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Determination of the optical bandgap of amorphous silicon

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ABSTRACT

The optical bandgap of glow-discharge and sputter-deposited a-Si has been deduced from measurements of the absorption coefficient α using a linear extrapolation of $(\alpha h\nu n)^{1/3}$ as a function of the photon energy $h\nu$. The exponent 1/3 is used instead of 1/2, resulting in a much better fit to the data. The influence of the method of extrapolation on the resulting value for the optical bandgap has been assessed.

§ 1. INTRODUCTION

The optical bandgap of amorphous semiconductors can be found from the dependence of the absorption coefficient α on the photon energy $h\nu$. The quantity $(\alpha h\nu)^{1/2}$ is usually approximated by a linear function of $h\nu$, at least at photon energies well above the bandgap energy. Also the index of refraction n is sometimes incorporated in the formula :

$$(\alpha h\nu n)^{1/2} \sim (h\nu - E_0), \tag{1}$$

with E_0 the optical bandgap energy. In the case of amorphous semiconductors for which the k-selection rule is relaxed, this relation is in agreement with a simple model based on two assumptions. Firstly, the densities of electron energy states $N(E)$ in the valence and conduction bands near the bandgap have a parabolic distribution. Secondly, the matrix elements for interband transition associated with photon absorption are equal for all transitions. For amorphous silicon, this approximation has been used by various authors (see, for example, Brodsky, Title, Weiser and Pettit 1970, Thutupalli and Tomlin 1977, Cody, Abeles, Wronski, Brooks and Lanford 1980). However, for some amorphous semiconductors exceptions to the square-root formula have been found. One example is a group of multicomponent glasses investigated by Fagen and Fritsche (1970). As reported by Mott and Davis (1979), Fagen found the following relation for these glasses :

$$(\alpha h\nu)^{1/3} \sim (h\nu - E_0). \tag{2}$$

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Davis and Mott (1970) discussed the possibility of a linear distribution function $N(E)$ in the region of localized states and the consequences for the conductivity $\sigma(\omega)$. Assuming that transitions between localized states occur with the same probability as other transitions, it follows, with the relation $\alpha = \sigma(\omega)/\epsilon_0 nc$, that

$$(\alpha h\nu n)^{1/3} \sim (h\nu - E_0). \tag{3}$$

However, if transitions between localized states are excluded, an approximately parabolic function like (1) is again found for absorption of photons with energy just above the bandgap energy. In that case, E_0 denotes the energy gap between localized states in one band and extended states in the other.

Although in publications on amorphous silicon it is conventional to approximate the absorption by a square-root formula, this seems not to be a very good approximation. As far as we can conclude from graphs in publications, eqn. (3) is generally a much better approximation for the absorption in amorphous silicon than eqn. (1). In this paper we present measurements of the absorption coefficient for various amorphous silicon layers. Objective criteria from statistics are used to judge the quality of fitting of eqns. (1) and (3) to the data. The value of E_0 and its standard deviation are determined by linear extrapolation, using eqn. (3).

§ 2. Film preparation

Amorphous silicon films were prepared by glow-discharge decomposition of silane and by sputtering of pure silicon. For the films produced by decomposition of silane a capacitive glow-discharge reactor was used. Its symmetrical electrode system was connected to the balance output of an r.f. generator with an output power of 40 W. Glass or fused quartz substrates were attached to the two parallel electrodes. The electrodes had a diameter of 60 mm and were 30 mm apart. Both electrodes were heated by a resistance heater so that substrate temperatures T_s up to 400°C could be reached. Silane diluted in argon (95%) was injected in the reactor chamber. The pressure was maintained at 90 Pa by means of a rotary pump. The resulting growth rate was about 0·1 nm s^{-1}.

The sputtered films were produced in pure argon as well as in a mixture of argon and 5 vol.% hydrogen. The sputter cathode was made of five-nines pure silicon. The diameter of the cathode was 100 mm and its distance to the substrate was 37 mm. The sputtering system was pumped by a turbomolecular pump until a base pressure of about 2×10^{-5} Pa was achieved. The sputtering gas was admitted to the system through a needle valve and the pressure was maintained at 1·3 Pa. An r.f. power of 1 kW resulted in a growth rate of about 1 nm s^{-1}. During the sputtering the substrate was heated to 200 ± 30°C.

