attachment proved that all samples under study were amorphous silicon [11]. Thus, under controlling the deposition, the samples are under the threshold of the transition from amorphous Si:H to the tri-phasic microcrystalline Si:H that is reported to consist of crystalline and amorphous phase and voids [12].

Optical properties for this study were analyzed using UV Vis transmittance spectra of the series A on glass substrate (Fig.2) and UV Vis reflectance spectra of the series B on c-Si (Fig. 3) performed on the Specord 210 spectrophotometer. Apparent interference effects (Fig. 2, 3) are caused by the weak absorption of light above the absorption edge. The onset of the material transparency is obviously shifted what indicates the differences in optical band-gaps of the samples.

Hydrogen content was deduced from FTIR spectra measured by Nicolet 380 FTIR spectrophotometer with the single-bounce attenuated total reflection sampling accessory with diamond

element and trapezoidal silicon crystal of a beveled edge of 45° . The broad absorbance bands at $\sim 2000 \text{ cm}^{-1}$ assigned to stretching Si-H vibrations confirm the presence of silicon to hydrogen bonds [12].

3. OPTICAL BAND GAP ENERGIES

From transmittance T of the series A corrected to the glass substrate transmittance, the absorption coefficients α were determined through the expression $T = \exp(-\alpha d)$, where $d = 300 \text{ nm}$ is the film thickness. The calculated absorption coefficients versus photon energies are in Fig. 4. The wavy parts of the plots are due to interference effects and can not be taken into account. However, the linear parts of the plots in Fig. 4 are fully sufficient to determine the optical band gap energies by means of the so-called Tauc's plots.

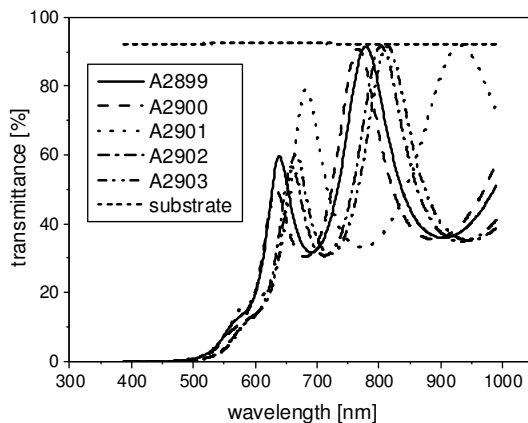


Fig. 2. Transmittance spectra of the series A (on glass)

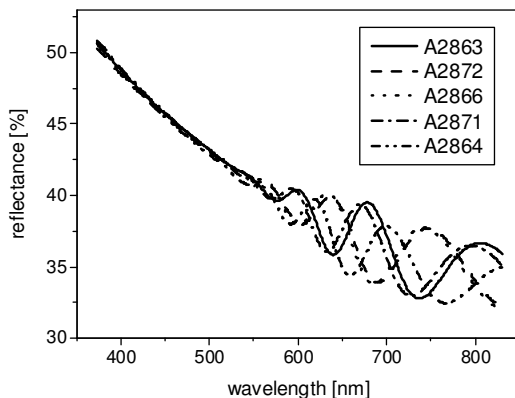


Fig. 3. Reflectance spectra of the series B (on c-Si)

Assuming parabolic band edges, optical band-gap energies E_g^{opt} were estimated from Tauc's plots $(\alpha h\nu)^{1/2} = B(h\nu - E_g^{opt})$. Here α is the absorption coefficient, $h\nu$ the photon energy and B is the constant indicating the sharpness of the band edge.

The task concerning the series B deposited on c-Si was more challenging, because only reflectance spectra could be used. A Delphi-based program based on an optimization procedure using genetic

algorithm was used. The optimization procedure minimized the differences between the experimental and theoretical reflectance in the broad spectral region including the region in the vicinity of the absorption edge. The theoretical reflectance was calculated using the theory in [13] and the Tauc-Lorentz dispersion model for refractive index and extinction coefficient [14] that is currently employed for the parameterization of the optical functions of amorphous materials [15].

