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OPTICAL PROPERTIES OF AMORPHOUS SILICON:  
SOME PROBLEM AREAS \*

N.M. Ravindra \*\*

International Centre for Theoretical Physics, Trieste, Italy,

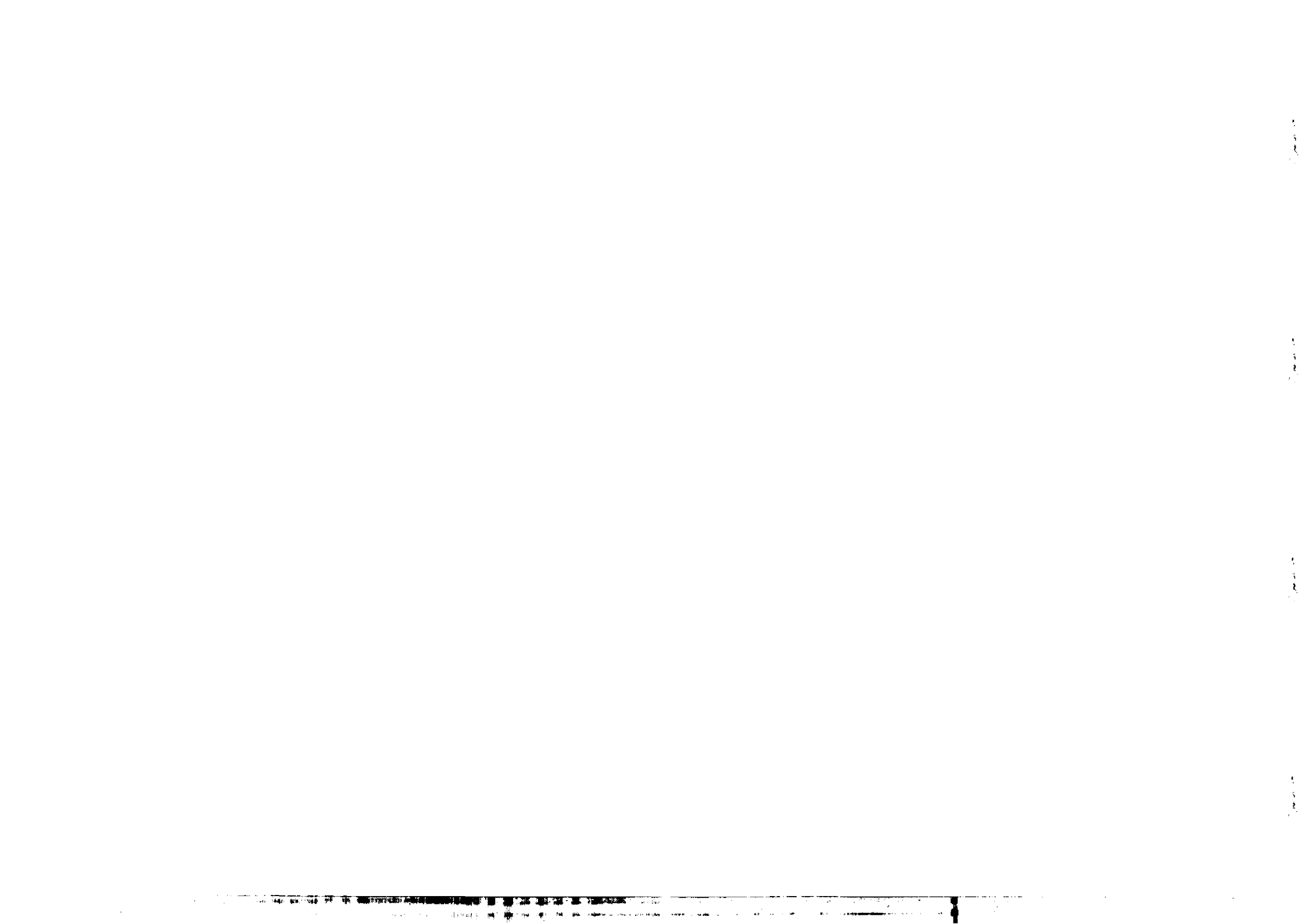
F. De Chelle, C. Ance, J.P. Ferraton, J.M. Berger and S.P. Coulibaly  
Laboratoire de Spectroscopie II, Université des Sciences et  
Techniques du Languedoc, Place E. Bataillon, Montpellier, France.

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\*\* Permanent address: Laboratoire de Spectroscopie II, Université des Sciences  
et Techniques du Languedoc, Laboratoire Associé au CNRS, Place E. Bataillon,  
34060 Montpellier, France.



