Published in Journal of Non-Crystalline Solids 198-200, 903-906, 1996
which should be used for any reference to this work

Enhanced optical absorption in microcrystalline silicon

N. Beck [a,*], J. Meier [b], J. Fric [a], Z. Remeš [a], A. Poruba [a], R. Flückiger [b], J. Pohl [c], A. Shah [b], M. Vaněček [a]

[a] *Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 00 Praha 6, Czech Republic*
[b] *Institute of Microtechnology, Rue A.-L. Breguet 2, 2000 Neuchâtel, Switzerland*
[c] *Faculty of Physics, University of Konstanz, 78434 Konstanz, Germany*

Abstract

An enhanced optical absorption, compared to crystalline silicon, was observed in the above gap region together with very low defect-connected absorption in microcrystalline silicon (μc-Si:H) prepared by very high frequency glow discharge technique at 70 MHz. As the μc-Si:H material has a very low fraction of amorphous phase, a 'crystalline silicon like' absorption model is proposed which associates most absorption properties of μc-Si:H to the crystalline phase in the material. Thereby the influence of internal strain, microcrystallite boundaries, hydrogen content and elastic light scattering on the absorption properties are discussed.

1. Introduction

Enhanced optical absorption in the IR region compared to a-Si:H together with very low defect-connected absorption, makes μc-Si:H produced by the very high frequency glow discharge technique (VHF-GD) at 70 MHz a promising material for solar cell applications. However, little is known about the physical processes which govern the absorption properties of μc-Si:H. Earlier models for the absorption spectra in μc-Si:H suggested an 'amorphous silicon like' absorption where the amorphous phase in the material determines the absorption properties [1]. In this paper we present a new, 'crystalline silicon like' absorption model which applies for high quality μc-Si:H material with a low amorphous fraction and crystallite boundaries well passivated by hydrogen.

2. Experimental

All μc-Si:H layers were produced by the VHF-GD deposition technique at 70 MHz on glass substrate (Corning 7059). The samples were selected from a compensation series of slightly boron doped μc-Si:H films presented in Ref. [2]. One undoped sample was produced using a gas purifier. Thicknesses of the films ranged between 1.60 and 1.85 μm. The absorption spectra of the films were determined by the constant photocurrent method (CPM), photothermal deflection spectroscopy (PDS) and transmission/reflection measurements. For the hydrogen evolution experiments the samples were annealed in ultrapure

* Corresponding author. Present address: Institut de Microtechnique, Université de Neuchâtel, Rue A.-L. Breguet 2, CH-2000 Neuchâtel, Switzerland. Tel: +41-38 234 121; fax: +41-38 254 276; e-mail: beck@imt.urine.ch.

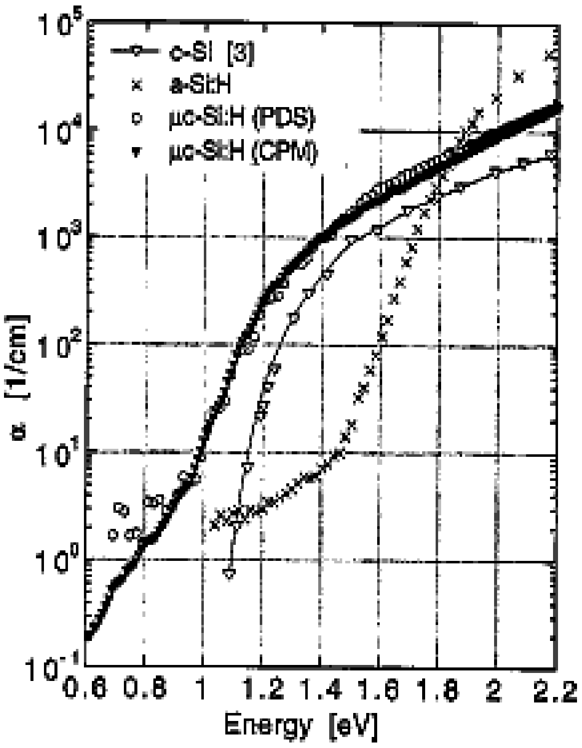

Fig. 1. Absorption coefficient of μc-Si:H deposited by the VHF-GD in comparison with crystalline and amorphous Si.

molecular hydrogen atmosphere for 2 h at temperatures between 300°C and 500°C.

