THE EFFECT OF STATIC ELECTRIC AND MAGNETIC FIELDS ON THE OPTOELECTRONIC PROPERTIES OF AMORPHOUS HYDROGENATED SILICON FILMS PRODUCED BY R. F. GLOW DISCHARGE (*)

R. MARTINS, A. G. DIAS and L. GUIMARÃES
Centro de Física Molecular das Universidades de Lisboa
Complexo I (I. S. T.), Av. Rovisco Pais, 1000 Lisboa, Portugal

(Received 21 December 1982; final form in 3 March 1983)

ABSTRACT — The paper deals with the interpretation of transport properties of amorphous hydrogenated silicon films (a-Si : H) through dark conductivity and photoconductivity measurements. a-Si : H films were produced by r. f. glow discharge coupled either inductively or capacitively to a 3 % SiH_4/Ar mixture at different crossed electromagnetic static fields. The data concerned with the dark activation energy, photoactivation energy and photosensitivity, $(\sigma_{ph}/\sigma_d)_{25^\circ C}$, of a-Si : H films can account for their optoelectronic properties, which are strongly dependent on the deposition parameters [1, 2, 3]. We also observed that crossed static electromagnetic fields applied during film formation influence hydrogen incorporation in a manner different from that proposed by Knights [4] or Fritzsche [5].

1 — INTRODUCTION

In recent years the electric and optical proprieties of a-Si : H films have received an increasing amount of attention. Work by Spear [6], Knights [7], Okamoto [8], Taniguchi [9] and Martins [1, 2], has pointed out the role played by the deposition conditions on the electric and optical properties of the films. Their results have shown that it is possible, by a correct arrangement

(*) Based on results presented at the Third General Conference of the Portuguese Physical Society (Coimbra, June 1982).

of the deposition parameters, to obtain a-Si : H alloys with a low density of defect gap states, high photoconductivities and well defined conduction paths. We observed that it is possible to produce a-Si : H films at high growth rates (~ 10 Å s^{-1}) [10], with good substrate adhesion and suitable optoelectronic properties. Films produced under static crossed electromagnetic fields are particularly suitable for use in photoelectric devices; their production would involve an industrial process faster and cheaper than those used for crystalline or polycrystalline materials.

2 — EXPERIMENTAL DETAILS

a-Si : H films were produced by r. f. glow discharge of a pre-mixed 3 % SiH_4/Ar mixture fed into a capacitively or inductively r. f. (signal) coupled deposition chamber using a gas flow rate lower than 1000 c.c. min^{-1}. The substrate temperature, reactor pressure, r. f. power and frequency of the discharge are kept constant, respectively of the order of 260°C, for inductive films (I. F.), 325°C for capacitive films (C. F.), 1 torr, 20 W and 12.9 MHz. For C. F. films, 7059 Corning Glass substrates are placed in both sides of the heated pedestal, A – C. F. and P – C. F. films [1].

Dark conductivity and photoconductivity measurements as a function of the reciprocal temperature were performed in samples provided with aluminium evaporated electrodes in a gap cell configuration. Air Mass 2 sunlight produced by a G. E. quartz-line ELH tungsten halogen lamp was used for photoconductivity measurements [1, 2].

3 — DARK CONDUCTIVITY AND PHOTOCONDUCTIVITY MEASUREMENTS

Dark conductivity (σ_d) and photoconductivity (σ_{ph}) *versus* the inverse of absolute temperature (T^{-1}) were measured in samples produced either capacitively or inductively coupled at different crossed static electromagnetic fields. In general σ_d *versus* T^{-1} plots show well defined activation energies (ε_σ), except for a few samples produced without or at low bias. For such samples

we observed that σ_d is proportional to $T^{-1/4}$. This means that the conduction mechanism is hopping assisted. Here the indicated ε_σ value must not be regarded as an activation energy since it is correlated with the asymptote to the σ_d *versus* T^{-1} curve containing the room temperature value.

Fig. 1 summarizes the ε_σ values as a function of holder's bias (V_{dc}) for C. F. and I. F. with B = 0 KG (Fig. 1-a) and