## ABSTRACT

In this presentation we essentially attempt to throw light on some problem areas concerning the various optical properties of amorphous silicon. The problems seem to emerge from the classical methods employed to determine the optical properties like the optical gap, Urbach tail parameter and other related characteristics. Additional problems have emerged in recent years by virtue of many attempts to generalize the property-behaviour relationships for amorphous silicon without attributing any importance to the method of preparation of the films. It should be noted here that although many authors believe disorder to be the controlling parameter, we are of the opinion that at least for films containing fairly large concentrations of hydrogen, the hydrogen concentration has an equally important role to play. The present study has been carried out for films prepared by glow-discharge and chemical vapour deposition.

## INTRODUCTION

The localized states in the energy gap of amorphous semiconductors have been theoretically seen to be the result of potential fluctuations caused by disorder (1-3). The tailing of the density of states in amorphous silicon is now attributed to disorder - topological and structural disorder(4). In his detailed studies of the properties of glow discharge deposited amorphous germanium and silicon, Chittick(5) reports that at room temperature(300K), electrical conduction is achieved by thermally activated hopping in a band of acceptor states. The conduction becomes intrinsic at higher temperatures when carriers get excited beyond the localised states into the high mobility region.

It is well-known that the glow discharge deposition technique provides non-crystalline films which are essentially contamination free. Further, although the hydrogen content in amorphous silicon films prepared by glow discharge technique decreases with increase in deposition temperature, it always remains higher than in chemically vapour deposited films. It is generally believed that at least a qualitative comparison of the results concerning the properties of the films prepared by various techniques should be possible. Here, we attempt such a study. This study has been inspired by the recent work of Cody(6), Dunstan(7), Sumi-Toyozawa(8), Klazes et. al.(9) and Bahl-Bhagat(10).

## THEORY, ANALYSIS and DISCUSSION

In general, for many crystalline and amorphous semiconductors, it is well known that the absorption coefficient  $\alpha$  varies as

$$\alpha(h\nu) \propto \exp(h\nu/E_0) \quad (i)$$

or

$$\alpha(h\nu) \propto (h\nu - E_0)^2/nh\nu \quad (ii)$$

where  $E_0$  represents an energy characterizing the distribution of electronic states in band-like regions while  $E_g$  is characteristic of such a distribution in tail like region,  $h\nu$  is the photon energy and  $n$  is the index of refraction. Expression (i) which is the well known result of Urbach(11) has been seen to be valid for amorphous semiconductors in the range  $1 < \alpha < 10^4 \text{ cm}^{-1}$  (12).

At values of  $\alpha$  higher than  $10^4 \text{ cm}^{-1}$ , expression (ii) is utilized to determine the so called optical gap. There have been various interpretations for the Urbach tail parameter  $E_0$  (13-16). Expression (i) may be written as (6),

$$\alpha(E, T) = \alpha_0 \exp\left[\frac{(E-E_1)/E_0(T, X)}{T}\right] \quad (iii)$$

where, according to Cody et.al. (6),  $\alpha_0 = 1.5 \times 10^6 \text{ cm}^{-1}$ ,  $E_1 = 2.2 \text{ eV}$  corresponding to the data for  $2 \times 10^2 \text{ cm}^{-1} < \alpha < 5 \times 10^3 \text{ cm}^{-1}$  with  $E_0(T, X)$  being the width of the exponential tail and  $X$  is a parameter describing structural disorder. Note that unlike earlier conclusions (14), the temperature dependence of  $E_0$  cannot be neglected by virtue of the exponential nature of the absorption coefficient. At values of  $\alpha > 10^4 \text{ cm}^{-1}$ ,  $\alpha$  varies as (12)

$$(\alpha E) \propto (E-E_G)^{n'} \quad (iv)$$

where  $n'$  has been found to lie between  $1 < n' < 3$ . Such a variation of  $n'$  is essentially due to deviations of the density of states function  $g(E)$  from the free-electron gas behaviour. Expression (iv) is slightly different from the classical Tauc formula (17)

$$(\alpha E) \propto (E-E_G)^2 \quad (v)$$

Conventionally, what one does is to plot  $(\alpha E)^{1/3}$  as a function of the energy for  $\alpha > 10^4 \text{ cm}^{-1}$  and then extrapolate the curve to  $\alpha = 0$ . The corresponding value of the energy is the 'optical gap'  $E_G$  of the material. In the wake of the absence of any alternative method to define the gap  $E_G$ , such a method as is generally used (expr.v) seems to be qualitatively understandable but at least not quantitatively. For example, one can plot  $(\alpha E)^{1/2}$  and  $(\alpha E)^{1/3}$  versus energy to obtain different values of the gap  $E_G$ . In the process, it may even be difficult to differentiate between the best possible fit to experimental data. The question is what exactly is the meaning of the numbers that one obtains with such plots? This may reflect on the deviation from the parabolic nature of the bands.

We consider here two sets of samples - five of them have been prepared by glow-discharge while two of them are CVD samples. One of the glow-discharge prepared samples has been doped with boron and one of the CVD samples has been post-hydrogenated. For details concerning the preparation of the films and the measurements, reference is made to our earlier reported studies (18,19). The samples were typically one micron thick and all the measurements have been made at room temperature ( $T_m = 300\text{K}$ ).

