

OPTICAL MODULATION SPECTROSCOPY

1. Introduction

The study of localized states in the gap of an amorphous semiconductor is a very important problem. Many methods were conceived to find the density of states (DOS) and their results are very much connected with the physical phenomena which are fundamental for the method. The energy distribution of electrons in a semiconductor is changed by illumination. This effect can be used for studying the positions in the energy scale of DOS and its distribution by **optical modulation spectroscopy** (OMS). Two optical radiation beams are used: one for producing the excited states (au laser light) and the second one for measuring the changes in the optical transmission that occur. These changes can be: i) photo-induced absorption (PA) and ii) photo-induced bleaching (PB).

The PA is associated with electronic transitions from initial energy states when their occupation is enhanced by illumination or with transitions to final states emptied by illumination; the PB is associated with transitions from initial states emptied by laser beams (they are occupied in dark conditions) or with transitions to final states filled by illumination (they are emptied in dark). Both processes PA and PB will affect the optical transmission spectrum.

The relative change of the transmission ($\Delta T/T$), which represents the OMS signal, is proportional to the photo-induced change $\Delta\alpha$ of the absorption if the intensity of the laser beam is low enough. The OMS signal may be described as superposition of PA (generally associated with charged dangling-bond (DB) states) and PB (associated with the neutral DB).

In this work OMS measurements and data analysis for a-SiC :H alloys containing different amounts of carbon are presented. At room temperature the PA contribution is dominant and it is explained in terms of DB states [1, 2]. For low temperatures the OMS signal has PA and PB contributions. For good-quality material, the band-tail contributions to optical transitions can be extracted. Information about the Fermi level and demarcation level positions is obtained and a connection with the optical absorption results [3] is made.

2. Theory

The photons absorption due to transitions from the initial states characterized by energy E and density of states $g_i(E)$, to the final states with energy $E+\hbar\omega$ and density $g_f(E+\hbar\omega)$, may be described for a disordered solid in which the \mathbf{k} vector conservation doesn't hold, by:

$$\alpha(\omega) = \frac{c}{\hbar\omega} \int |M|^2 g_i(E) \cdot g_f(E + \hbar\omega) \cdot [f(E) - f(E + \hbar\omega)] dE \quad (1)$$

where C is a constant, M is the momentum matrix element and f is the equilibrium occupancy function. Such a relation may be written for the sample irradiated with laser light (the photon energy is greater than the energy gap) but $f(E)$ must be replaced by a non-equilibrium occupancy function $f^*(E)$. The absorption coefficient can be calculated by

$$\Delta\alpha(\omega) = \frac{C}{\hbar\omega} \int |M|^2 g_i(E) \cdot g_f(E + \hbar\omega) \cdot [\Delta f(E) - \Delta f(E + \hbar\omega)] dE \quad (2)$$

where $\Delta f = f^* - f$ is the changes produced by illumination.

It's very important to observe that in the expression of α , the refractive index, n , is present by the relation between the imaginary part of dielectric constant and the absorption coefficient: $\varepsilon_2 = nc\alpha/\omega$. Normally we take into account the dependence of n on frequency. Since we study only the region near the absorption edge, we can consider $n(\omega) \approx \text{constant}$ and we find the refractive index in the constant C expression.

Grevendonk et al. [1] made a short review of the theoretical expression of $\Delta\alpha(\omega)$ for different DOS functions, $g_i(E)$ and $g_f(E + \hbar\omega)$. The PA contribution to the OMS signal may be described if we consider for g_i the states localized above the equilibrium Fermi level E_F and the final states as the states into the conduction band. Generally, the last one is parabolic in energy: $g_f(E) \sim (E - E_F)^{1/2}$ and the distribution of the DB states we will take a Gaussian function:

$$g_i(E) = \frac{N_T}{\sigma(2\pi)^{1/2}} \cdot \exp\left[-\frac{1}{2} \cdot \left(\frac{E-\mu}{\sigma}\right)^2\right] \quad (3)$$

where σ is the standard deviation.

Under these conditions, Eqn. (2) may be written as:

$$\Delta\alpha(\omega) \sim \int \exp\left[-\frac{1}{2} \cdot \left(\frac{E-\mu}{\sigma}\right)^2\right] \cdot (E + \hbar\omega - E_C)^{1/2} dE \quad (4)$$

where E_C is the bottom of the conduction band. Rel. (4) may be used to fit the experimental results. A good fit is obtained if we consider the super position of PA and PB contributions. The Eqn. (2) is a general expression, and it describes also the photo-induced bleaching of absorption. The neutral DB states are localized below the equilibrium Fermi level E_F and they are responsible for PB signal (the final states being the conduction band, too).