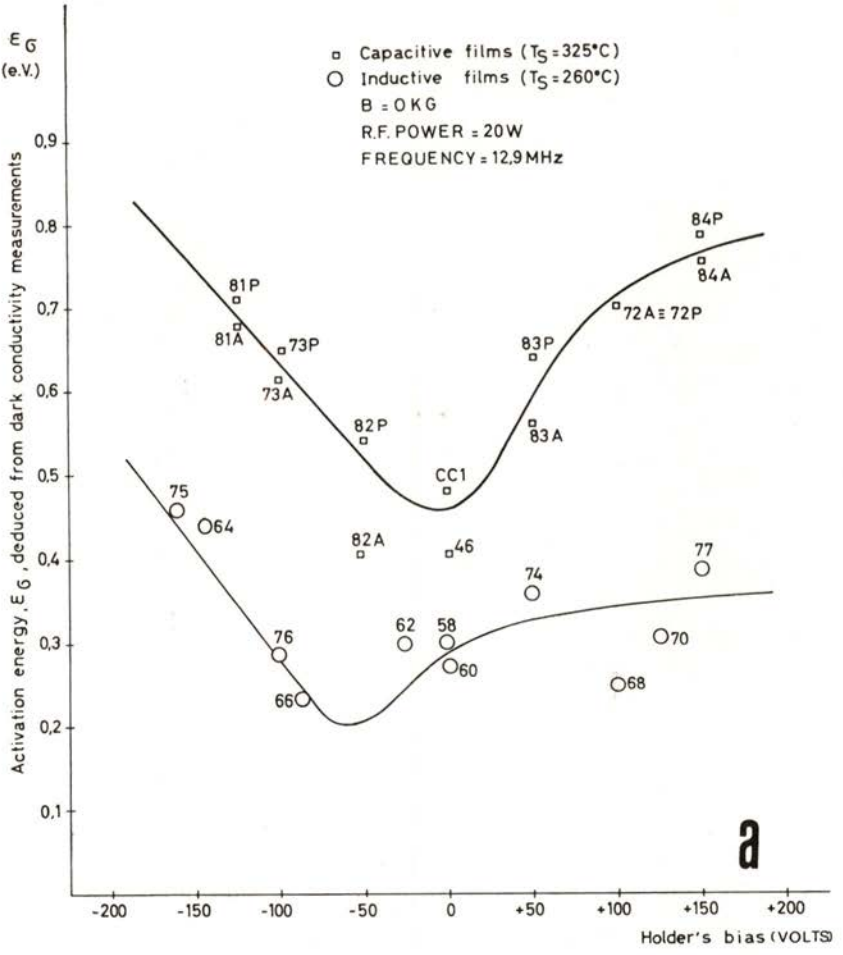

Fig. 1-a — Activation energy as a function of holder's bias (B = 0) .

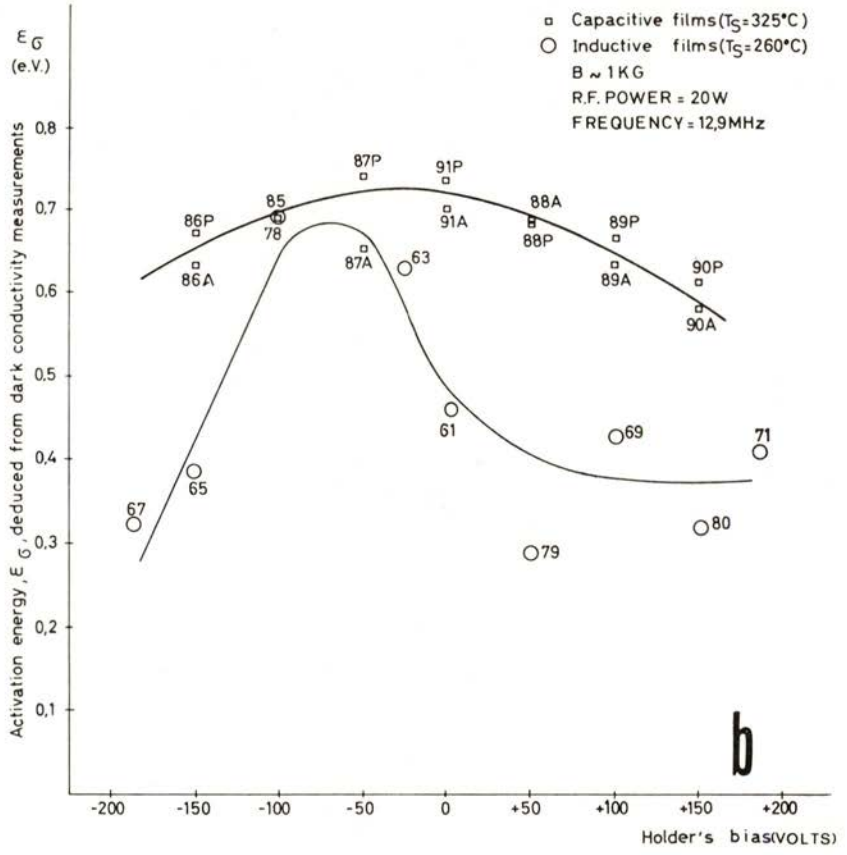

Fig. 1-b — Activation energy as a function of holder's bias (B ~ 1 KG) .