In figures 1 and 2, we plot  $(\alpha E)^{1/2}$  and  $(\alpha E)^{1/3}$  versus  $E$  respectively. Essentially the  $(\alpha E)^{1/3}$  versus  $E$  plots yield lesser values for  $E_G$  compared to  $(\alpha E)^{1/2}$  versus  $E$  plots (by 0.15 eV). Unfortunately, both the plots fit in equally well with the experimental data. The Urbach tail parameter  $E_0$  is then determined from the plots of  $\log \alpha$  versus  $E$  in the low energy range ( $E < E_G$ ) (figure 3). This optical absorption edge  $E_0$  has earlier been explained in terms of an electric field broadening of an exciton (15). Attempts have also been made to understand the Urbach rule by utilizing a configuration-coordinate model which is essentially based on an analogy between the electronic excitation of a molecule and optical absorption in amorphous materials (8,13,14). It is to be noted here that at spite of the universality of the Urbach rule, sometimes the exponential tail to the absorption curve has been reported to be completely missing for some forms of amorphous germanium (20).

Cody et. al. find that the variation of the width of the Urbach tail  $E_0$  with temperature and the gap  $E_G$  with  $T$  are similar except that the sign is opposite, that is,  $(dE_0/dT) < (dE_G/dT)$  (6). The change in  $E_0$  is about 27% for a change in temperature of  $350^\circ$ . In general, Cody et. al. (21) report a linear variation of  $E_G$  with  $E_0$ . The relation is given by,

$$E_G(E_0) = E_G(0) - 6.2 E_0 \quad (vi)$$

where  $E_G(0)$  is the zero disorder limit for the optical gap equal to 1.94 eV for the a-Si:H<sub>x</sub> ( $x=0.09$  to  $0.19$ ) films. In figure 4, we attempt to extrapolate the results of Cody to our samples. As can be seen in the figure, such a linear variation of  $E_0$  with  $E_G$  just does not seem to hold good. Of course, this could be due to various reasons. First of all, it should be noted that the optical absorption measurements in amorphous semiconductors differ notoriously depending on the method of preparation, conditions during preparation and subsequent treatment (22). It has generally been observed that the optical absorption and the photoconductivity spectra of a-Si films prepared by CVD are similar to those of glow-discharge films (23-25). Sputter deposited and evaporated films exhibit properties similar to one another. Sputter deposited films have been the most studied ones and are understood fairly well.

In spite of such gross similarities in sputter deposited and evaporated films, it remains doubtful whether one could just extrapolate the structural models proposed for sputter deposited films to vacuum deposited films. This is especially so with respect to concept of voids. Films prepared at

low temperatures generally tend to have more voids explaining thereby a decreased density but with an increased index of refraction  $n$ . Such a conclusion is in complete accord with the studies reported by Bahl et.al.(26) for films prepared by electron beam evaporation. Bahl et. al. (26) find that with increase in deposition rate, the index of refraction increases. Understandably, films deposited at high rates tend to have more voids (hence a decreased density).

The problems with glow-discharge or chemically deposited films assume a different dimension altogether probably by virtue of the fact that here, the deposition proceeds atom by atom resulting thereby in a less imperfect structure (less disorder) or the influence of the defects may be compensated by certain active impurities. Further, with decrease in temperature of deposition  $T_D$ , the hydrogen concentration in a-Si:H films increases. The question now is if one can attribute all such property-behaviour relationships to disorder (like Cody) and treat disorder as the independent and the deciding parameter?

Broadly speaking, disorder can be classified into three types (27);

- (i) topological disorder - due to the atoms being displaced in a non-periodic way at the same time retaining the coordination as in the crystal resulting in new structural features
- (ii) quantitative disorder - which always accompanies topological disorder and results from fluctuations in bond lengths and deviations in bond angles with respect to the regular tetrahedral value
- (iii) extrinsic disorder - due to foreign impurities, defects etc.

In general, the first two types of disorder have been found to decrease with increase in temperature  $T_m$  (measurement temperature). For glow-discharge deposited films, it is well known that the hydrogen exo-diffusion starts at temperatures of  $T_m = 350^\circ\text{C}$ . This results in creation of dangling bonds (which were otherwise saturated; at  $T_m < 350^\circ\text{C}$ ). Thus, the structural disorder (due to the creation of dangling bonds) increases with increase in temperature at high temperatures ( $T_m = 350^\circ\text{C}$ ) while the thermal disorder (i & ii) decreases with increase in  $T_m$ . Thus, at least at high  $T_m$ , disorder is controlled by the hydrogen in a-Si:H films. Further, it seems to us that with such high concentrations of hydrogen, the role of hydrogen in a-Si:H films prepared by glow-discharge is different from its role in other kinds of films. Thermodynamically, it seems more logical to treat temperature as the only independent parameter ( $T_D$  or  $T_m$ ) with disorder and hydrogen concentration being a function of temperature. This kind of approach may be able to explain many of the problems associated with a-Si:H films produced by glow-discharge. In fig.5, we plot  $E_G$  and  $E_0$  as a function of the hydrogen concentration.