The determined absorption coefficients are in Fig. 5. A typical Tauc's plot is in Fig. 6. Optical band gap energies are summarized in Tab. 1, 2. We note that E_g^{opt} for both series deposited either on glass or on c-Si are an increasing function of the hydrogen dilution.

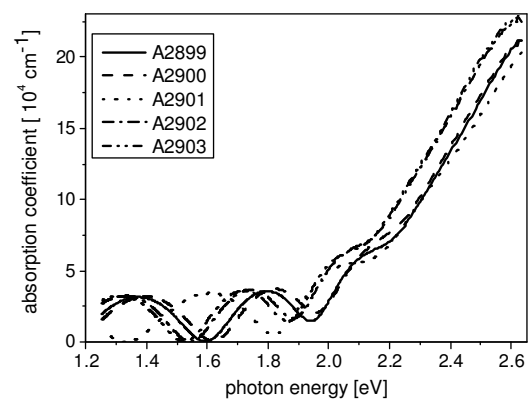


Fig. 4. Absorption coefficients, the series A on glass

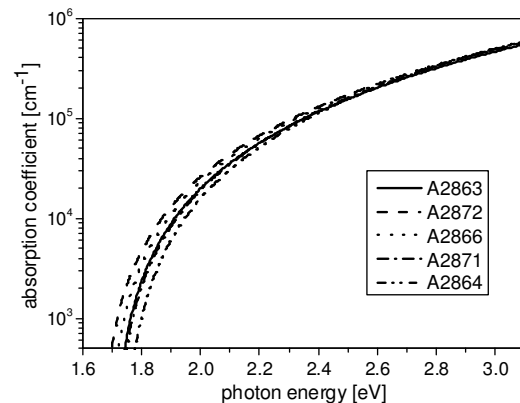


Fig. 5. Absorption coefficients, the series B on c-Si

4. THE HYDROGEN CONTENT

The hydrogen content c_H was deduced from FTIR absorbance spectra of the series A (Fig. 7). The area under the absorbance curves (Fig. 7) is proportional to the total hydrogen atoms bonded to silicon. The hydrogen content can be determined according to the formula

$$c_H = \frac{A_x}{N_{\text{int}}} \int \frac{\alpha(\bar{\nu})}{\bar{\nu}} d\bar{\nu}$$

where $A_x = 9 \times 10^{19} \text{ cm}^{-1}$ is the proportionality constant for the stretching vibrations of Si – H bonds at $\sim 2000 \text{ cm}^{-1}$ [16], $N_{\text{int}} = 5 \times 10^{22} \text{ cm}^{-3}$ is the total number of Si atoms in c-Si per cm^3 , $\alpha(\bar{\nu})$ is the wavenumber ($\bar{\nu}$) dependent absorption coefficient calculated from the FTIR absorbance. The values of hydrogen content c_H are in Table 1. We see that in general c_H decreases with increasing dilutions at the deposition, thus the samples obtain less hydrogen.

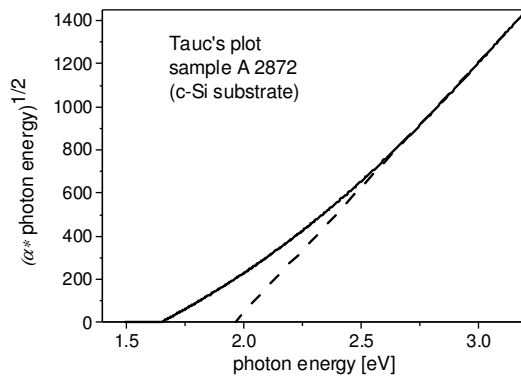


Fig. 6. Tauc's plot for the sample A 2872

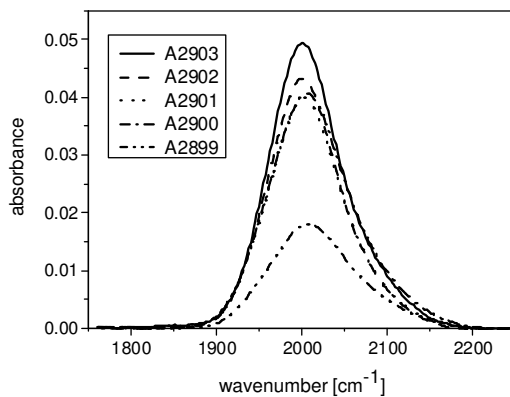


Fig. 7. FTIR absorbance (experimental spectra were smoothed and baseline corrected)

5. QUANTUM SIZE EFFECT

The question how the QSE or the so-called quantum confinement of carriers modifies optical properties of amorphous Si is long-standing [3]. QSE is accompanied by an increase of the light absorption and the blue-shift of the optical band-gap due to a reduction in the crystallite size.

