HYDROGEN CONTENT AND THE OPTICAL BANDGAP IN AMORPHOUS SILICON

K.M.H. MAESSEN, M.J.M. PRUPPERS, J. BEZEMER, F.H.P.M. HABRAKEN AND W.F. VAN DER WEG.
Department of Atomic and Interface Physics, University of Utrecht, P.O. Box 80.000, 3508 TA Utrecht, the Netherlands.

ABSTRACT

The dependence of the optical bandgap on the hydrogen concentration is measured for amorphous silicon films prepared under different glow-discharge conditions. A deviation from the usually accepted linear dependence is found for hydrogen concentrations above 12 at.%. We find that in this concentration region an increase of hydrogen incorporated as SiH_2 is responsible for this behaviour.

INTRODUCTION

As a part of a systematic investigation of the influence of the composition and structure on the optical properties of amorphous silicon, the dependence of the optical bandgap on the hydrogen concentration is investigated. In order to achieve general conclusions, it is necessary to prepare amorphous silicon films with a large variety of preparation and doping conditions. It will be shown, that the binding configuration of hydrogen in the film will be of importance for the relation between the optical bandgap and the hydrogen concentration.

SAMPLE PREPARATION

The amorphous silicon samples were deposited in a capacitively coupled radio frequent (rf) glow-discharge reactor. In order to achieve a large variety of amorphous silicon films the deposition conditions were systematically varied. The rf-power was varied between 0.005 and 0.07 W/cm^3. The pressure was adjusted between 10 and 50 Pa. The silane gasflow was changed from 0.001 to 0.05 Pa m^3/s. The films were deposited at substrate temperatures ranging from 300 K up to 650 K. Phosphorus and Boron doped films as well as undoped films were deposited. The concentration of dopant atoms amounted to 1 at.%.

ANALYSIS

The hydrogen content of the amorphous silicon films was determined by nuclear reaction analysis (NRA) using the reaction $^1H(^{15}N,\alpha\gamma)^{12}C$ [1].

Mat. Res. Soc. Symp. Proc. Vol. 95. ©1987 Materials Research Society

In addition, infrared absorption spectroscopy was used to obtain information about the various hydrogen to silicon bonding modes (SiH, SiH_2, SiH_3).

The optical constants of the film were measured by optical transmission and reflection experiments. From the measured absorption coefficient, for photon energies above the bandgap energy, a value of the optical bandgap is found. The value of the optical bandgap is obtained by a linear extrapolation of the absorption coefficient to zero absorption.

RESULTS AND DISCUSSION

For a theoretical deduction of the optical bandgap it is necessary to make an assumption for the density of delocalised states in the conduction and valence band. Frequently the density of states distribution is chosen to be parabolic. This distribution leads to the well known Tauc plot for the determination of the optical bandgap ($(\alpha \times n \times h\nu)^{1/2} = c' \times (E - E_o)$). When the distribution of delocalised states is taken linear, the optical bandgap can be deduced from the relation

$$(\alpha \times n \times h\nu)^{1/3} = c \times (E - E_o) \qquad (1)$$

with α = the absorption coefficient
$h\nu$ = the photon energy
E = the energy
E_o = the optical bandgap
n = the refractive index
c = a constant.

As was pointed out earlier by us [2], a linear density of states distribution in the valence and conduction band of amorphous silicon appears to be more appropriate than a parabolic distribution for a large variety of deposition conditions.

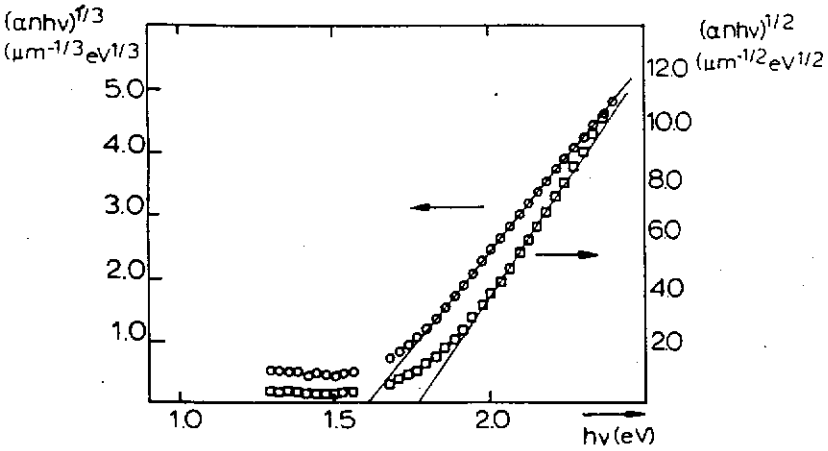

fig. 1 Determination of the optical bandgap according to $(\alpha nh\nu)^{1/2}$ (i.e. Tauc plot) or $(\alpha nh\nu)^{1/3}$

Bremsstrahlung Isochromat Spectroscopy and photoemission experiments recently described by Jackson et al. [3] confirm the linearity of the density of states distribution in amorphous silicon. For these reasons we determine the optical bandgap using relation (1).