The above studies lead us to believe that the model of Cody may have limited applicability. In fact a look at the results of Brodsky (28) does not seem to indicate any kind of focussing of  $\ln\alpha$  versus  $E$  plots at  $E = 2.2$  eV (see Cody (6) for details). In fact, there does not seem to be any physical reason to accept this value of  $E$  at which  $\alpha = \alpha_0 = 1.5 \times 10^6 \text{ cm}^{-1}$  ( $E = E_1$ ). The results of Cody seems to indicate that annealing at temperatures as high as  $625^\circ\text{C}$  has not significantly changed the general behaviour of the sample (evidently accounting for the importance of disorder rather than the hydrogen content). But, all these results may be true for sputter deposited films. As such, it seems difficult to extrapolate these results to glow-discharge deposited films.

As a last part of the present study, we present in figure 6 a plot of index of refraction  $n$  versus the density  $\rho$ . As can be seen in the figure, as the index of refraction increases, the density also increases. Note that this behaviour is just the opposite of vacuum deposited films. However, such a behaviour seems to be understandable in terms of decreased hydrogen content with increase in deposition temperature. The densities have been evaluated theoretically elsewhere(29). Further, this behaviour of an increased refractive index with increased density seems to be easily understandable. After all, considering voids as absolutely transparent medium, with increasing deposition temperatures, one obtains films with less voids thus resulting in increased density and index of refraction.

Just in passing, we look at the definition of activation energy  $\Delta E$  (determined from electrical conductivity measurements) in terms of the optical gap  $E_G$ . Generally, it is accepted that  $\Delta E = (E_G/2)$  (12). The results of Hasegawa et. al. (30) concerning the annealing temperature effects on  $E_G$  and  $\Delta E$  do not seem to indicate any such relation. The problem could be with the very definition of  $\Delta E$ . If one considers a conventional model wherein the Fermi level is pinned to the centre (or middle) of the gap, then the activation energy  $\Delta E$  may be representative of energy levels corresponding to states in the gap and the bottom of the conduction band (rather than the Fermi level and the bottom of the conduction band).

#### CONCLUSION

An attempt has been made in the above study to identify some problems concerning the various properties of amorphous silicon. Let alone the  $\sigma_0$  problem, there seem to be more simpler problems which need to be tackled with care. At times, it could be very difficult to separate the effects of

disorder or hydrogen content on the properties of a-Si:H. At least for glow-discharge deposited films, they seem to be more acceptable as alloys. Detailed work in this direction is now being taken up. But, as long as most of the parameters remain as fitting parameters (determined from extrapolation procedures), it might be very difficult to attribute any precise physical meaning to the numbers. Until and unless both the electrical and optical measurements are made in the same laboratory conditions, it may be difficult to confirm the experimental results. Such studies hardly exist in literature. Further, the role of voids in different types of films is yet to be well understood.

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FIGURE CAPTIONS :

FIGURE 1 :  $(\alpha E)^{\frac{1}{2}}$  versus Energy. Note that on every figure, the samples are numbered in the following manner; (1) and (2) are CVD samples before and after post-hydrogenation respectively. Samples (3),(4), (5),(6) and (7) are prepared by glow-discharge at temperatures of 350,280(doped),280(undoped),150 and 50 °C respectively. All the measurements have been made at room temperature (300 K).

FIGURE 2 :  $(\alpha E)^{\frac{1}{3}}$  versus Energy.

FIGURE 3 :  $\text{Log} \alpha$  versus Energy.

FIGURE 4 :  $E_g, E_o$  versus the hydrogen concentration.

FIGURE 5 :  $E_g$  versus  $E_o$  - note the nonlinear variation.

FIGURE 6 : Index of refraction  $n_o$  (referred to as  $n$  in the text) versus density for different samples. (see reference (29) for details concerning calculations.

Note : In figures 4 and 5, Circles and Squares represent values of  $E_g$  from figures 1 and 2 respectively. The triangles represent  $E_o$  values. It may further be noted that  $E_g$  and  $E_o$  have the same meaning.