B ~ 1 KG (Fig. 1-b). The configuration of the dependence of ε_σ on V_{dc} changes completely, either for I. F. or C. F., when we apply a crossed magnetic field ~ 1 KG. This change is associated with a shift upward in ε_σ values, for I. F. and C. F., of the order of 0.25 eV, for any value of the V_{dc} signal. The maximum value of ε_σ (~ 0.73 eV) for C. F. corresponds to V_{dc} ~ 0 V. For I. F. ε_σ maximum (~ 0.7 eV) corresponds to V_{dc} ~ — 75 V. Both films were produced under the action of a static magnetic field ~ 1 KG.

Fig. 2 shows photoactivation energy values (ε_{ph}) deduced from photoconductivity measurements for I. F. and C. F. deposits

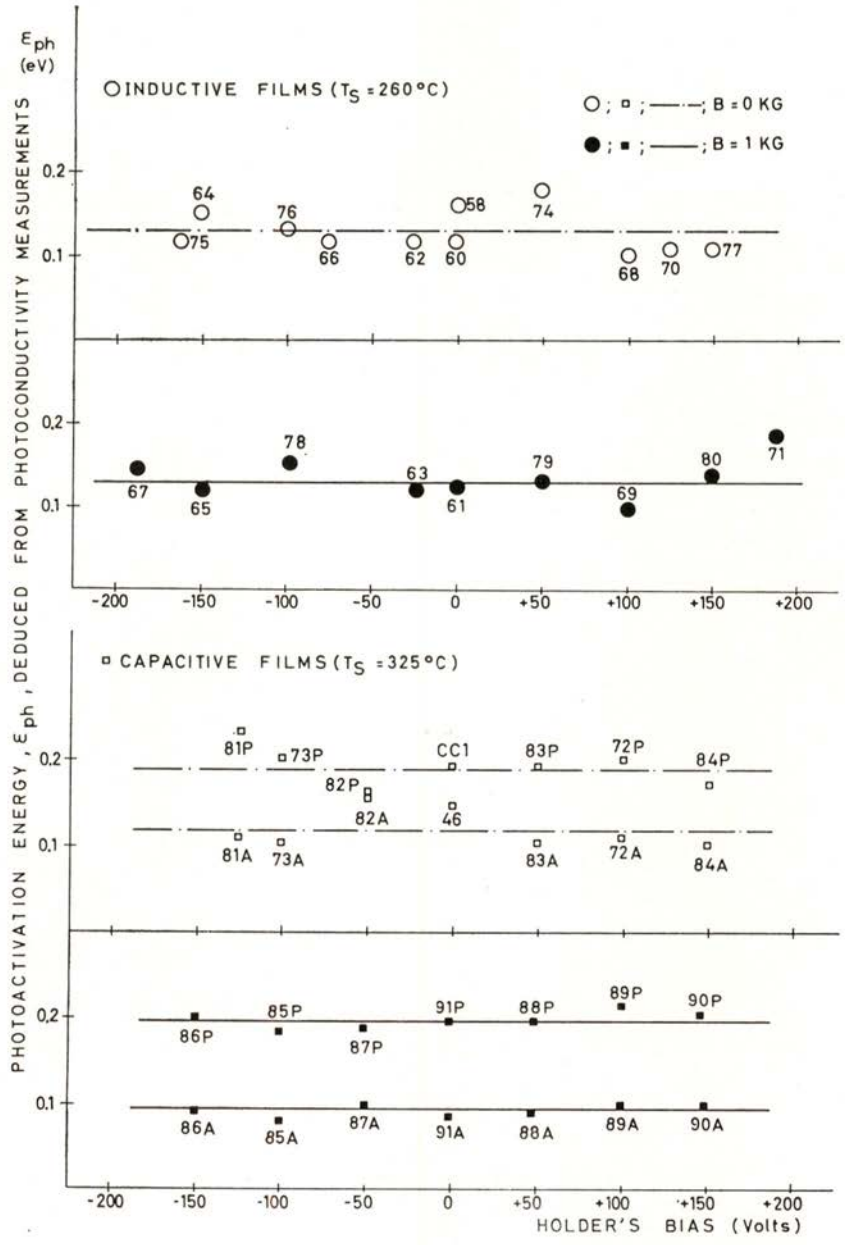

Fig. 2 — Photoactivation energy as a function of holder's bias under AM 2 excitation (75 mw cm^{-2}).