For hydrogenated amorphous silicon it is generally accepted, that the value of the optical bandgap depends linearly on the hydrogen concentration of the amorphous film [4]. This is supposed to be related to a shift of the valence band edge with increasing hydrogen concentration [5]. We have investigated this relation for numerous amorphous silicon films prepared under different glow-discharge conditions. For all samples the hydrogen concentration, measured with the NRA technique, and the optical bandgap are determined. The results are shown in figure 2.

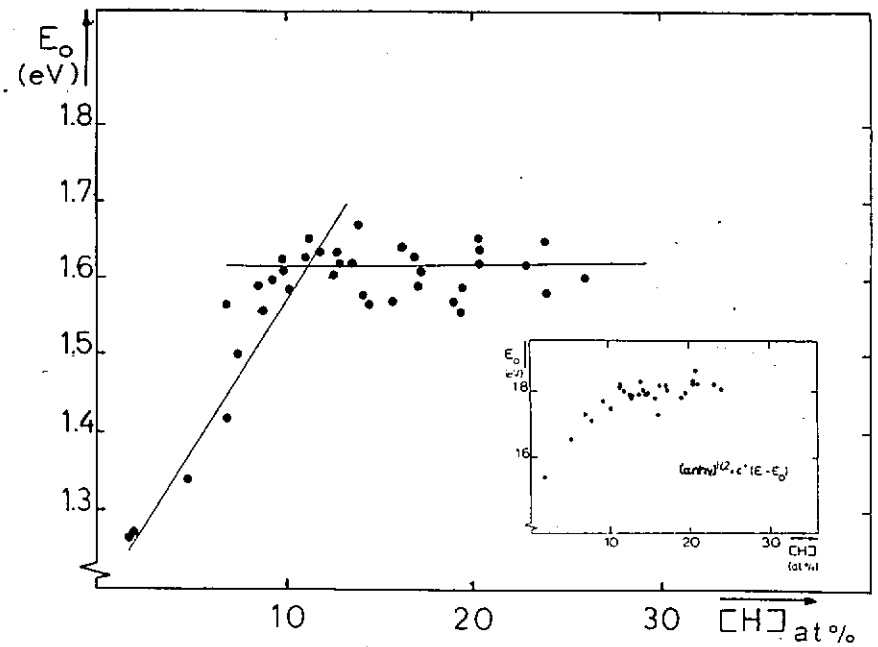

fig. 2 The optical bandgap as a function of the concentration of incorporated hydrogen for amorphous silicon films prepared at different glow discharge conditions.

It is clear from this figure, that the linear increase of the bandgap with hydrogen concentration is valid over a limited region of hydrogen concentration. For hydrogen concentrations below 10–12 at.% indeed a linear increase of the bandgap with hydrogen concentration is found, which is given by

$$E_o = 0.056 \times [H] + 1.1 \qquad (2)$$

with E = the optical bandgap in eV
[H] = the hydrogen concentration in at. %.

However, for hydrogen concentrations above 12 at.% we find the optical bandgap to be independent of the hydrogen concentration. This feature is especially interesting, because the hydrogen concentration at the intercept of the two regions in figure 2 (10 at.%) is comparable with the hydrogen concentration usually found in high quality amorphous silicon for device applications. It should be remarked, that the same dependence of the optical bandgap as a function of the hydrogen content is found, when the bandgap is determined by the Tauc plot as is illustrated in the inset of figure 2.

It is interesting to compare this work with theoretical calculations performed by Papaconstantopoulos et al. [6]. They deduced a linear dependence of the optical bandgap on the hydrogen concentration, by assuming that only clusters with Si-H bonds are present. Their calculations also showed a decrease of the slope for hydrogen concentrations above 10 at. %. However the model did not predict a constant optical bandgap with hydrogen concentration above a hydrogen concentration of 10 at. %.