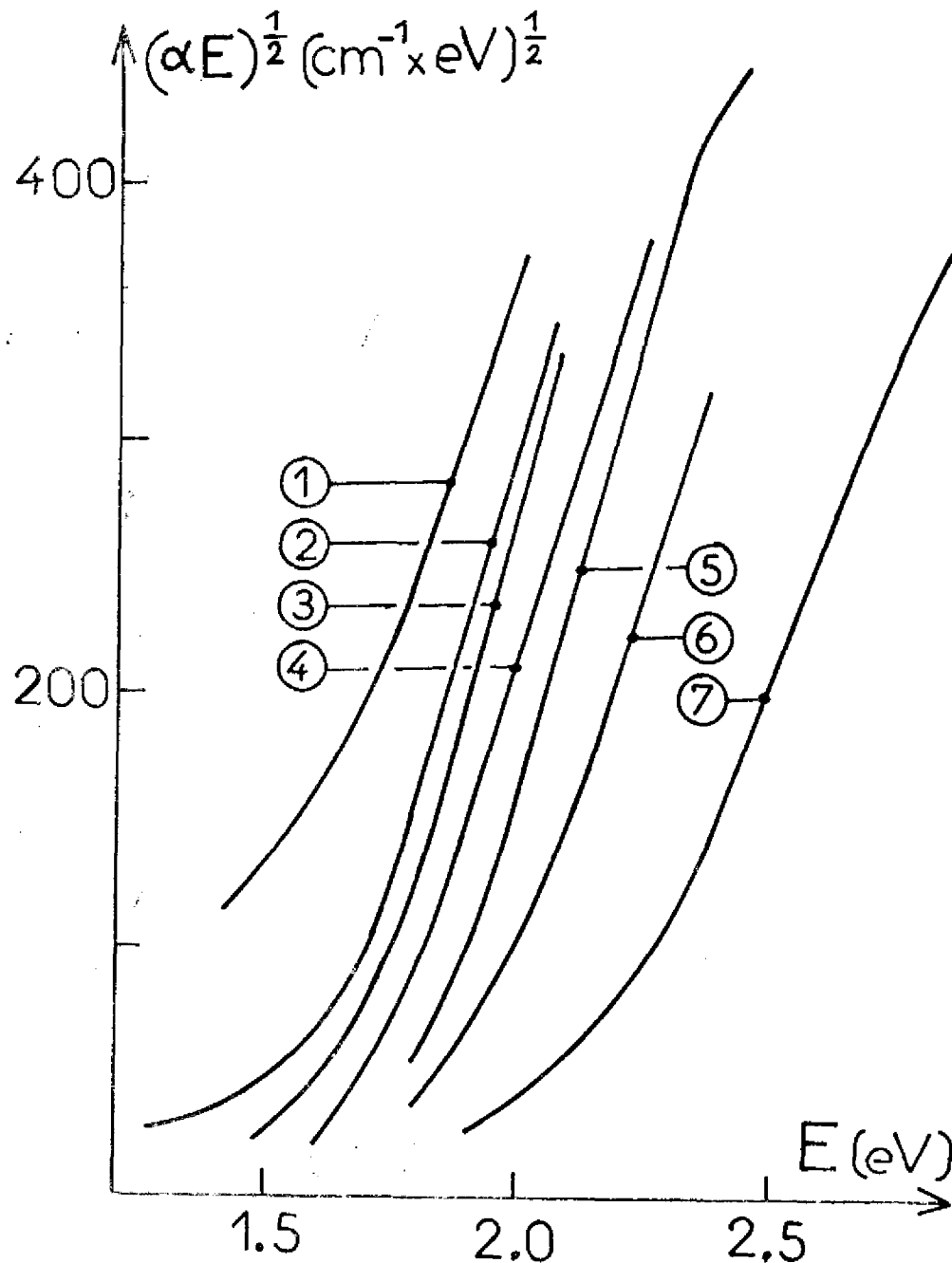


Fig.1

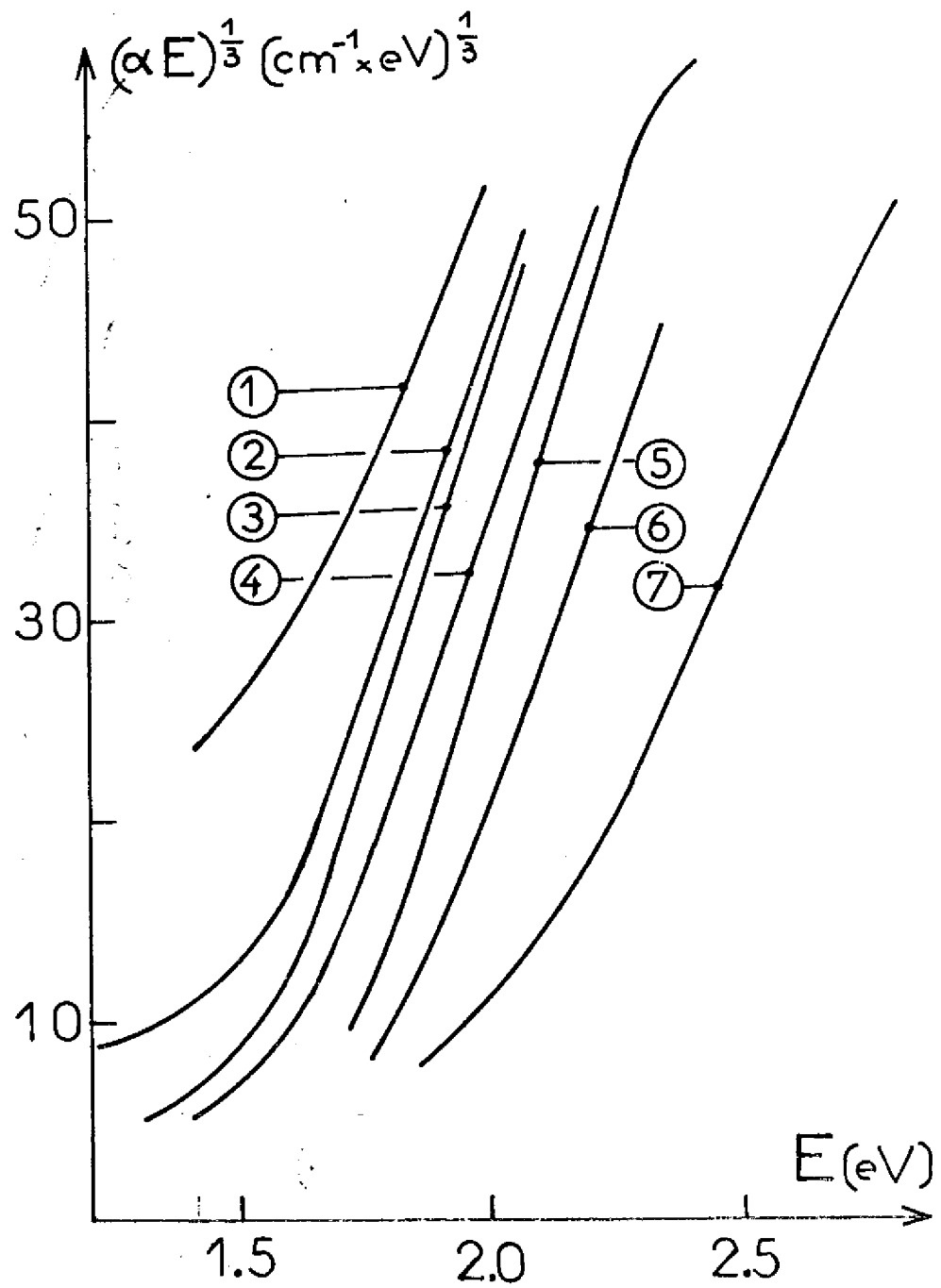


Fig. 2  
