Published in Journal of Non-Crystalline Solids 227-230, 876-879, 1998
which should be used for any reference to this work

Optical determination of the mass density of amorphous and microcrystalline silicon layers with different hydrogen contents

Z. Remeš [a], M. Vaněcek [a,*], P. Torres [b], U. Kroll [b], A.H. Mahan [c], R.S. Crandall [c]

[a] *Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, CZ-16253 Praha 6, Czech Republic*
[b] *Institute of Microtechnology, Neuchatel University, Rue A.L. Breguet 2, CH-2000 Neuchatel, Switzerland*
[c] *National Renewable Energy Laboratory, Golden, CO 80401-3393, USA*

Abstract

We have measured the density of amorphous and microcrystalline silicon films using an optical method. The mass density decreases with increasing hydrogen content, consistent with a hydrogenated di-vacancy model that fits the data for amorphous silicon. Material produced by hot wire assisted chemical vapour deposition, with low hydrogen content, has a higher density and is structurally different from glow discharge material with hydrogen content around 10 at.%. The lower density microcrystalline silicon seems to be porous.

Keywords: Mass density; Silicon layers; Hydrogen contents

1. Introduction

Further progress in a continuing effort to improve the stability of the efficiency of hydrogenated thin film amorphous (a-Si:H) and microcrystalline (μc-Si:H) silicon solar cells is dependent on our understanding of the growth process and material structure. Deposition conditions determine the silicon and hydrogen bonding, multivacancies and voids in the material; and all these affect the electronic properties of the material, namely the defect density and the material stability. The mass density of the material affects, indirectly, all these changes, as we have already reported [1]. Here we present a detailed study of the density of thin amorphous and microcrystalline layers deposited on glass substrates, as a function of deposition technique, deposition conditions and hydrogen content.

* Corresponding author. Tel.: +42-2 2431 1137; fax: +42-2 312 3184; e-mail: vanecek@fzu.cz.

2. Experimental details

Amorphous silicon films were deposited by hot wire assisted chemical vapor deposition (HW) technique (HW26 and HW59) that differ in hydrogen content [1]. Sample GD23 was produced by the conventional plasma-enhanced chemical-vapour deposition with void fraction (0.01%), as measured by small angle X-ray scattering (SAXS) [2]. Samples HW59 and GD23 were later annealed at 500°C for 24 h in a hydrogen atmosphere to reduce their hydrogen content. Microcrystalline samples (D15, P13, P06, P05) were prepared by hydrogen dilution of silane using several frequencies (70–130 MHz) in a glow discharge technique (VHF-GD). Samples D20 and D28, prepared by VHF-GD, are amorphous.

All measurements of transmittance (T) and reflectance (R), as a function of wavelength λ, were made using a single beam spectrophotometer allowing illumination of a small part of the sample (1 mm^2) without its movement. This procedure is crucial for the accurate estimation of the index of refraction, n.

Following Tomlin [3], the function $(1+R)/T$ is given by:

$$\frac{1+R}{T} = \frac{(n^2+1)(n^2+s^2)-(n^2-1)(n^2-s^2)\cos\frac{4\pi nd}{\lambda}}{4n^2 s} \quad (1)$$

where s is index of refraction of the glass substrate and d is thickness of a thin film.

Approximating the imaginary part of the complex dielectric constant by a delta function resonance absorption at an energy, E_R (Penn gap), it is easy to show from the Kramers–Kronig equations and the plasma sum rule [4] that:

$$n^2(E) = 1 + \frac{E_P^2}{E_R^2 - E^2} \quad (2)$$

The Penn gap, E_R, represents an average separation between valence and conduction bands and is a measure of the covalent bond strength. E_P is the plasma energy. We made the first approximation of these two parameters from the reflectance measurement in an absorbing region where no interferences are present. If E_P, E_R and d are approximately known, the function (1) can be used in a fitting procedure providing a better estimate of parameters, error estimate on the parameters and a statistical measure of goodness-of-fit.

The refractive index at long wavelengths, n_∞ can be written in terms of individual oscillators. This classical approach is described by the Clausius–Mossoti equation [5]. In the case of a-Si:H or μc-Si:H, the oscillators are Si–Si bonds and Si–H bonds. The bond polarizability of a Si–Si bond in the crystalline phase, $\alpha_1 = 1.96\ 10^{-24}$ cm^3, and the bond polarizability of a Si–Si bond in the amorphous phase, $\alpha_2 = 1.87\ 10^{-24}$ cm^3, were estimated from the corresponding refractive indexes, n_∞ (c-Si) = 3.42 and n_∞ (a-Si) = 3.67 and the mass densities ϱ(c-Si) = 2.33 g cm^{-3} and ϱ(a-Si) = 2.29 g cm^{-3} [6,2]. The bond polarizability, $\alpha_3 = 1.36\ 10^{-24}$ cm^3 of the Si–H bond, is taken from the polarizability of the SiH_4 molecule [5]. Hence, knowing the concentration of bonded hydrogen (c_H), from IR absorption measurements [7], it is possible to determine the film mass density (ϱ) from the measured index of refraction. Finally, we obtained after the substitution:

$$\frac{n_\infty^2 - 1}{n_\infty^2 + 2} = \frac{4\pi\varrho}{3m_{Si}}\left(4\xi + \frac{c_H}{1-c_H}(\alpha_3 - \xi)\right) \quad (3)$$

where $\xi = 1/2((1-p)\alpha_1 + p\alpha_2)$, m_{Si} is the mass of the Si atom and p is the amorphous fraction.