3. Experimental measurements and discussions

3.1 Samples description

The hydrogenated silicon-carbon alloys were prepared with the conventional glow-discharge technique. The gas-flow ratios defined by

$$r = \frac{Q_{[CH_4]}}{Q_{[CH_4]} + Q_{[SiH_4]}} \quad (5)$$

were 42% and 60%.

The carbon content in alloys is function of this ratio. Some parameters of the deposition process are presented in Table 1.

Table 1: Some parameters of a-SiC:H deposition

| | |
|-----------------------|------------------------------|
| Substrate temperature | 200C |
| r.f. power | 12.5 – 25 mW/cm ² |
| Gas concentration (r) | 42% - 70% |
| Total pressure | 0.1mbar |

The substrates have been optical glass.

3.2 Measurement setup

The setup to measure the optical transmittance within the OMS experiments is presented in Figure 1 : the light emitted from an incandescent source passes through a monochromator and then through the sample. To reduce the stray light, before the detector, a second monochromator is used.

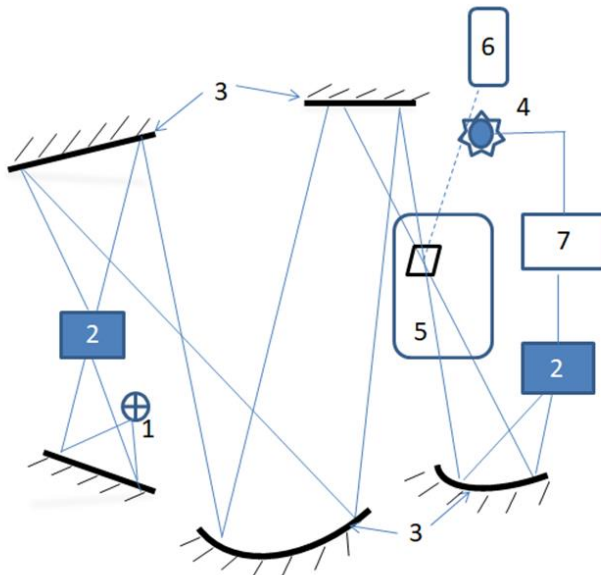


Figure 1. Schematic representation of an OMS setup: 1=light source, 2=monochromator, 3=mirror, 4=chopper, 5=cryostat with sample on the sample-holder, 6=Ar laser, 7=detector + lock-in amplifier

A lock-in amplifier will measure the detector signal. Since the OMS signal is the difference between the transmission characteristic of the sample with and without the pump light - an Ar laser, the measurement begins by placing a chopper between the first monochromator and the sample.

Without laser light, the transmission T is measured. With the chopper between the laser and the sample, the transmission of the sample in the presence of the pump light is measured. All these measurements are controlled by a computer and the OMS signal is averaged for each wavelength.

3.3 Experimental data and analysis

For thin films the OMS curve presents an interference pattern and we will take the mean value of maxima and minima envelope at each wave length.

Figure 2 presents the OMS signal of a-SiC:H sample with $r = 42\%$ for room temperature and Figure 3 shows the fit with Rel. (4) of the OMS signal for both samples. From experimental data we can observe the influence of the carbon content. More carbon means a deeper distribution of DB and a higher optical gap. Eqn. (4) allows to obtain the values of some important parameters like: the position of equilibrium Fermi level E_F , of quasi-Fermi levels E_{Fn} and E_{Fp} , of the maximum of the DB Gaussian distribution. All these parameters are presented in Table 2 and the energy amounts are measured from the conduction band edge. Therefore, the Fermi level position is 1.2 eV, for the sample with $r = 42\%$ and 1.35 eV for the sample with $r = 60\%$. Elsewhere [2] we show that these values are in good agreement with the values of the optical gap of the samples measured in Wemple and DiDomenico version [4], and in this way the undoped character of the samples is proved.

Table 2 also shows the thermal activation energy of the carriers on the same samples, obtained by dark conductivity measurements. It's very important to observe that the thermal activation energy is lower than the Fermi level value. This fact can be explained by the difference between the optical and thermal processes. Since the optical excitation of electrons is realized in a much shorter time than that in which the structure can relax, the optical transitions are vertical in the configuration-coordinate diagram [5]. After the optical transition, the system relaxes by interactions with phonons until the potential minimum is reached. The thermal excitation means the relaxation of the system, because the nature of this transition involves the lattice participation. Therefore, in a configuration-coordinate diagram, the thermal transition is an oblique transition directly to the minimum potential position.