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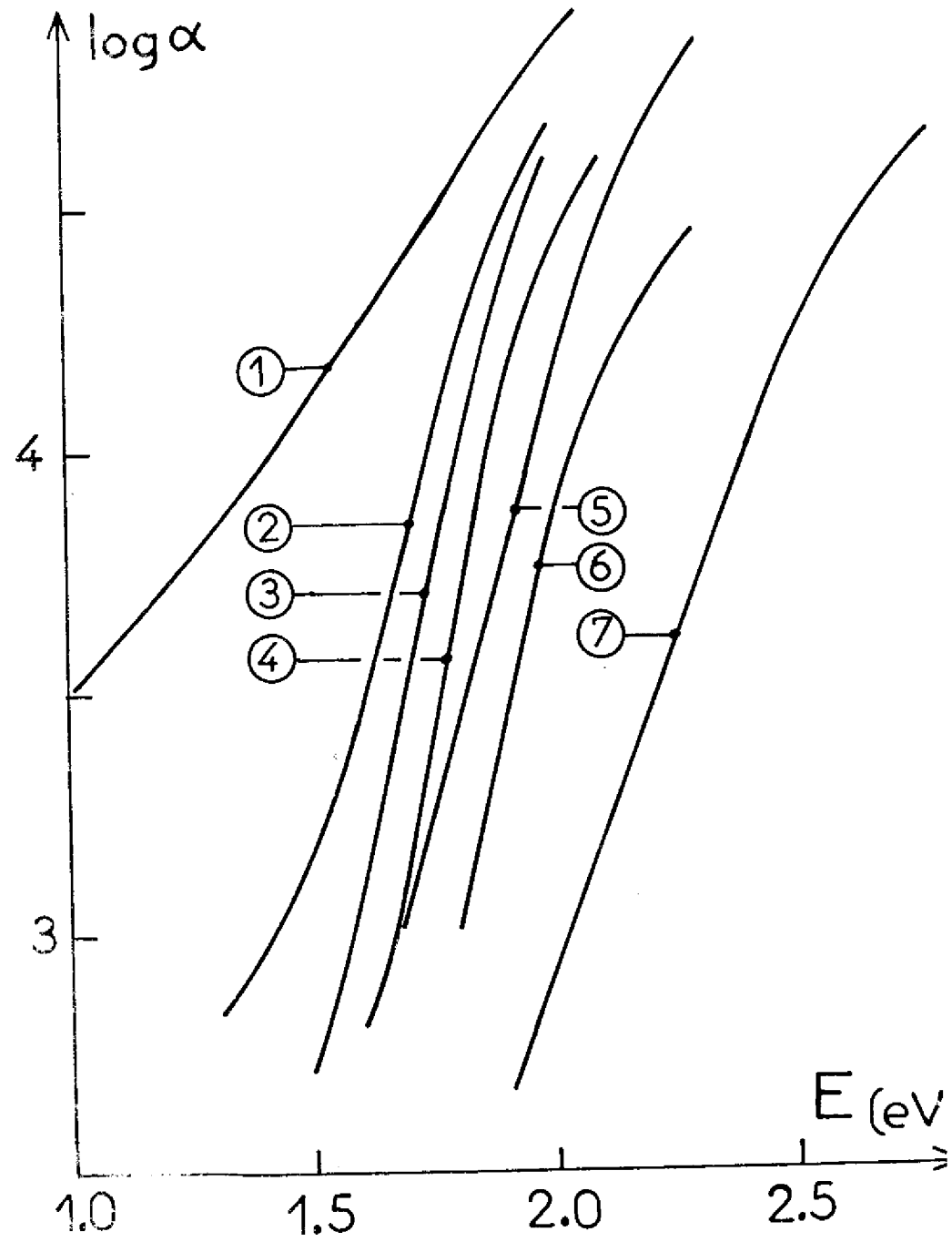


