OPTOELECTRONIC PROPERTIES PRESENTED BY DOPED AND UNDOPED AMORPHOUS SILICON FILMS

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ABSTRACT -This work deals with transport and structural properties of undoped and doped a-Si:H films produced by plasma enhanced chemical vapour deposition techniques and their dependence on deposition conditions. Namely, the effect of plasma conditions substrate temperature (T_s), deposition pressure (p) and power used (P), on dark conductivity (σ_d), optical gap (E_{op}), activation energy (ΔE), photosensitivity (σ_{ph}/σ_d) and the way in which the [SiH], [SiH_2] and [SiH_3] species are incorporated, will be discussed. Overall we observe that undoped films with good performances are obtained when during the deposition process T_s=260 C, P=10 - 20 W and p=0.1 Torr. As far as doped films are concerned, the best film performances are obtained using p=0.5 Torr and high dilution ratios of silane in hydrogen. We also studied the behaviour of a-Si:C:H alloys based on methane/silane mixtures, doped or not with boron and produced at low powers ($P \simeq 5W$).

1. INTRODUCTION

Since Spear in 1975 [1] doped effectively a-Si:H films, the interest in using such semi-conductors in several photovoltaic and nonphotovoltaic applications has been growing . Nevertheless, most of the work done is based on trials that experience demonstrates to lead to films with good performances for their particular applications. Most of the problems concerned with films produced for device applications are due to the way in which hydrogen is incorporated and with density of states (DOS) within the mobility gap.

In this work we intend to determine the best deposition conditions that lead to the production of stable a-Si:H films with optoelectronic properties suitable for producing photovoltaic devices. This will be done either for films produced by conventional diode or by TCDDC (Two Consecutive Decomposition and Deposition Chamber) systems, respectively.

2. EXPERIMENTAL ANALYSIS OF THE PLASMA

Priori to deposit a-Si:H films, Paschen curves [2] corresponding to plasma discharges on hydrogen and silane were taken in order to characterize the plasma. In Fig.1 we show the behaviour of four of those typical Paschen curves.

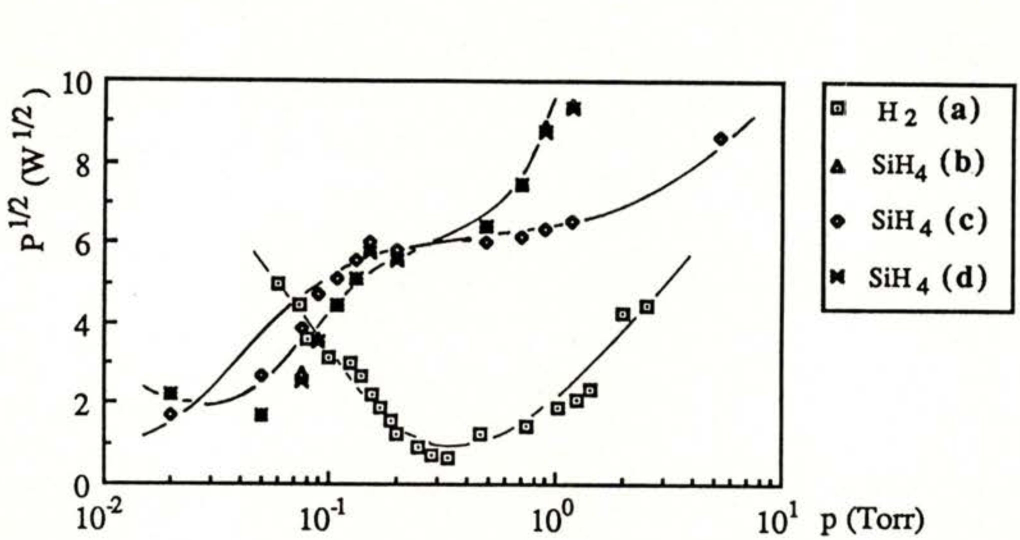

Fig. 1 -Paschen Plots for H_2 (a) and for silane at different electromagnetic static films (b: I_B=0, V_G=- 50 V; c: I_B= 3 A, V_G=- 50 V; d: I_B=0, V_G=0 V).