Table 2 OMS results of undoped a-SiC :H sample

| R (%) | E_F (eV) | E_{Fn} (eV) | E_{Fp} (eV) | E_a Wemple (eV) | E_0 (eV) | E_{Do} (eV) | E_{D-} (eV) | E_{bt} (eV) | E_{dm} (eV) |
|---------|------------|---------------|---------------|-------------------|------------|---------------|---------------|---------------|---------------|
| 42 | 1.2 | 0.54 | 1.84 | 2.48 | 1.0 | 1.54 | 0.9 | 0.15 | 0.57 |
| 60 | 1.35 | 0.50 | 2.30 | 2.77 | 1.1 | 1.72 | 1.0 | 0.19 | 0.69 |

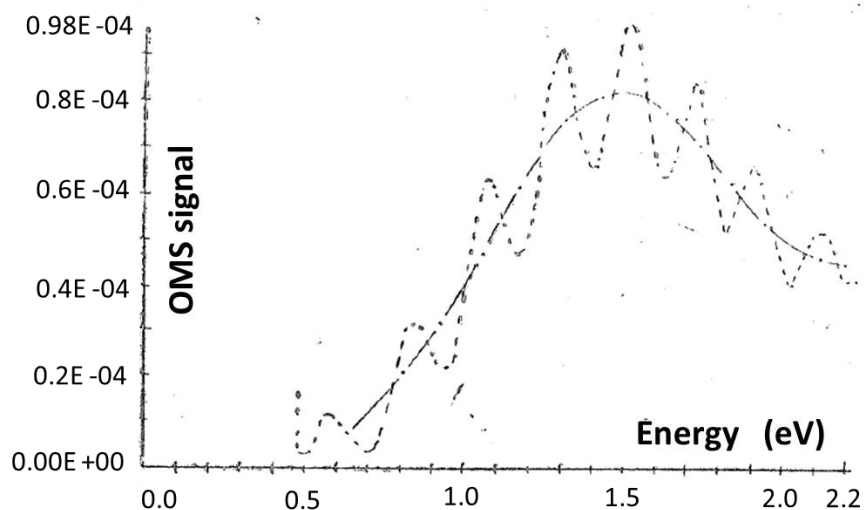


Figure 2. OMS signal in a-SiC:H sample, $r = 42\%$. The Oscillations in the photo-induced transmission as a function of photon energy and the results of averaging, are presented.

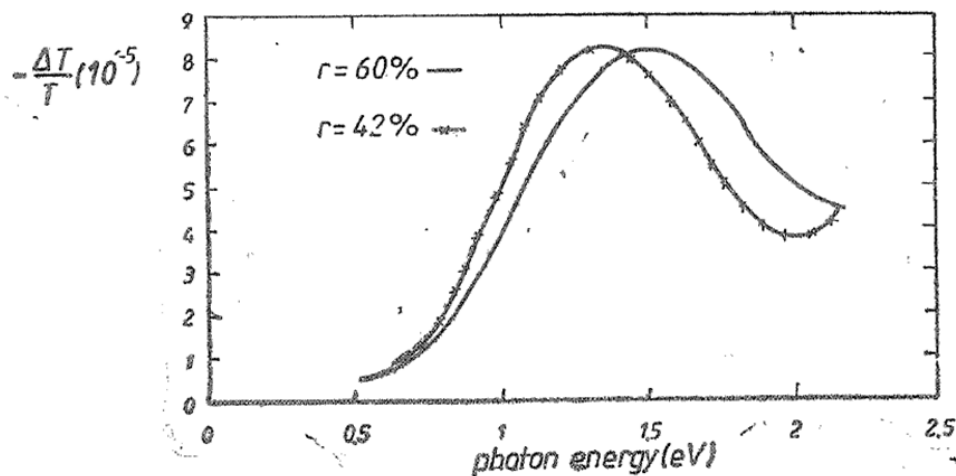


Figure 3. OMS averaged signal and its fit for sample with different carbon content.

The position of neutral DB, D^0 , and negative charged DB, D^- , are in Table 2, too. The D^- states peak at 0.9 eV and 1 eV below the conduction band for sample with $r = 42\%$ and respectively $r = 60\%$. They have a broad distribution ($\sigma_{D^-} = 0.2$ eV and 0.3 eV respectively) for the film with more carbon. We can see that more carbon means also a deeper position of D^- states (under Gaussian distribution). Bullot and Schmidt [6] suggested that $(sp^3)C - (sp^3)C$ bonds may be responsible for

a high optical gap. This idea is in good agreement with a deeper state of $(sp^3)D^-$ than $(sp^2)D^-$ when the energy origin is the conduction band edge.

The maximum of the Gaussian peak D^0 states was found at 1.57 eV and respectively 1.72 eV. Both of them have the same standard deviation $\sigma_{D0} = 0.12$ V. It's important to note the symmetry of D^- and D^0 positions as against the Fermi level position. For example, if we take the Fermi level energy as energy reference, the D^- dangling bonds are placed at 0.3 eV while the D^0 has the maximum of the Gaussian distribution at -0.3 V.