§ 3. Optical measurements

The optical constants were determined by measuring the spectral transmittance T and the spectral reflectance R of the films at photon energies between 0·6 and 3·2 eV. The apparatus consisted of a surface-mirror system.

A tungsten strip lamp was used as a light source. The detector system was a diffraction grating monochromator in combination with a PbS cell, a Si photodiode or a photomultiplier. The optical beam was chopped and the signals were detected with a lock-in amplifier. The transmittance and reflectance were measured at an angle of incidence of about 5°, using polarized light. The direction of polarization was normal to the plane of incidence and reflection.

The procedure for calculating the optical constants has been outlined by Denton, Campbell and Tomlin (1972). Formulae giving R and T as functions of the refractive index n and the absorption coefficient α were derived, taking into account all multiple reflections in the film as well as in the substrate. The values of n, α and the film thickness d were computed from the measurements of R and T by an iterative method. The standard deviations of n and α were also determined, assuming an uncertainty of 0·5% in the measured values of R and T.

In determining the optical constants, more complicated formulae had to be applied because of the oblique incidence of the optical beam. However, if the small angle of incidence had been neglected, an error of less than only 0·4% would have been introduced in terms of R and T. The computations were performed for one fixed angle of incidence. The divergence of the optical beam, which was 3°, caused a negligible error in the results.

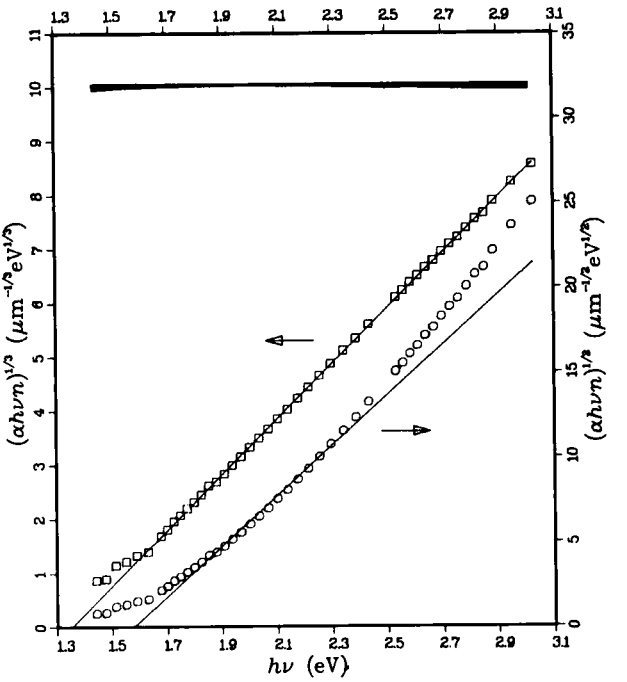
§ 4. Results and discussion

Figures 1 and 2 represent the photon absorption of a sputtered sample (number 2) and of a glow-discharge sample (number 3), respectively. In both figures $(\alpha h\nu n)^{1/2}$ and $(\alpha h\nu n)^{1/3}$ are linearly extrapolated to zero in order to find an optical bandgap energy E_0. The extrapolation was performed by a least-squares method, weighting the errors of the individual measuring points. In the case of a cube-root approximation the points in the low-energy tail were excluded. The limiting point was the first point from the high-energy side which contributed significantly to the resulting standard deviation of the value of E_0. To compare the two extrapolation methods, for a square-root approximation the same measuring points were considered as for the cube-root approximation. The figures clearly show that the cube-root approximation gives a much better fit to the experimental data. To judge the quality of the fit of both approximations, we computed