This study allows us to determine the minimum potential needed to obtain the glow, and so, the power that we must use in order to promote plasma formation, as well as to separate the high pressure from the one of low pressure (e.g. the kind of collisions undertaken by the formed species) [3]. Besides this, we also inferred the behaviour of such curves under electromagnetic crossed static fields [4],[6]. From this analysis, we see that the presence of a dc bias voltage (V_G) and a magnetic static field (I_B) during plasma formation, shifts the minimum of Paschen curves towards lower pressures. We also observe that the minimum of Paschen curves for H_2 discharges is ascribed with pressures almost one order of magnitude higher than the one for silane. This means that hydrogen when present during the discharge process acts mainly as a "buffer-gas" since the threshold of decomposition is superior to that one of silane, at low pressures. Once defined the best plasma conditions, we determine the correlation between power used and growth rate, either for undoped or doped a-Si:H films. These results are shown in Fig.2, where we observe that, by diluting carrier gas in hydrogen, the growth rate decreases by a factor of seven when $SiH_4/H_2 < 5\%$.

3. EXPERIMENTAL DETAILS

The films analyzed were produced by plasma enhanced chemical vapour deposition either using a diode-type system

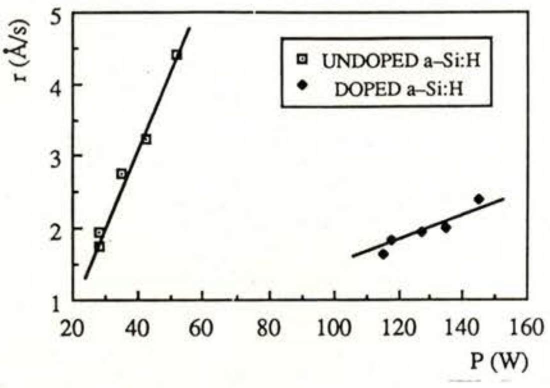

Fig.2 - Growth rate as a function of power used for undoped(◻) and doped (♦) (with $Si_4H_2 < 5$ %) for a-Si:H films.

or TCDDC system, where plasma chemistry is separated from that one of the deposition [4]. The obtained films were grown on glass substrates. Dark conductivity and photoconductivity measurements were performed on films using a gap-cell electrode configuration. Optical gap was inferred from Tauc's plot [4] through the absorbance measurements obtained by a double beam spectrophotometer. Hydrogen content was inferred through IR measurements performed on films grown onto high resistivity policrystalline silicon wafers.

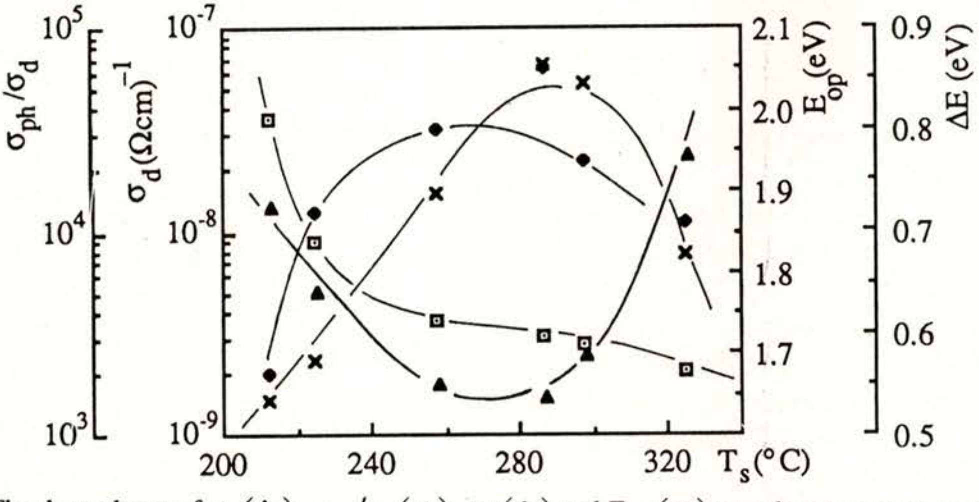

Fig.3 - The dependence of σ_d (▲), σ_{ph}/σ_d (×), ΔE (♦) and E_{op} (◻) on substrate temperature used for undoped a-Si:H films.