as a function of V_{dc} with B = 0 KG and B of the order of 1 KG. The ε_{ph} values are of the order of 0.1 eV for I. F. deposits and respectively 0.1 eV and 0.2 eV for A – C. F. and P – C. F. deposits, independently of the applied voltage. Using a discrete model like those proposed by Rose [11] and Spear and coworkers [6] we can ascribe ε_{ph} values to transitions between localized states located near the valence and conduction band edges. Thus for I. F. and A – C. F. deposits ε_{ph} values of the order of 0.1 eV can be correlated with the existence of an activated recombination lifetime (τ_R) associated with a high density of defect-gap-states [12, 13], high concentration of charged centres located near the valence band and/or hydrogen content [7]. However when τ_R is unactivated ε_{ph} is of the order of 0.2 eV (P – C. F.), which can be associated with a low density of defect-gap-states and/or hydrogen positively charged centres.

4 — THE NORMALIZED PHOTOCONDUTIVITY AT ROOM TEMPERATURE – $\eta . \mu . \tau$ PRODUCT

Considering the importance of the normalized photoconductivity at room temperature – $(\eta . \mu . \tau)_{25°C}$, the product of the quantum efficiency, η, the drift mobility, μ and excess carrier lifetime, τ – in the characterization of photovoltaic materials, we studied its dependence on the crossed static electromagnetic fields applied during formation of the films. The quantity under consideration may be written

$$(\eta . \mu . \tau)_{25°C} = (I_{ph})_{25°C}\ L^2/(e f V)$$

where I_{ph} is the photocurrent, L the electrode spacing, e the electron charge, f the number of incident photons per unit area and second and V the applied voltage.

For I. F. deposits we observed bias dependent $(\eta \cdot \mu \cdot \tau)_{25°C}$ values reaching a maximum in the V_{dc} range [+ 50 , + 100 V] as can be observed in Fig. 3-a. For C. F. deposits the $(\eta \cdot \mu \cdot \tau)_{25°C}$ maximum value, located in the same range as observed for I. F.

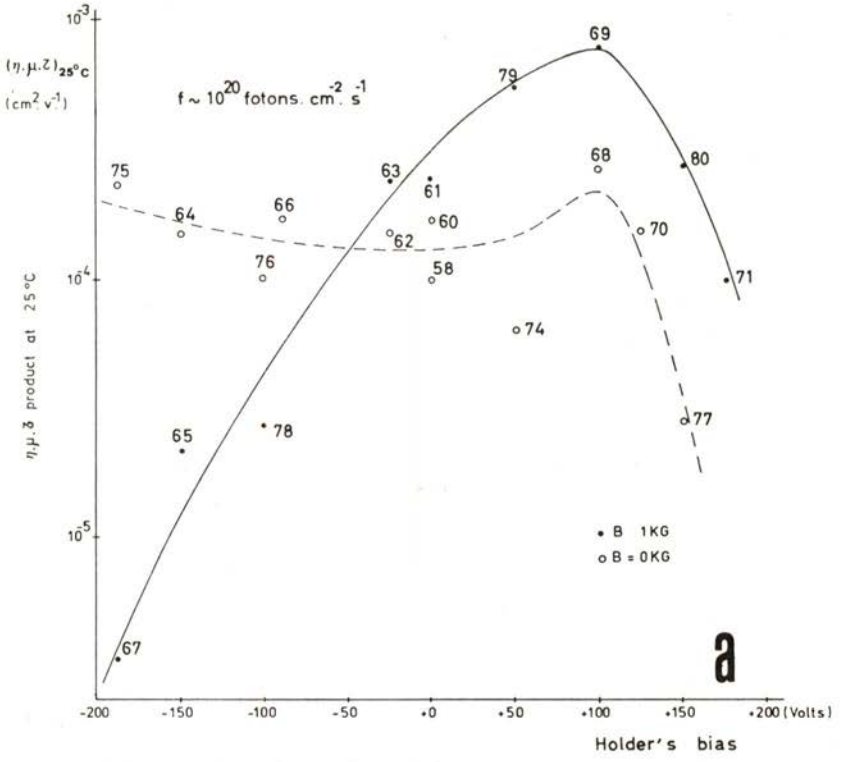

Fig. 3-a — $(\eta \cdot \mu \cdot \tau)_{25°C}$ product as a function of holder's bias for inductive films.

deposits, is shifted towards a V_{dc} range [− 30 ; − 60 V] through application of a crossed static magnetic field of the order of 1 KG during film deposition (see Fig. 3-b).