$$\chi^2 = \sum_n (Y_n - Y_{Ln})^2/\sigma_n^2, \tag{4}$$

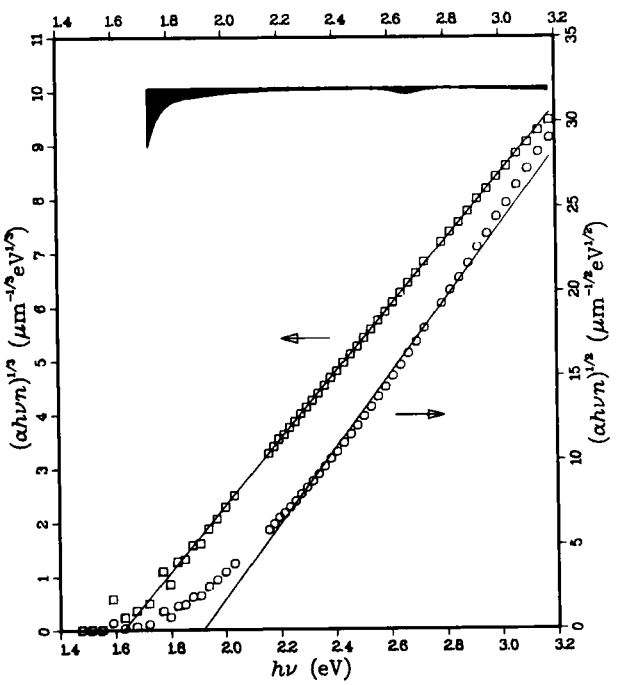
where Y_n is the ordinate of the nth measuring point and Y_{Ln} is its approximation by the straight line. The standard deviation of the nth point is σ_n. For a good fit and a proper estimation of the measuring errors, χ^2 must be equal to k within a standard deviation of about $(2k)^{1/2}$, in which k is the number of measuring points minus two. The 38 measuring points of sample number 2 that were considered yielded $\chi^2 = 45$ for the cube-root approximation and $\chi^2 = 1591$ for the square-root approximation. For sample number 3, using 42 measuring points, $\chi^2 = 25$ and $\chi^2 = 1261$ were found, respectively. Roughly speaking, the deviation of the square-root approximation from the

Fig. 1



Photon absorption of an a-Si sample (number 2), sputtered at 200°C in the presence of H_2. Two linear approximations are shown to determine an optical bandgap. The height of the inset indicates the experimental error (standard deviation) on the left-hand scale.

Fig. 2



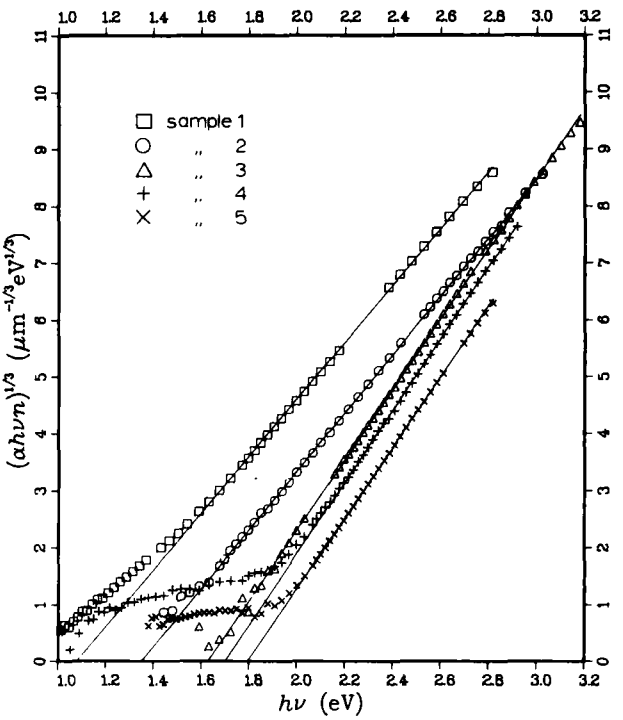
Photon absorption of an a-Si sample (number 3), produced by glow-discharge decomposition of SiH_4. Two linear approximations are shown to determine an optical bandgap. The height of the inset indicates the experimental error (standard deviation) on the left-hand scale.

measuring points amounts to six times the standard deviation of these points. The fit of the cube-root approximation is consistent with the estimated standard deviation of the measuring points.

The latter approximation was applied to measurements on five samples, as shown in fig. 3. Two of these samples were sputtered, one in the presence of hydrogen and one in pure argon. The other three samples were produced by a glow-discharge decomposition of silane at different substrate temperatures. The computed optical bandgap energies are listed in the table. The slopes of the graphs in fig. 3 are indicated by a constant c which is defined by

$$\alpha h\nu n = c(h\nu - E_0)^3. \tag{5}$$

Fig. 3



Photon absorption of five a-Si samples. Preparation methods and numerical details are as listed in the table.

The results as shown in fig. 3 are similar to those mentioned in the literature. It is remarkable that the same slope is found for samples produced by the same method, whereas an important difference in slope exists between sputtered and glow-discharge samples. The two production methods apparently yield essentially different materials, probably due to a different structure or to incorporated impurities.