4. RESULTS AND DISCUSSION

a) Effect of substrate temperature:

In Fig.3 we show the dependence of σ_d and σ_{ph}/σ_d on substrate temperature used for undoped a-Si:H films produced at discharge pressures of the order of 0.2 Torr and constant powers. There, it is

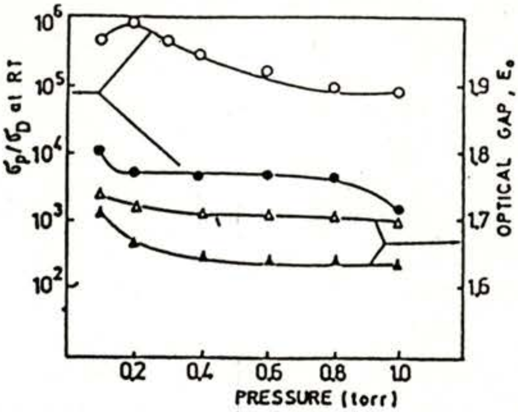

Fig. 4 - Dependence of σ_{ph}/σ_d and E_{op} on p for undoped films deposited by TCDDC system (o) and by a conventional diode-system (o).

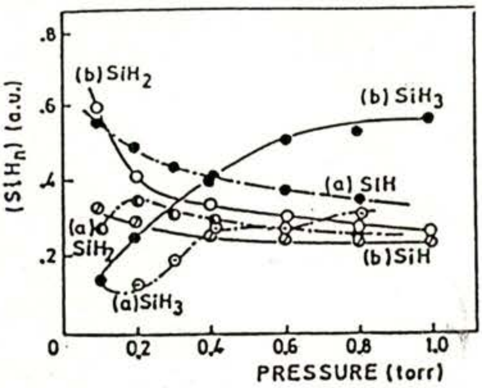

Fig. 5 - Dependence of species concentration (arbitrary units) on p, a) Films deposited by TCDDC system. b) Films deposited by a conventional diode-system.

also shown the corresponding behaviour of the optical gap, E_{op} , and of the activation energy, ΔE. The results show that σ_d has its minimum at substrate temperatures of the order of 260 C, which corresponds to the maximum in σ_{ph} $/\sigma_d$ with $\Delta E \simeq 0.8$ eV and $E_{op} \simeq 1.73$ eV, at T_S=260 C. For $T_S \gtrless 260$ C, σ_d increases while σ_{ph} $/\sigma_d$ decreases. From the obtained results we see that:

- at substrate temperatures, T_s , below 260 C there is a high hydrogen incorporation related to a high DOS [1] which is responsible for the high Eop and σ_d results obtained as well as the low σ_{ph} $/\sigma_d$ values recorded.
- at T_s above 260 C σ_{ph} $/\sigma_d$ decreases and σ_d increases, while E_{op} remains almost constant. This is explained by the decrease in hydrogen content on the film as well as by the reduction on μτ product [5].

b) Effect of the pressure:

In Fig. 4 we show the dependence of σ_{ph}/σ_d and Eop on the deposition pressure, p, for films deposited at T_S = 260 C by a TCDDC system (open circles) and by a conventional diode-system (dark circles). The data show that films produced by the TCDDC system have photosensitivities more than one order of magnitude higher than those ones produced by the conventional system [6]. The best σ_{ph} $/\sigma_d$ are obtained for p in the range of 0.1-0.2 Torr, which to corresponds values of the order of 10^6 (with $E_{op} \simeq 1.73$ eV) for the TCDDC system and of the order of 10^4 (with E_{op} 1.65 eV) for the conventional diode-system. In Fig.5 we also show the qualitative dependence of species concentration (deduced from IR spectra) on p, ei-