The band tail contributions are noticeable at low temperature OMS data measurements. At this temperature ($T = 20$ K) the release of the carriers trapped in band-tail states occurs at a much slower rate and transitions involving these states and the allowed bands dominate the spectrum. In Fig. 3 it is presented the OMS spectrum of a-SiC:H sample with $r = 42\%$ for room temperature and for $T = 20$ K. The low temperature curve can be fitted by a convolution of a distribution $\rho(E)$ of carriers trapped in band-tail states with a parabolic valence band density of states. To describe the carrier thermalization by hopping in an exponential band-tail, Stoddard et al., [7], have used for the $\rho(E)$:

$$\rho(E) = K \cdot \exp\left(-\frac{E}{E_1}\right) \cdot \exp\left[-\exp\left(-\frac{E-E_{dm}}{E_1}\right)\right] \quad (6)$$

where K is a constant, $E_1 = \left(\frac{3}{2}\right) \cdot E_{bt}$ (with E_{bt} the width of the band-tail) and E_{dm} the demarcation energy separating the recombination states from trapping states. From [8], the **demarcation level** is close to the quasi Fermi level ; our experimental data show $E_{dm} = 0.57$ eV and $E_{Fn} = 0.57$ eV.

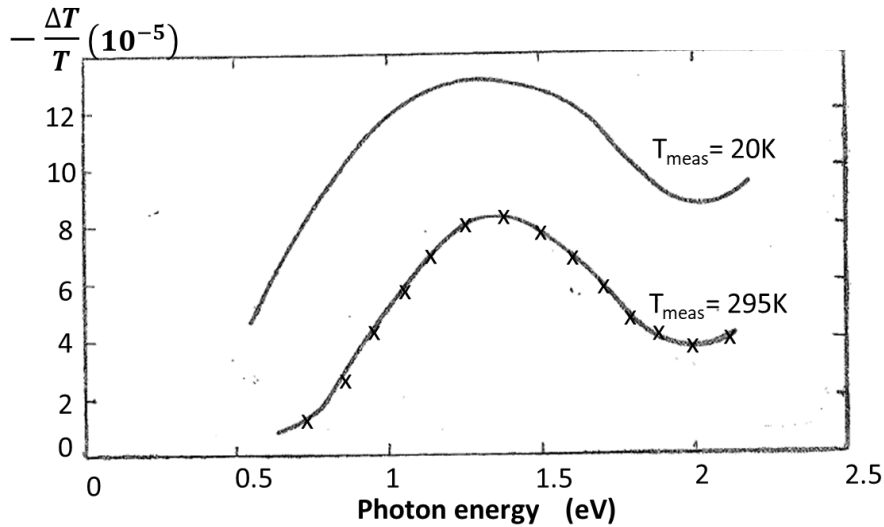


Figure 4. OMS spectra measured on a-SiC:H ($r = 42\%$) at room temperature and $T=20K$.

Concerning the band-tail width of the valence band, values as 150 meV ($r = 42\%$) and 190 meV ($r = 60\%$) are large. In [9] the authors explain the small values of E_{bt} as 70 - 90 meV for a-SiC:H alloys with a low carbon content, by a very high quality of the material. We observe that the band-tail parameter increases with the increasing carbon content. This is mainly due to the increase in the amount of micro-voids, which are also connected with the content of (sp^3)C sites [10].

REFERENCES

- [1]. W. Grevendonk M. Verluyten, J. Dauwen, G. J. Adriaenssens and J. Bezemer, *Phil. Mag.* B61, 393 (1990).
- [2]. J. Tauc and Z. Vardeny. *Phil., Mag.*, B52, 313 (1985).
- [3]. N.Tomozeiu, H.Herremans, N.Qamhieh and W.Grevendonk - "*Electronic, Optoelectronic and Magnetic Thin Films*", Ed.: Prof. J.M. Marshall, Research Studies Press, England, and John Wiley & Sons, New York, 1995, p. 660-663. ISBN 0 86380 173 0;
- [4]. S. H. Wemple and M. DiDomenico Jr., *Phys. Rev.*, B4, vol 3. 1338 (1971).
- [5]. S. R. Elliot, "(Physics of amorphous materials" Longman Scientific & Technical, England (1990), p. 392.
- [6]. J. Bullot and M. P. Schmidt, *Phys, stat sol. (b)*, 143. 345 (1987).
- [7]. H. Stoddart, Z. Vardeny and J. Tauc. *Phys. Rev.*, B38, 1362 (1988).
- [8]. A. Rose, *Concepts in Photoconductivity and Allied Problems*, Interscience, New York, 1963.
- [9]. H. Herremans, W. Grevendonk, R. A.C.M.M. van Swarj, W.G.J.H.M. van Sark, A.J.M. Arnold Bik and J. Bezemer, *Phil. Mag.*, B6G, 8787 (1992).
- [10]. D. L., Wilianison, A.H. Maban, P. B. Nelson and R. S. Crandall. *Appl. Phys. Lett.*, 55, (8), 783 (1989).