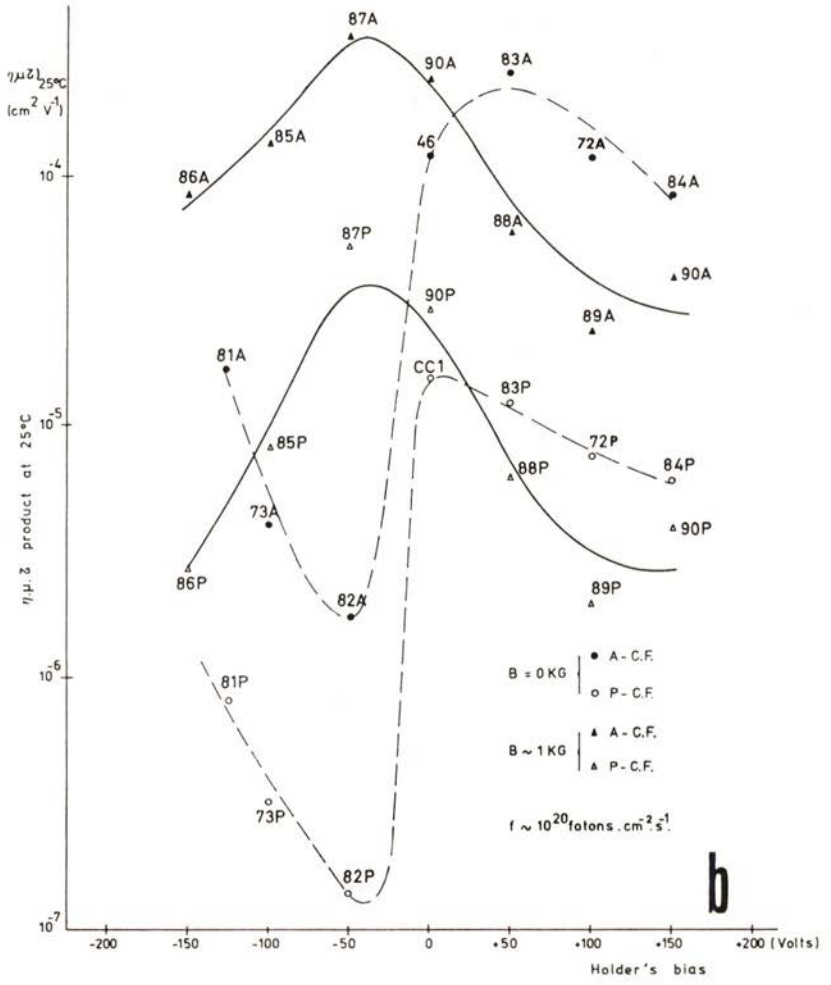

Fig. 3-b — $(\eta \cdot \mu \cdot \tau)_{25°C}$ product as a function of holder's bias for capacitive films.

5 — PHOTOSENSITIVITY. PLASMA KINETICS AND SURFACE REACTIONS

We found bias dependent photosensitivity ratios $(\sigma_{ph}/\sigma_d)_{25°C}$ either for C. F. or I. F. deposits produced with B = 0 KG and B of the order of 1 KG (see Fig. 4). Thus it seems important to