In order to explain the experimental results we have performed infrared absorption measurements on the amorphous silicon films. The infra red absorption spectrum of amorphous silicon shows a Si-H stretching mode at 2000 cm^{-1} and a $Si-H_2$ stretching mode at 2090 cm^{-1}. Due to the broadening of the absorption peaks the seperate modes can hardly be resolved. However the experimental peak position can be used as an indication for a variation of the SiH/SiH_2 ratio in the film. The measured peak position is illustrated in figure 3 as a function of the hydrogen concentration of the film.

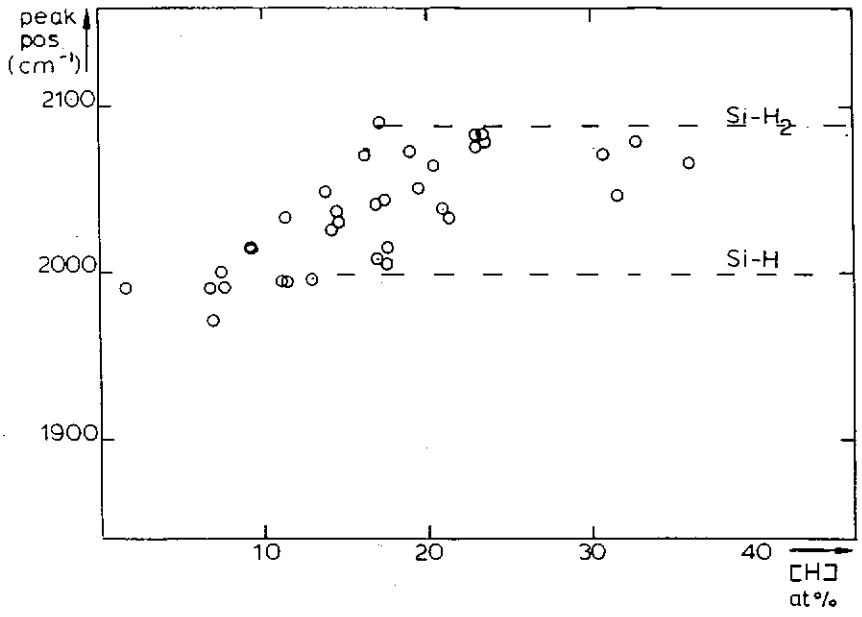

fig. 3 The experimental peak position of the combined SiH (2000 cm^{-1}) and SiH_2 (2090 cm^{-1}) stretching modes, as a function of the hydrogen concentration.

For low hydrogen concentration it is found that the peak position is located at the frequency of the SiH stretching mode. Apparently, for low values of [H], the hydrogen is predominantly bound as SiH. For increasing hydrogen concentration the peak position increases, indicating that the relative amount of SiH_2 in the film increases.

CONCLUSIONS

We conclude from a combination of these results, that the additional incorporated hydrogen above 10-12 at.% does not influence the optical bandgap. From figure 3 it is clear, that most of the hydrogen in the amorphous silicon film above 10-12 at.% is incorporated as SiH_2. Therefore only hydrogen bound as SiH appears to influence the optical bandgap, while hydrogen incorporated as SiH_2 does not alter the optical bandgap. In terms of the microstructure of amorphous silicon we therefore suggest, that up to a concentration of about 10 at.% hydrogen incorporation leads to a reduction of internal stress and defects which improves the material. Above a hydrogen concentration of 10 at.% addition of hydrogen leads to an increase of the void fraction in amorphous silicon. The influence of the incorporation of SiH_2 on the structure should lead to a change in the refractive index and the density of amorphous silicon, which is an aim of future investigations.

REFERENCES

1. W.A. Lanford, Solar Cells 2 445 (1980).
2. R.H. Klazes, M.H.L.M. van den Broek, and J. Bezemer, Phil. Mag. B45 377 (1982).
3. W.B. Jackson, S.-J.Oh, C.C.Tsai, and J.W. Allen, Phys. Rev. Lett. 53 1481 (1984).
4. L. Ley,in Hydrogenated amorphous silicon, Vol 2, ed. J.D. Joannopoulos and G.Lukovsky (Springer, Berlin 1984).
5. B. von Roedern, L. Ley, M. Cardona, Phys. Rev. Lett. 39, 1576 (1977).
6. D.A. Papaconstantopoulos, E.N. Economou, Phys. Rev. B24 7233 (1981).