3. Results

The spectral dependence of the optical absorption coefficient $\alpha(E)$ in our μc-Si:H material is plotted in Fig. 1 together with data from the literature for crystalline and amorphous silicon. The most striking feature of the absorption in this material is its extremely low defect-connected absorption compared to μc-Si:H material produced in other laboratories (i.e. Refs. [1,4–6]). Annealing of the material leads to an increase of the optical absorption for photon energy E below 1 eV (Fig. 2). The most interesting part of the absorption spectra for PV applications, however, is the strongly enhanced absorption in the infrared region, compared to a-Si:H and c-Si. Thus, μc-Si:H has already successfully been integrated as a low gap cell into a tandem solar cell [2].

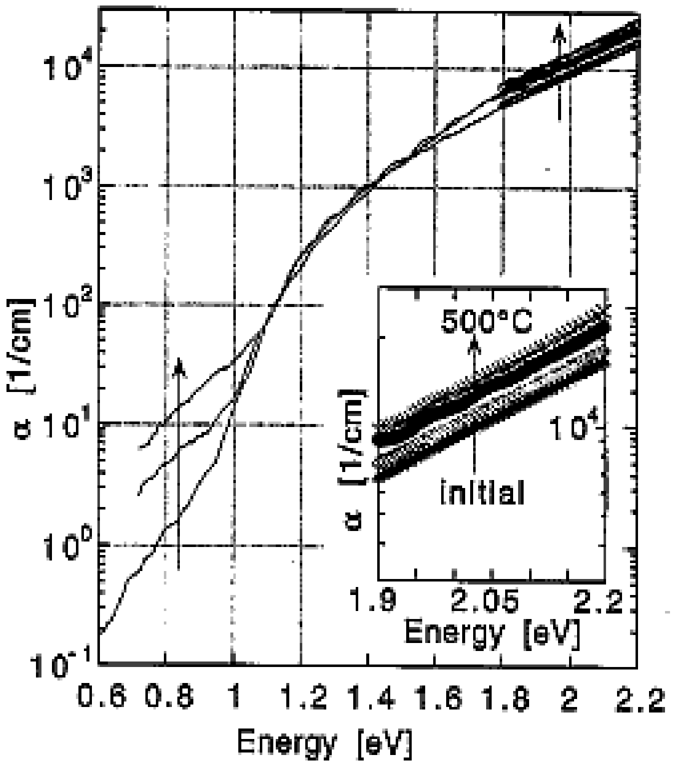

Fig. 2. Hydrogen evolution by stepwise annealing up to 500°C of μc-Si:H leads to a prominent increase of the subbandgap absorption as well as the absorption in the visible region as indicated by the arrows.

4. Discussion

4.1. *Defect-connected absorption*

The defect-connected absorption in our high quality μc-Si:H material is extremely low with a value of about 1 cm^{-1} at the shoulder ($E \approx 0.8$ eV) which, according to Refs. [1,7] should correspond to a spin density in the material of about 5×10^{15} cm^{-3} only. Raman spectra measurements of similar samples indicate an amorphous phase of much less than 10% [2] and the diameter of the cigarlike crystallites (⟨220⟩ orientation) is about ≤ 200 Å [2]. All the studied films contained about 6 mol% hydrogen which play an important role for the passivation of defect states at the grain boundaries. Evolution of the hydrogen by annealing leads to a prominent increase of the defect-connected absorption (Fig. 2). An opposite effect has been used in Ref. [1]: annealing of CVD polysilicon in the atomic hydrogen reduced its high, defect-connected absorption and spin density.

An earlier study on μc-Si:H material, prepared by a DC discharge [8], found an important contribution of scattered light to the apparent $\alpha(E)$. Even if our μc-Si:H material looks mirrorlike to the eye, the measured contribution of scattered light to the apparent $\alpha(E)$ also turned out to be important (Fig. 3). Thereby, we performed CPM measurements on a sample with different interelectrode spacings (0.5 mm and 4.5 mm) to estimate the value of the optical scattering coefficient $\alpha_s(E)$ in the low absorption region ([9,10]). The basic principle of this approach is quite straightforward and relies on the waveguiding properties of silicon thin films. We perform 2 CPM measurements with 2 different interelectrode spacings, thus changing the optical path of the scattered light. A part of the scattered light is finally absorbed in between the electrodes and gives a contribution to the photocurrent (small for the 0.5 mm spacing, quite large for the 4.5 mm spacing) that is additive to the directly absorbed light and that is functionally dependent on the spacing. From that dependence we can calculate the scattering coefficient using the simple theory [9]. With a decrease of the interelectrode spacing to or below 0.5 mm the measured α approaches the true optical absorption. The scattering coefficient α_s for energies below 1.0 eV was estimated to be of the order of 10^1 cm^{-1}. Difference in PDS and CPM spectra (Fig. 1) is due to the absorption of our substrate (Corning 7059) which dominates PDS spectra at energies less than 0.9 eV [11].