3. Results

Typical transmittance and reflectance are shown in Fig. 1 for a microcrystalline and an amorphous sample. The spectral dependency of the index of refraction is calculated from the spectral dependency

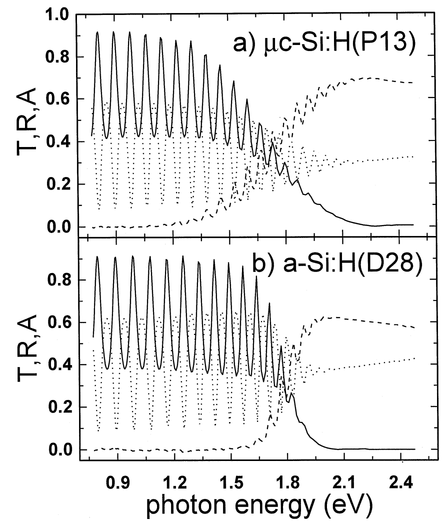

Fig. 1. Spectral dependence of transmittance, T, (solid line), reflectance R (dotted line) and absorptance $A = 1 - T - R$ (dashed line) spectra of (a) sample P13 (μc-Si:H, calculated thickness is ≈ 2034 nm) and (b) sample D28 (a-Si:H, calculated thickness is ≈ 1744 nm).

Table 1
Penn gap, E_R, long wavelength limit of the index of refraction, n_∞, and density, ϱ, of measured samples with hydrogen content, c_H, and amorphous fraction, p

Sample	c_H (at.%)	p (%)	E_R (eV)	n_∞	ϱ (g cm^{-3})
HW26	0.3	100	3.42	3.66	2.28
HW59	1.6	100	3.51	3.63	2.27
HW59b	≈ 0	100	3.34	3.67	2.29
GD23	9	100	3.49	3.49	2.22
GD23b	≈ 0	100	3.33	3.67	2.29
D28	11	100	3.53	3.47	2.20
D20	12	100	3.80	3.46	2.19
D15	3.0	12.5	4.02	3.44	2.31
P06	4.2	18	4.01	3.26	2.24
P13	5.0	23	4.02	3.26	2.23
P05	5.8	16	4.03	3.31	2.26

of $(1+R)/T$ using Eq. (1). Calculated values of n, E_R and ϱ for all measured samples are summarized in Table 1. The hydrogen content has been determined by infrared spectroscopy, and the amorphous fraction was determinate from Raman scattering [8].

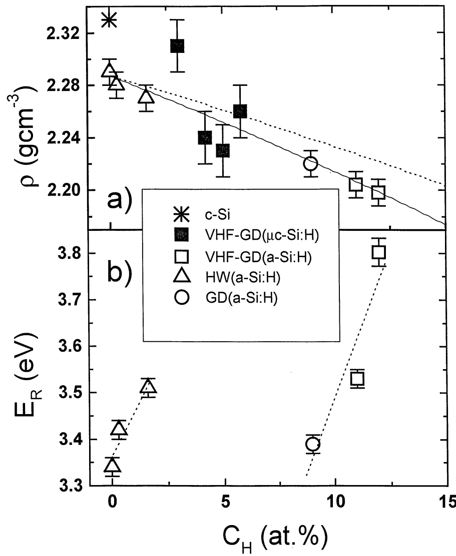

Fig. 2. (a) Mass density of measured samples compared with the mono-vacancy (dotted line) and di-vacancy model (solid line) as a function of hydrogen density. (b) Penn gap of measured samples as a function of the hydrogen content. Two linear regression functions (dotted lines) show two different linear dependencies of the Penn gap on the hydrogen content. Mass density of c-Si was added for comparison.

In Fig. 2a, we display the dependence of the density of all measured layers on hydrogen content. To describe this behaviour, two simple models are presented. In the mono-vacancy model, four hydrogen atoms replace one silicon atom, in the di-vacancy model, six hydrogen atoms replace two silicon atoms. The measured density is compared with the density of crystalline silicon (2.33 g cm^{-3}). Error bars have been estimated from errors of fitted parameters E_P and E_R.

In Fig. 2b, we display the dependence of E_R of amorphous silicon on hydrogen content.