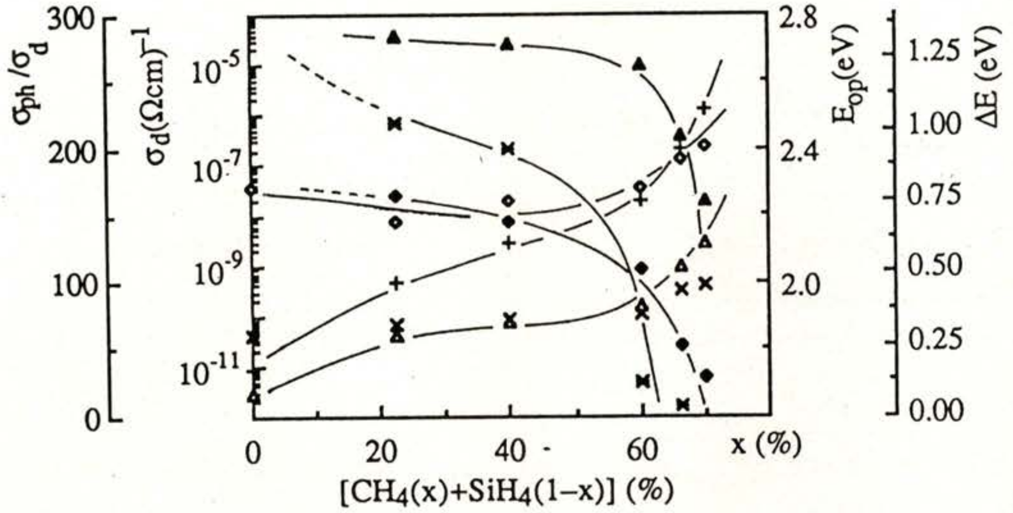

Fig. 6 - The dependence of σ_{ph}/σ_d (✱), σ_d (◆,▲), E_{op} (+,△) and ΔE (◇,×) on the dilution ratio used for undoped (a-Si:C:H (✱,◆,+,◇)) and doped (a-Si:C(B):H (▲,△,×)) samples produced at low powers, respectively.

ther for the TCDDC system (a) or the conventional diode-system (b). There, we observe that species incorporation is dependent on pressure used, being the main percurssor ascribed to SiH species, for TCDDC system, and, with SiH_2 species for the conventional diode system. For pressures below 0.2 Torr, the ratio between [SiH]/[SiH_2] is higher than a factor of nine for films produced by the TCDDC system.

c) Performances presented by a-Si:C:H doped and undoped alloys:

In Fig. 6 we show the dependence of σ_{ph}/σ_d, σ_d, E_{op} and ΔE on the ratio x = [CH_4/(SiH_4 + CH_4)] used, for undoped and doped samples produced at low powers ($P \simeq 5$ W). Overall we see that:

- E_{op} increases as x increases while σ_d decreases behind the detectable limits of the apparatus used. The same happens with σ_{ph}/σ_d.

- As far as doped samples with 1% of boron are concerned, E_{op} also increases with x, but more slowly. ΔE presents values between 0.25 and 0.4 eV while σ_d though higher than that one for undoped samples, it still decreases as x increases.

d) Behaviour of phosphorous doped samples:

In Fig. 7-a) we show the dependence of σ_d, E_{op}, and ΔE on the dilution ration (y = H_2/SiH_4) using P > 100 W and p = 0.5 Torr. Overall we observe that for 0 < y < 10, σ_d decreases while ΔE and Eop are