4.2. Absorption in the near infrared region

Thanks to the very low subbandgap absorption in our material, the shape of the absorption edge becomes clearly visible: $\alpha(E)$ follows a square root dependence on photon energy, E, characteristic for monocrystalline silicon [3] (Fig. 4). Hence, we attribute this absorption edge in μc-Si:H to the indirect optical transition with the assistance of phonons, as it is in the crystalline material. This hypothesis is further supported by the unchanged absorption edge between 1.1 and 1.4 eV with hydrogen evolution. The indirect gap, E_g, obtained by extrapolation, 1.08 eV in monocrystalline silicon at room temperature [3], is shifted to the IR by about 0.1 eV in our material. Scattering contributes a small part to this shift, as can be deduced from Fig. 3 and the approach used in Ref. [9].

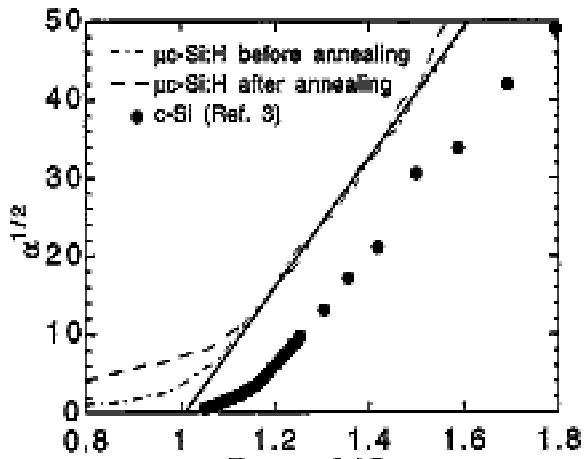

Fig. 4. Square root dependence of the absorption coefficient of μc-Si:H in comparison with the crystalline silicon data.

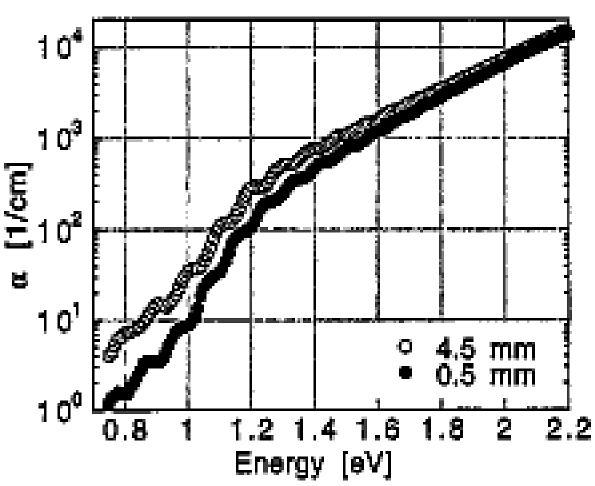

Fig. 3. CPM absorption curve for two different spacings of contact electrodes. The apparent α measured with 4.5 mm interelectrode spacing reflects the contribution of light scattering [10].

X-ray diffraction experiments with a $CuK_{\alpha 1}$ source on VHF-GD μc-Si:H revealed an enhanced interatomic Si–Si spacing: 5.46 Å in μc-Si:H compared to the lattice constant of 5.43088 Å in c-Si. This fact indicates important tensile strain within the crystallites which leads to a distortion of the band structure. Studies about the effect of pressure on c-Si indeed found measurable changes in the band gap minima [12] and data on non-stress relieved monocrystalline silicon shows a shift of $\alpha(E)$ towards the IR compared to the stress relieved c-Si [13].