Fig. 3  
-12-



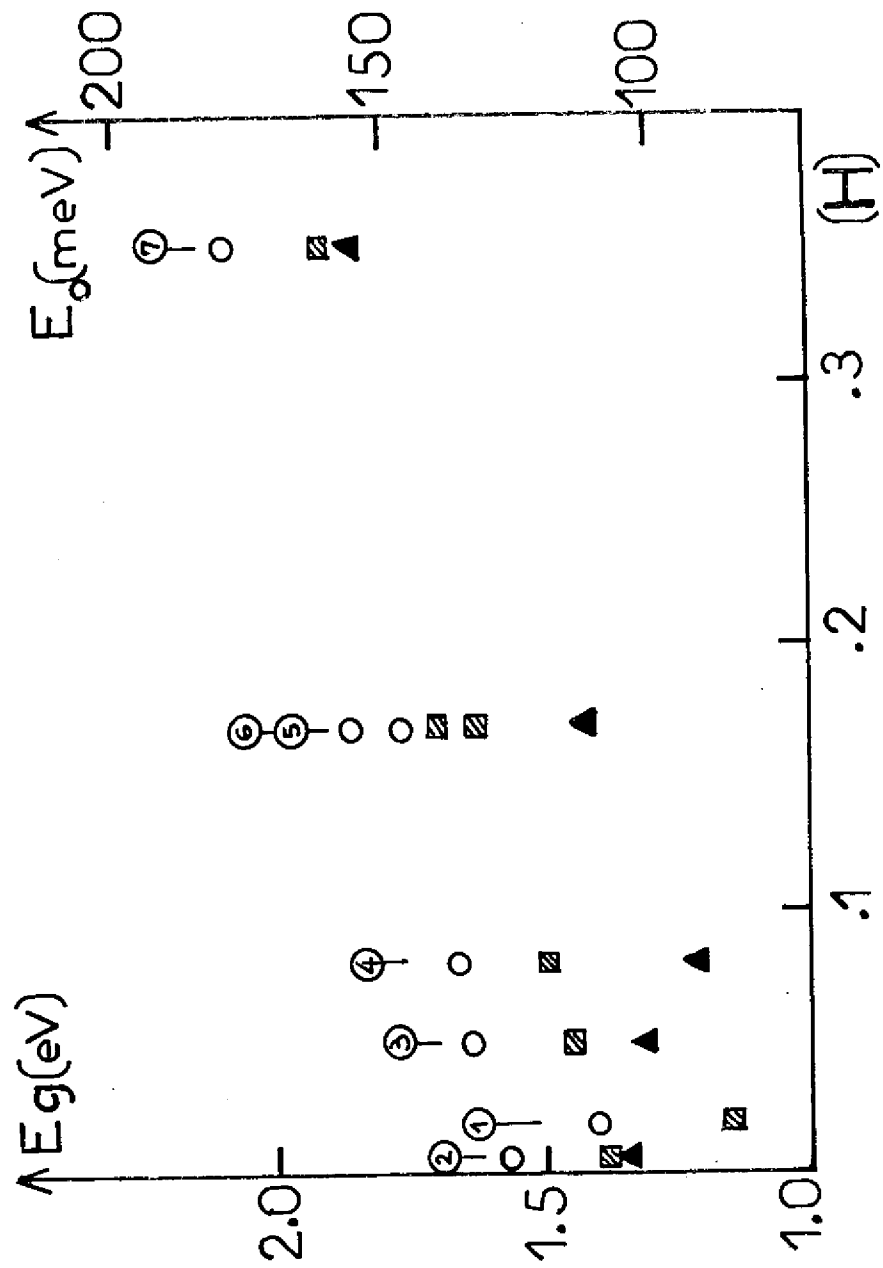


Fig. 4