From results summarized in Tab.1, 2 the influence of the dilution on the band-gap energies can be seen. With the increasing dilution, the blue-shift of the band-gap energies (towards higher energies that is towards smaller wavelengths) is observed. The probable explanation of the band-gap

shift is a 3D confinement related to nanocrystalline Si quantum dots (QDs) embedded in amorphous Si.

Understanding the nature of the nanometer size-induced properties is of fundamental importance for advanced technological applications. Various mechanisms are discussed to be responsible for unusual behaviour QDs, e.g. bond-order-length-strength correlation [17]. The confinement effect on the band-gap is agreed to arise from the kinetic energy of electron-hole pairs separated by a distance of the QD dimension and the Coulomb interaction [17]. The values of E_g^{opt} expand due to the QD dimensions a according to Kayanuma's equation the modification of which is [2]

$$E_g^{opt} = 1.56 + 2.2/a^2$$

The calculated QD dimensions a are in Tab.1, 2 and represent the nanometer ordering in the samples.

Thus, we deduce that the blue-shift of optical band-gap energies in a-Si:H of both series is due to nanocrystalline Si clusters of dimensions of 2 – 4 nm that represent the medium-range order or nanometer ordering and are subject to QSE.

Tab.1. The series A (glass substrate)

Sample on glass	dilution	c_H [%]	E_g^{opt} [eV]	a [nm]
A2903	0	16.49	1.68	4.28
A2902	5	14.20	1.70	3.96
A2901	10	13.24	1.73	3.60
A2900	15	14.61	1.75	3.40
A2899	20	6.82	1.77	3.24

Tab. 2. The series B (c-Si substrate)

Sample on c-Si	dilution	E_g^{opt} [eV]	a [nm]
A2863	0	1.97	2.32
A2872	5	1.96	2.35
A2866	10	1.99	2.26
A2871	15	2.00	2.23
A2864	20	2.02	2.19

Recently, we have investigated the QSE of a thickness series of a-Si:H on glass (deposited at the dilution = 30) [18]. The QDs dimensions were found to be from 2.71 nm (the sample thickness of 100 nm) to 2.58 nm (the sample thickness of 25 nm). For the series A here, the sample thickness is greater (of 300 nm), but still the QSE is observable. However, the QD dimensions increase probably due to the sample thickness, although lower dilutions have been used at the depositions. Owing to this comparison, a more complex and thorough study is necessary to complete the knowledge of the nanometer ordering in a-Si:H of varied thicknesses deposited under varied deposition conditions.

Another observed fact is that the medium-range order in the samples deposited on glass and on Si differ slightly. The QD dimensions in samples on c-Si are smaller in comparison with the QD dimensions in samples on glass. The influence of the substrate is as follows – the c-Si substrate opens more the band-gap (Tab. 1 and Tab. 2).

Owing to the decreasing hydrogen content we speculate that the grain boundaries effect may also play role. The grain boundaries of smaller QDs obviously obtain less hydrogen passivating the surface. Therefore, optical band gaps are affected by a-Si:H microstructure and hydrogen content.

4. CONCLUSION

The results show that optical band gaps of a-Si:H thin films of the thickness of ~ 300 nm deposited under hydrogen dilutions are higher than optical band gaps of undiluted material whichever substrate was used. Increasing hydrogen dilution at the a-Si:H deposition activated the growth of nanograins of 2 – 4 nm in size within the amorphous matrix. By increasing the hydrogen dilution from 0 to 20, tunable band gaps from 1.68 eV to 1.77 eV were obtained in a-Si:H films deposited on glass substrate, band gaps from 1.97 to 2.02 in case of c-Si substrate.

Acknowledgements

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