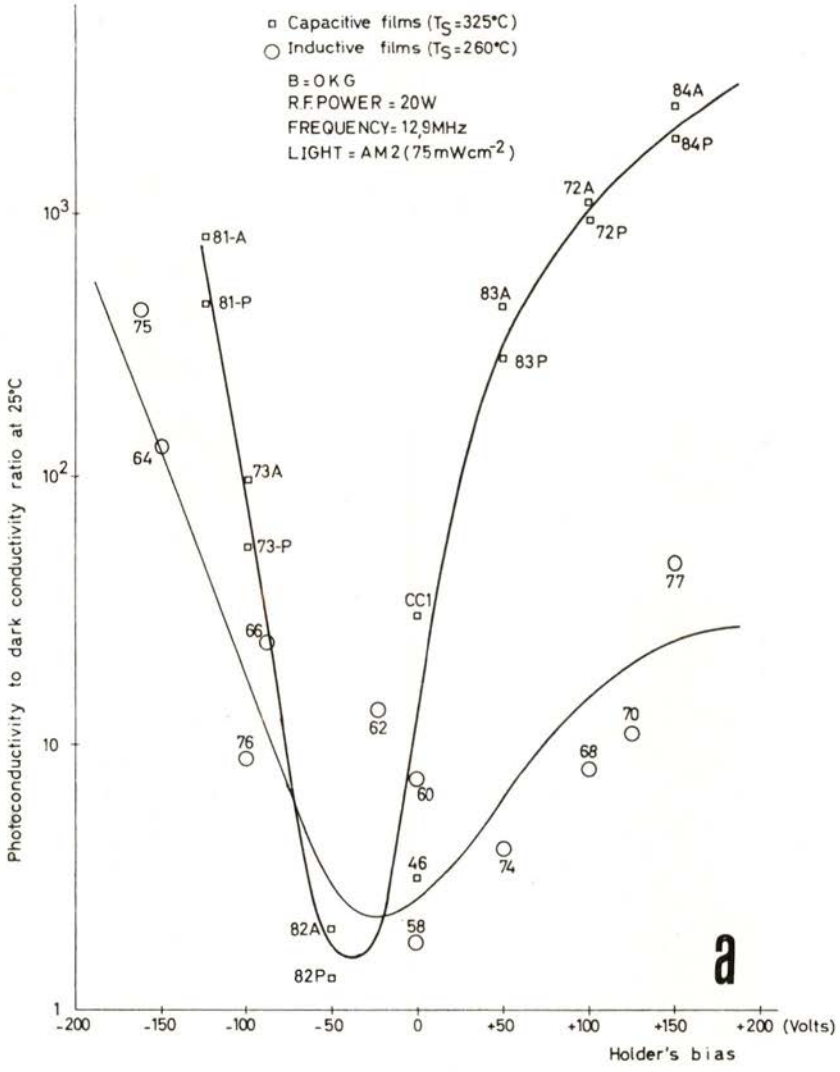

Fig. 4-a — Photosensitivity ratio $(\sigma_{ph}/\sigma_d)_{25°C}$ as a function of holder's bias (B = 0).

know the holder's potential with respect to the plasma, as well as the holder's floating potential (for the unbiased case), since both plasma kinetics and surface reactions depend on such values. In order to know the plasma potential and the holder's floating

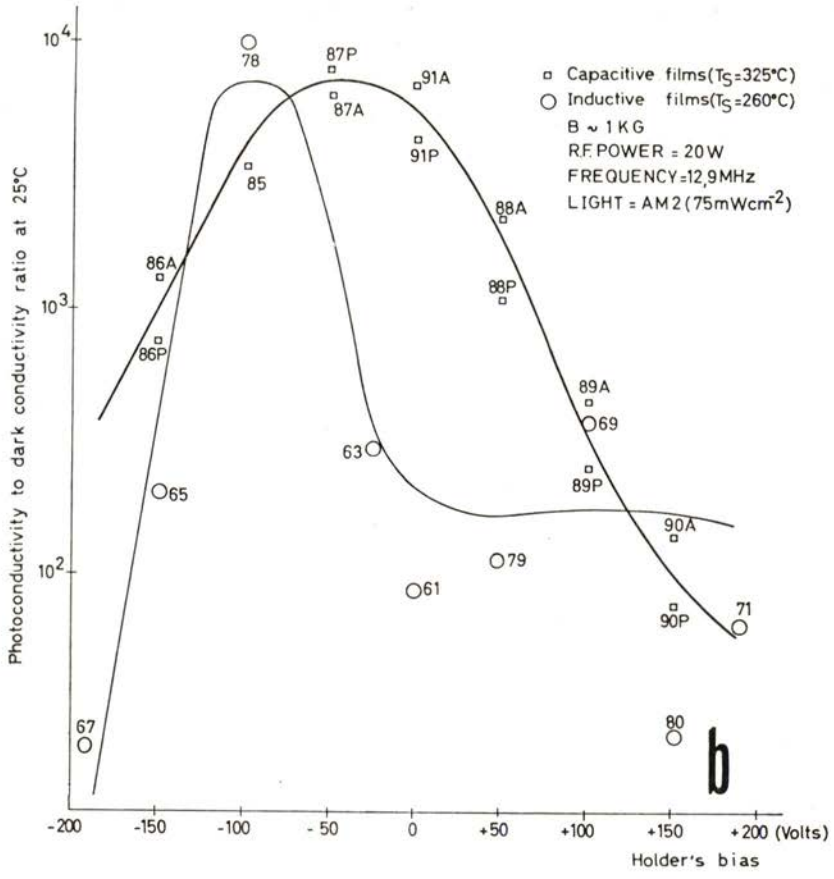

Fig. 4-b — Photosensitivity ratio $(\sigma_{ph}/\sigma_d)_{25°C}$ as a function of holder's bias (B ~ 1 KG).

potential we obtained the I(V) characteristic curves of the plasma at a fixed gas temperature (~ 280°C) and discharge pressure (~ 1.5 torr) as a function of r. f. power delivered to the discharge for B = 0 KG and B of the order of 1 KG (see Fig. 5). Such measurements have been carried out using a Langmuir plasma diagnostic probe placed near the substrate.