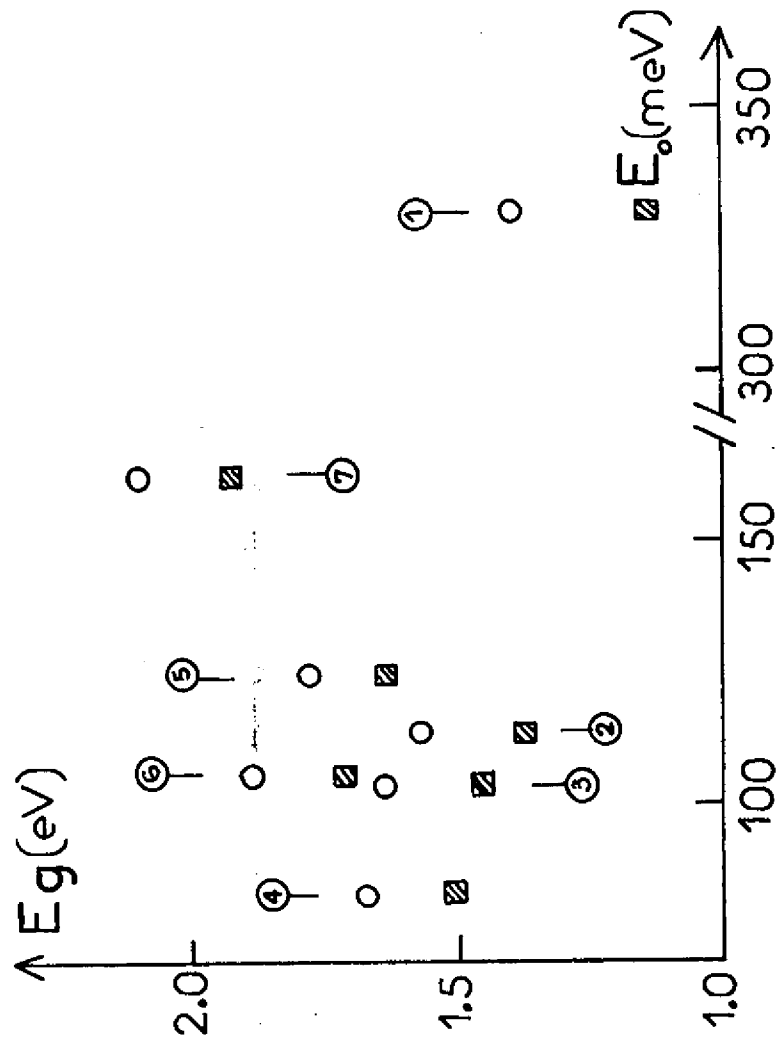


Fig. 5

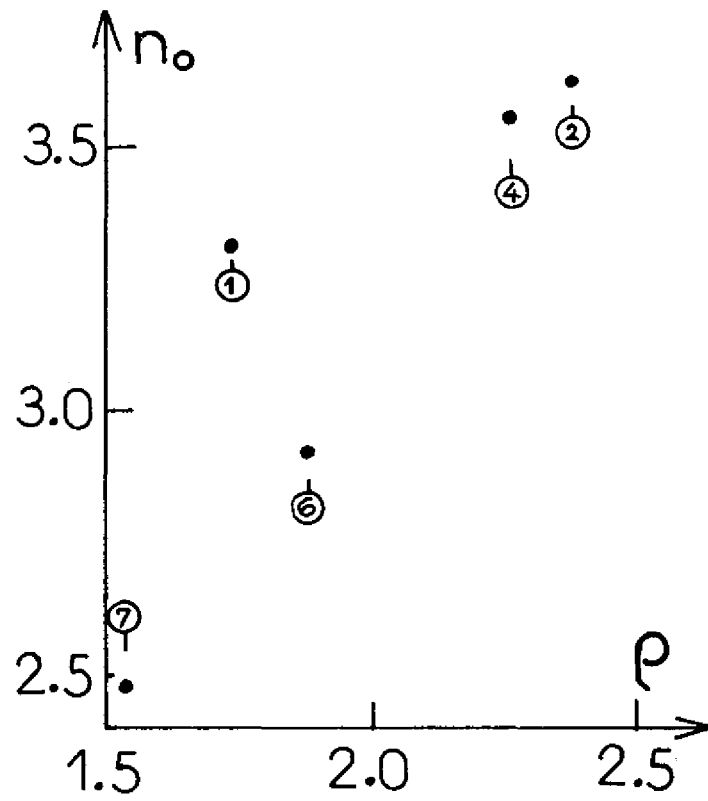


Fig. 6