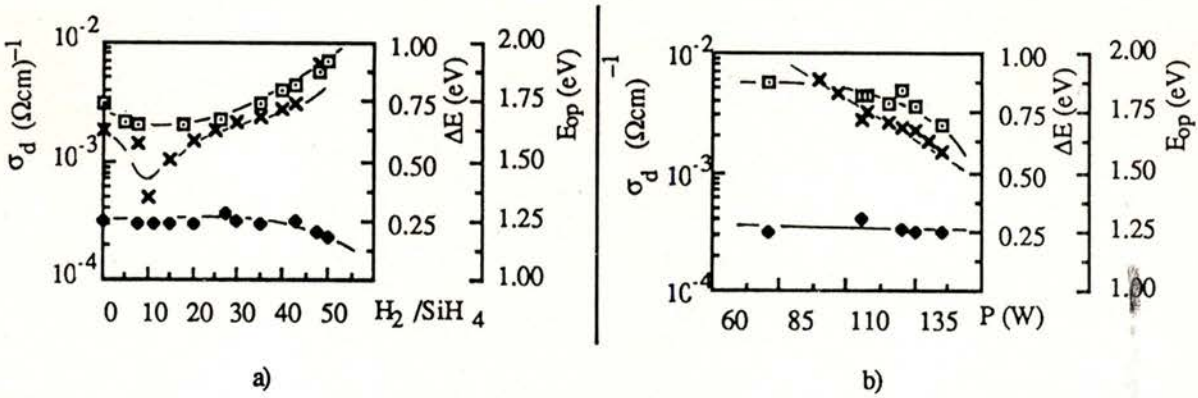

Fig. 7 - a) Dependence of σ_d (×), E_{op} (▣) and ΔE (◆) on H_2/SiH_4. b) The same dependence as a function of the power used.

kept almost constant, For y >10, σ_d starts increasing while ΔE and E_{op} present significant changes for y > 35 (ΔE decreases and E_{op} increases). This means that the dilution of the carrier gas in hydrogen will improve the optoelectronic performances of doped films, and so, that film properties are dependent on the residence time of hydrogenionic species present during the discharge process [4]. In Fig. 7-b) we show the same dependence as above but for the power used, having p = 0.5 Torr and y≥30. The obtained data show a decrease in σ_d and E_{op} as P increases while ΔE is kept almost constant. This can be explained by the ionic bombardment of the growing surface that will enhance the number of DOS, whilst the number of active species incorporated in active matrix, decreases. Similar behaviour was observed for boron doped films.

5. CONCLUSIONS

1 - Plasma behaviour during the deposition process can be determined by knowing the corresponding Paschen curves. Indeed, as low as the potential needed to promote plasma ignition as less as will be the effect of ionic bombardment on the growing surface. This means that for producing good quality material, the power at which the plasma is produced must be at or near the minimum of the Paschen curves.

2 - Overall we observe that deposition conditions play a significant role on film performances. Concerning T_s, the best value that leads to undoped films with good optoelectronic properties is in the range of 250-260 C, while 0.1 < p <0.2 Torr.

3 - a-Si:C:H undoped and boron doped films present valence controllability by changing the composition of methane/silane mixtures. High optical

gaps and high resistivities are obtained (for undoped films) in rich methane mixtures.

4 - For amorphous doped films, good optoelectronic properties are obtained by using low P and high hydrogen dilutions. As the power increases, the growing surface is under intense bombardment which enhances DOS and so leads to poor quality films. This is related to the residence time of species during the growth process [4]. Thus, for getting good doped films at high powers, the growth surface must be under atomic hydrogen bombardment and the residence time must be higher than the reaction time, in order to promote plasma chemical equilibrium conditions [3], which can lead us to mycrocrystallization.

5 - The species incorporated depend on reactor used. [SiH] and [SiH_2] species are assigned as being the main percursors for films produced by TCDDC and conventional diode type systems, respectively.

6 - We also observe that films produced by the TCDDC system present better performances than those ones produced by the conventional diode-system.

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REFERENCES

[1] Spear, W. E. and Le Comber, P. G., Phil Mag., Vol. 33, **6**, 935-949 (1976).

[2] Von Engel, A., Ionized Gases, Second Edition, Oxford at the Clarendon Press.

[3] Veprek, S., et. al., J. de Physique, **42 C4**, 251 (1981).

[4] Martins, R. and Guimarães, L. Proc. of 5th E.C. Photov. Solar En. Conf. (Athens 1983), 146; Martins, R., et. al., "Performances Presented by a-Si:C:H Films produced by a TCDDC System for PV Applications" (invited), Proc. of 8th E.C. Photovoltaic Solar En. Conf. (Florence 1988).

[5] Hamakawa, Y., "Amorphous Silicon Solar Cells", Current Topics in Photovoltaics, **3**, 111 (1985).

[6] Martins, R., Dias, A. G. and Guimarães, Portugal. Phys. - **14**, fasc. 1-2 , 81-94 (1983).