Our results show that when B = 0 KG the $(\sigma_{ph}/\sigma_d)_{25°C}$ ratio improves as $|V_{dc}|$ increases both for C. F. and I. F. deposits. This indicates that positive holder's bias do not enhance the amount of

hydrogen or the number of polysilicon dihydride molecules $(SiH_2)_n$ incorporated into the films, as suggested by Knights [4] and Fritzsche [5]. This result agrees with the raising photoconductivity values for such films which is indicative of a low density of

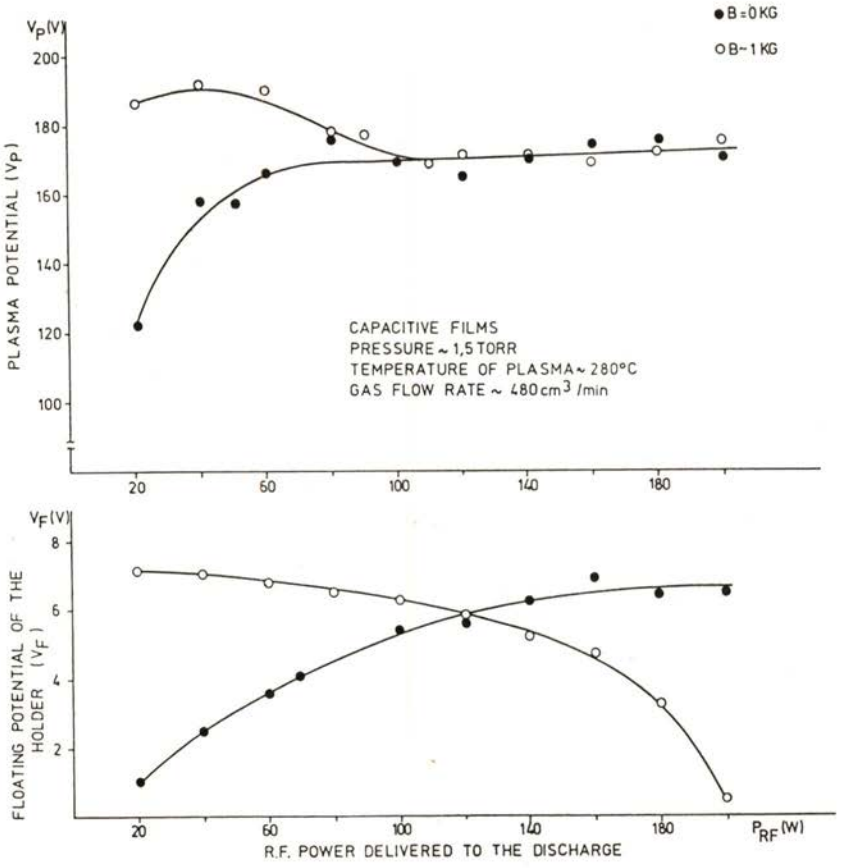

Fig. 5 — Plasma potential and floating potential as a function of R. F. power delivered to the discharge.

recombination centres related with few polymerization centres and voids [14]. Similar results have been reported by Hamakawa et al. [15] who observed a maximum in $(\sigma_{ph}/\sigma_d)_{25°C}$ ratio as a

function of V_{dc} for B = 0 KG at V_{dc} in the range [0; + 50 V], associated with a substrate potential of the order of − 60 V with respect to the plasma. As we can see plasma kinetics and surface reactions are not ruled only by the r. f. power delivered to the discharge which in fact controls the plasma potential; the holder's bias is also important. This means that ion damage and electron bombardment, which will influence the number of incorporated defects and the local H binding, will depend on the holder's potential with respect to the plasma.

When B is of the order of 1 KG the dependence of $(\sigma_{ph}/\sigma_d)_{25°C}$ on V_{dc} is opposite to that obtained for B = 0 KG. This result means that, avoiding ion damage or electron bombardment of the substrate, the number of dihydride molecules (SiH_2) decreases as the number of monohydride molecules increases [5, 1].

This can be explained by the differences observed in the plasma potential values at B = 0 KG and B ~ 1 KG (Fig. 5).