As our μc-Si:H material is constituted of crystallites of small dimensions, also possible quantum confinement effects should be taken into consideration. However, quantum confinement would lead to a blue shift of the absorption edge [14] and this is not the case here.

4.3. Absorption in the visible region

In the region above 1.8 eV the absorption coefficient of μc-Si:H is higher than in c-Si but also considerably lower than in a-Si:H. The most obvious attempt to explain this enhanced absorption compared to c-Si would be by the amorphous fraction in the material which has a large α. However, the low volume fraction of amorphous phase of much less than 10% contradicts this explanation. We have not investigated the elastic light scattering in this spectral region yet, but starting with our α_s value for the 0.8 to 1.0 eV region and expecting a Mie type of scattering for our crystallite size [15], scattering should contribute less than 10% to the measured absorption coefficient here.

The absorption coefficient of our μc-Si:H material in the high energy range is a function of the hydrogen content. Similar as in a-Si:H, the evolution of hydrogen by annealing increases the absorption coefficient (Fig. 2). This behaviour imposes the assumption, that the increased absorption for energies higher than 1.8 eV is indeed somehow related to the grain boundary regions where the hydrogen is located.

5. Conclusions

High quality μc-Si:H material with small amorphous volume fraction was prepared by the VHF-GD at 70 MHz. Its absorption properties have turned out to be qualitatively similar to crystalline silicon, yet quantitatively different. The very small absorption related to deep defects allowed us to observe the indirect absorption edge of the crystallite phase: we deduced a reduced energy gap of slightly below 1.00 eV due to the tensile strain in the crystallite grains. Elastic light scattering in the μc-Si:H material was much higher than in a-Si:H with scattering coefficient of the order 10^1 cm^{-1}.

Further investigations will be necessary in order to understand the enhanced absorption of high quality μc-Si:H in the above gap region (compared to c-Si). In this paper, however, light scattering as well as the amorphous phase in the material could be excluded from a dominant role. Furthermore, it has been shown, that $\alpha(E)$ in this region is dependent on the hydrogen content. Two suggested explanations for the observed enhanced absorption will need more experimental evidence to be approved or rejected: strain-induced change of the absorption (α should correlate with strain) and relaxation of the k vector selection rule for grain boundary atoms [1] (α should correlate with grain size).

Acknowledgements

This work was supported by the Swiss Federal Renewable Energy Program (EF-REN(93)032), the Swiss National Science Foundation grant FN-39377 and AV CR grant No. 110102.

References

[1] W.B. Jackson, N.M. Johnson and D.K. Biegelsen, Appl. Phys. Lett. 43 (1983) 195.
[2] J. Meier, S. Dubail, R. Flückiger, D. Fischer, H. Keppner and A. Shah, Proc. of the 1st WCPVEC, Hawaii, HI (1994) p. 405.
[3] R. Braunstein, A.R. Moore and F. Herman, Phys. Rev. 109 (1958) 695.
[4] C. Godet, PhD Thesis, Université de Paris-Sud, Centre d'Orsay (1987).
[5] H.N. Liu, Y.L. He, F. Wang and S. Grebner, J. Non-Cryst. Solids 164–166 (1993) 1005.
[6] H. Richter and L. Ley, J. Appl. Phys. 52 (1981) 7281.
[7] N. Nickel, N.M. Johnson and W.B. Jackson, Appl. Phys. Lett. 62 (1993) 3285.
[8] Z. Iqbal, F.A. Sarott and S Vepřek, J. Phys. C: Appl. Phys. 16 (1983) 2005.
[9] M. Favre, H. Curtins and M. Vaněček, J. Non-Cryst. Solids 114 (1989) 405.
[10] M. Vaněček, D. Cervinka, M. Favre, H. Curtins and A. Shah, Mater. Res. Soc. Symp. Proc. 192 (1990) p. 639.
[11] S. Nonomura, T. Nishiwaki and S. Nitta, Philos. Mag. B69 (1994) 335.
[12] W. Paul, J. Appl. Phys. 32 (1961) 2082.
[13] M. Saritas and H.D. McKell, J. Appl. Phys. 61 (1987) 4923.
[14] I. Sagnes, A. Halimaoui, G. Vincent and P.A. Badez, Appl. Phys. Lett. 62 (1993) 1155.
[15] H.C. Van de Hulst, Light Scattering by Small Particles (Wiley, New York, 1957).