It should be noted that the photon energies which contribute to the absorption in the linear range as shown in fig. 3 lie from 0·3 to 1·3 eV above the experimental bandgap energy. This result suggests that the assumption

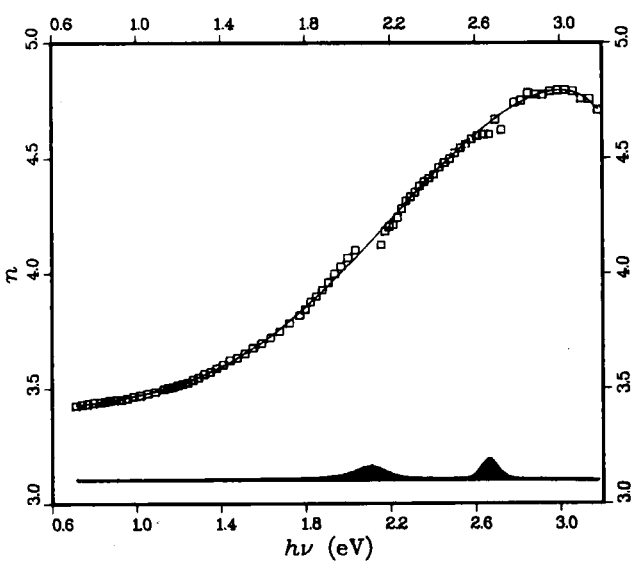
Optical bandgap energy E_0 as defined by $\alpha h\nu n = c(h\nu - E_0)^3$.

Sample number	Preparation	Temperature (°C)	Thickness (μm)	Extrapolation range (eV)	E_0 (eV)	c ($\mu m^{-1} eV^{-2}$)
1	Sputtered	200	0·108	1·6–2·8	1·080 ± 0·009	125 ± 2
2	Sputtered	200	0·087	1·7–3·0	1·352 ± 0·008	136 ± 2
3	Glow discharge	370	0·047	1·9–3·2	1·630 ± 0·007	238 ± 2
4	Glow discharge	240	0·060	2·1–2·9	1·702 ± 0·013	250 ± 3
5	Glow discharge	145	0·167	1·9–2·8	1·796 ± 0·006	241 ± 2

made by Davis and Mott (1970) concerning the linear distribution function $N(E)$ in the region of localized states can be generalized to extended states. Owing to the better fit of eqn. (3) at high energies, the low-energy tails seem to become more pronounced. However, accurate measurements on thicker samples are needed to study these tails in more detail.

As follows from figs. 1 and 2, the optical bandgap can differ by about 0·3 eV, depending on the method of extrapolation and on the range of measurements used for the extrapolation. The optical bandgap also changes, when it is defined by eqn. (2) instead of eqn. (3). The effect of the omission of the refractive index n was computed for sample number 3. The refractive index of this sample is shown in fig. 4. We found that the influence on the

Fig. 4



Index of refraction n of an a-Si sample (number 3), produced by glow-discharge decomposition of SiH_4. The height of the inset indicates the experimental error (standard deviation).

linearity was negligible. The bandgap energy, however, was 0·05 eV lower when eqn. (2) was used in place of eqn. (3).

An alternative possibility to improve the fit of the extrapolation function to measurements was suggested by Thutupalli and Tomlin (1977), who measured the optical constants of evaporated amorphous silicon. They applied eqn. (1), but supposed that the measured photon absorption spectrum was the result of a superposition of two processes arising from two energy gaps. One gap (of 1·4 eV) could be the gap between the localized states near one band and the extended states of the other band. The other gap (of 1·8 eV) was supposed to be the gap between the extended states of the conduction and the valence band. Using the cube-root approximation as proposed here, they probably would have found a single bandgap of about 1·2 eV.

§ 5. Conclusions

Experimental evidence has been given for a surprisingly good approximation to the absorption edge of amorphous silicon by eqn. (3). The approximation holds, at least for photon energies between 0·3 and 1·3 eV above the bandgap energy. This result can be explained by a linear distribution of energy states near the bandgap and equal matrix elements for interband transitions. However, more complicated models may lead to the same results. Although the theoretical foundations of the assumptions made in the proposed model are not well established, the cube-root approximation has the practical advantage over the square-root approximation that it defines unambiguously an optical bandgap which depends little on the range of photon energies above the bandgap where absorption measurements are made.

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