6 — CONCLUSIONS

Taking into account the results concerning the dark conductivity and photoconductivity measurements we can conclude that film properties are strongly influenced by the electrode geometry (I. F. or C. F. deposits) and the kind of static electromagnetic fields used [10]. We also observe (see Fig. 3 and Fig. 4) that, for inductive or capacitive films produced under the action of negative holder's bias (B = 0 KG), while the $(\sigma_{ph}/\sigma_d)_{25°C}$ ratio increases (which is indicative of increasing SiH/SiH_2 ratios) the $(\eta . \mu . \tau)_{25°C}$ products decrease or remain almost constant. On the other hand, P − C. F. deposits, although related with an amount of incorporated H lower than A − C. F. or I. F. deposits [2] present a poor photoconductivity. Both results show that the SiH/SiH_2 ratio is not a good measure of film quality for photovoltaic application, as suggested by Knights [4] and Fritzsche [5].

As a matter of fact, our previous work [1, 2, 3] confirms that the application of static electromagnetic fields during film formation disturbs the plasma decomposition process and the surface reactions, controlling the growth rate [10] and optoelec-

tronic properties [1, 2, 16] of the films. Thus, it seems that the best films for photovoltaic purposes are the capacitive ones produced with $V_{dc} \in [0; -50\,V]$ and B of the order of 1 KG or $V_{dc} \in [+50; +100\,V]$ and $B = 0$ KG, corresponding to holder's potentials, with respect to the plasma, of the order of $[-180; -230\,V]$ and $[-20; -70\,V]$, respectively (see Fig. 3, 4 and 5).

According to our results the most convenient deposition technology of amorphous silicon hydrogenated alloys for photovoltaic applications is the static electromagnetic controlled r. f. glow discharge.

The authors wish to thank Instituto Nacional de Investigação Científica, Junta Nacional de Investigação Científica e Tecnológica (research contract no. 321.81/71), Universidade Nova de Lisboa, Fundação Calouste Gulbenkian and Direcção Geral de Energia for their financial support of this project.

We should also like to express our gratitude to Eng. C. Nunes de Carvalho, J. Figueiredo and M. Quintela for technical assistance.

REFERENCES

[1] MARTINS, R., DIAS, A. G. and GUIMARÃES, L., *AIP Conf. Proc.*, **73** (1981), 36.

[2] DIAS, A. G., GUIMARÃES, L. and MARTINS, R., *Thin Solid Films*, **89** (1982), 307.

[3] GUIMARÃES, L., MARTINS, R. and DIAS, A. G., *Journal de Physique*, Colloque, **C4**, Supplément au n.° 10, Tome **42** (1981), C4-609.

[4] KNIGHTS, J. C., *Appl. Phys. Lett.*, **35** (1979), 244.

[5] FRITZSCHE, H., TSAI, C. C. and PEARSONS, P., *Solid State Tech.*, **21** (1978), 55.

[6] MADAN, A., LE COMBER, P. G. and SPEAR, W. E., *J. of Non-Cryst. Sol.*, **20** (1976), 239; ANDERSON, D. A. and SPEAR, W. E., *Phil Mag.*, **36** (1977), 695; LOVELAND, R. J., SPEAR, W. E. and AL-SHARBATY, A., *J. of Non-Cryst. Sol.*, **13** (1973/74), 55.

[7] KNIGHTS, J. C., *J. of Non-Cryst. Sol.*, **35-36** (1980), 159.

[8] OKAMOTO, H., YAMAGUCHI, T., NITTA, Y. and HAMAKAWA, Y., *Proc. of 8th Int. Conf. on Am. and Liq. Semic.* (Boston 1979), 201.

[9] TANIGUCHI, M., HIROSE, M. and OSAKA, Y., *Proc. of 8th Int. Conf. on Am. and Liq. Semic.* (Boston 1979), 189.

[10] MARTINS, R., *Thin Solid Films*, **90** (1982), 307.

[11] ROSE, A., *Concepts in Photoconductivity and Allied Problems*, Interscience, (New York 1970).

[12] FUHS, W., MILLEVILLE, M. and STUKE, J., *Phys. Status Solidi*, **B89** (1978), 495.

[13] WRONSKY, C. R. and CARLSON, D. E., *Proc. 7th Int. Conf. on Am. and Liq. Semic.* (Edinburgh 1977), 452.

[14] HOHEISEL, B., FISCHER, R. and STUKE, J., *Journal de Physique*, Colloque, **C4**, *Supplément* au n.° 10, Tome **42** (1981), C4-819.

[15] HOTTA, S., TAWADA, Y., OKAMOTO, H. and HAMAKAWA, Y., *Journal de Physique, Colloque*, **C4**, Supplément au n.° 10, Tome **42** (1981), C4-631.

[16] GUIMARÃES, L., MARTINS, R., DIAS, A. G. and BARRADAS, F., in «A model for analysis of optical measurements carried on a-Si : H films for photovoltaic applications», *4th European Photovoltaic Solar Energy Conference*, Italy 1982.