4. Discussion

Carlson [9] suggested that one way to improve the stability of a-Si:H is to increase the density of the material by systematically varying the deposition conditions. We have already reported that HW material prepared at 350 to 390°C with about ~2 at.% hydrogen shows a strongly reduced susceptibility to the creation of thermal and light-induced defects [1,10].

We have correlated this increased stability with larger material density [1] and a different hydrogen microstructure of this material, as determined by nuclear magnetic resonance (NMR) [11]. Another difference can be seen from Fig. 2b. We can see two different linear dependencies of E_R on c_H, for a 'stable' HW material with a $c_H < 4$ at.% and the glow discharge material with $c_H \geq 9$ at.%. All the above data reported on the 'more stable HW material' point to the conclusion that the material is structurally different from GD material with c_H of around 9 at.%.

Another important observation is presented in Fig. 2a. It can be seen that the density of the amorphous material with negligible void fraction monotonically decreases with increasing H content [12]. We obtain the best fit with the hydrogenated di-vacancy model in which six H atoms replace two Si atoms and the hydrogenated mono-vacancies make a minor contribution [12]. Our results show that the density deficiency compared to the crystalline Si density $\varrho = 2.33$ g cm^{-3} comes from a difference between crystalline and amorphous phase of the unhydrogenated Si ($\varrho = 2.29$ g cm^{-3}) [6] and from 'substitution' of Si

atoms by H atoms. Our data are consistent with a picture of one hydrogen atom occupying the space of approximately 1/3 of the silicon atom in a dense, void-free material.

We have also extended our approach to microcrystalline material, which was successfully used in microcrystalline solar cells [13]. Unfortunately, we cannot investigate strongly textured material which gives the highest efficiency solar cells due to increased light trapping because the rough surface suppresses the interference fringes. Our data for mirror like microcrystalline samples show that again, the density decreases with increasing hydrogen content.

Some samples have a smaller density than those that would correspond to the simple picture, presented above (samples P06, P13). We assume that this difference is connected with a porosity (smaller density) of these samples, compared to the samples prepared under 'optimal' conditions.

5. Conclusions

The mass density decreases with increasing hydrogen content, hydrogenated di-vacancies being mainly responsible for this. On the average, one hydrogen atom occupies the space of approximately 1/3 of the silicon atom.

More stable HW material with a low hydrogen content has a higher density and is structurally different from glow discharge material with c_{H} of around 9 at.%.

Microcrystalline silicon with lower densities seems to be porous.

Acknowledgements

Authors acknowledge support of the project JOR3-CT97-0145.

References

[1] M. Vanecek, Z. Remes, J. Fric, R.S. Crandall, A.H. Mahan, in: R. Hill, W. Palz, P. Helm (Eds.), Proc. 12th European Photovoltaic Solar Energy Conf., Amsterdam, Stephens, Bedford, UK, 1994, p. 354.
[2] D.L. Williamson, MRS Symp. Proc. 377 (1995) 251.
[3] S.G. Tomlin, Br. J. Appl. Phys. (J. Phys. D) 1 (1968) 1667.
[4] G.D. Cody, in: J. Pankove (Ed.), Hydrogenated Amorphous Silicon, Semiconductors and Semimetals, 21C, Academic Press, New York, 1984, p. 11.
[5] J.C. van den Heuvel, M.J. Geerts, J.W. Metselaar, Solar Energy Mater. 22 (1991) 185.
[6] J.S. Custer, M.O. Thompson, D.C. Jacobson, J.M. Poate, S. Roorda, W.C. Sinke, F. Spaepen, Appl. Phys. Lett. 64 (1994) 437.
[7] A.H. Mahan, E.J. Johnson, R.S. Crandall, H.M. Branz, MRS Symp. Proc. 377 (1995) 413.
[8] A. Poruba, Z. Remes, V. Vorlicek, M. Vanecek, N. Beck, P. Torres, J. Meier, A. Shah, to be published.
[9] D.E. Carlson, Appl. Phys. 41 (1986) 305.
[10] A.H. Mahan, M. Vanecek, in: B.L. Stafford (Ed.), Amorphous Silicon Materials and Solar Cells, AIP Conf. Proc., Vol. 234, American Institute of Physics, New York, 1991, p. 195.
[11] Y. Wu, J.T. Stevens, D.X. Han, J.M. Rutland, R.S. Crandall, A.H. Mahan, Phys. Rev. Lett. 77 (1996) 2049.
[12] Z. Remes, M. Vanecek, A.H. Mahan, R.S. Crandall, submitted to Phys. Rev. B.
[13] J. Meier, S. Dubail, R. Fluckiger, D. Fischer, H. Keppner, A. Shah, Proc. IEEE 1st World Conference on Photovoltaic Energy Conversion, Hawaii, 1994, p. 409.