



**HAL**  
open science

# PHOTOLUMINESCENCE VERSUS BORON DOPING AND PREPARATION CONDITIONS

J. Bruyère, A. Deneuve

► **To cite this version:**

J. Bruyère, A. Deneuve. PHOTOLUMINESCENCE VERSUS BORON DOPING AND PREPARATION CONDITIONS. *Journal de Physique Colloques*, 1981, 42 (C4), pp.C4-339-C4-342. 10.1051/jphyscol:1981472 . jpa-00220929

**HAL Id: jpa-00220929**

**<https://hal.science/jpa-00220929>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## PHOTOLUMINESCENCE VERSUS BORON DOPING AND PREPARATION CONDITIONS

J.C. Bruyère and A. Deneuve

*Groupe des Transitions de Phases, C.N.R.S., B.P. 166, 38042 Grenoble Cedex, France*Abstract.-

The variations of the intensities of the various components of the photoluminescence spectrum of undoped and boron doped a-Si:H are reported versus preparation parameters. They are discussed in the framework of two phases (grain like and grain boundary like) of hydrogenated amorphous silicon. We conclude that the grain like zone is weakly modified by the deposition rate or substrate temperature in undoped a-Si:H while it is strongly changed by boron doping and that the grain boundary like zone is very sensitive to any preparation parameters.

I. INTRODUCTION

Photoluminescence in undoped amorphous hydrogenated silicon (a-Si:H) was first reported by Engemann and Fisher (1). It has been generally found in both glow discharge and reactively sputtered undoped a-Si:H. However, the number of the luminescence peaks and their relative intensities vary widely with the conditions of preparation (2-5). From the variations of the luminescence intensity with the temperature of measurement or with time, several models have been proposed with the implicit assumption of an homogeneous material with a single distribution of states. The photon energies corresponding to the peaks in photoluminescence have been attributed to a number of different mechanisms : convolution of the state distributions in the conduction (unoccupied) and valence (occupied) band tails (1), band to band transitions with polaronic effects (4), trapping on defects and subsequent radiative recombination towards the valence band (3). The decrease of luminescence intensity with boron doping (5) was attributed to a parallel increase in the dangling bonds density. In the same time, the intensity of the line at 0.93 eV (attributed to catch and loss of an additional electron by dangling bond) increases.

We believe that many results such as those of photoluminescence, thermally stimulated currents, optical absorption and electrical conductivity are not consistent with the description of the a-Si:H by a single distribution of states (6). On the contrary, they are quite consistent with the existence of at least two distributions of states in an inhomogeneous material. TEM and RMN (7) studies give evidence for two zones of different physicochemical properties, one grain like (G.L.) and the other grain boundary like (G.B.L.) and so independent support of this picture. We have discussed the constancy of the energy of the luminescence components in another paper (6) and proposed a picture according to which in photoluminescence experiments, the light absorption takes place in the G.B.L. zone, and the carriers are transferred to the G.L. zone where the luminescence takes place. In this paper, we study the variations of the intensities of the various peaks due to changes in the deposition rates  $v$ , the deposition temperature  $T_s$  and in boron doping concentration to see if they are consistent with our picture.

II. PREPARATION AND CHARACTERISATION

The films are prepared by RF diode cathodic sputtering of a Si target in a reactive gas 20 % H<sub>2</sub> / 80 % Ar and 0, 10<sup>-5</sup>, 10<sup>-4</sup>, 10<sup>-3</sup> of B<sub>2</sub>H<sub>6</sub>. About 1 μm of a-Si:H was deposited onto roughened c-Si to remove the interferences fringes. We have selected three typical deposition rates 30 Å/mn, 70 Å/mn, 100 Å/mn corresponding to different RF powers (8) and substrate temperature of 190°C and 250°C.

The total hydrogen content is determined by resonant nuclear reaction with boron (8) or nitrogen (9). The boron content is determined by the resonant nuclear reaction with hydrogen (9). The argon and Si densities are determined by Rutherford Backscattering with He<sup>4</sup> (9). Results for undoped a-Si:H were already published (8).

As  $v$  increases, the hydrogen content decreases. RMN (7) experiments suggest that this is due mainly to changes in G.B.L. zone in undoped material. Optical absorption experiments confirm this picture (6). Results for B doping are given on Fig. 1.

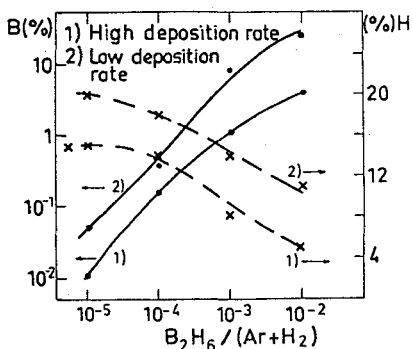


Fig. 1.

There is an important interaction between boron, hydrogen, silicon and argon (9) resulting, for instance, from boron atoms which do not give additional carriers as they would have done if they were in substitutional positions.

The films are excited by a D.C. argon laser emitting at 5328 Å with 1.3 w on 3 mm<sup>2</sup>. The light emitted by the sample is dispersed by a grating monochromator and detected by a cooled PbS cell. We report here the measurements at 4.2°K.

III. RESULTS AND DISCUSSION

A typical photoluminescence spectrum is shown in Ref. 6. A computer program determines the best fit for the positions and intensities of four lines with identical width. At 4.2°K, we get 1.36 eV, 1.2 eV, 1.08 eV and 0.93 eV with a full width at middle height of 0.3 eV. The positions and width are similar to those reported in the literature (1-5).

a) Undoped a-Si:H

The variations of the intensities of the various lines versus  $v$  are shown on Fig. 2a for T<sub>s</sub> = 190°C. At 190°C, when  $v$  increases the intensities of the 1.08 and 0.93 eV components remain nearly constant, while that of the 1.36 eV component decreases and that of the 1.2 eV component increases slowly then decreases. At 250°C (Fig. 2b) when  $v$  increases, the intensity of the 0.9 eV component remains constant, while that of the 1.36 and 1.2 eV components decreases and that of the 1.08 eV line slowly increases then decreases.

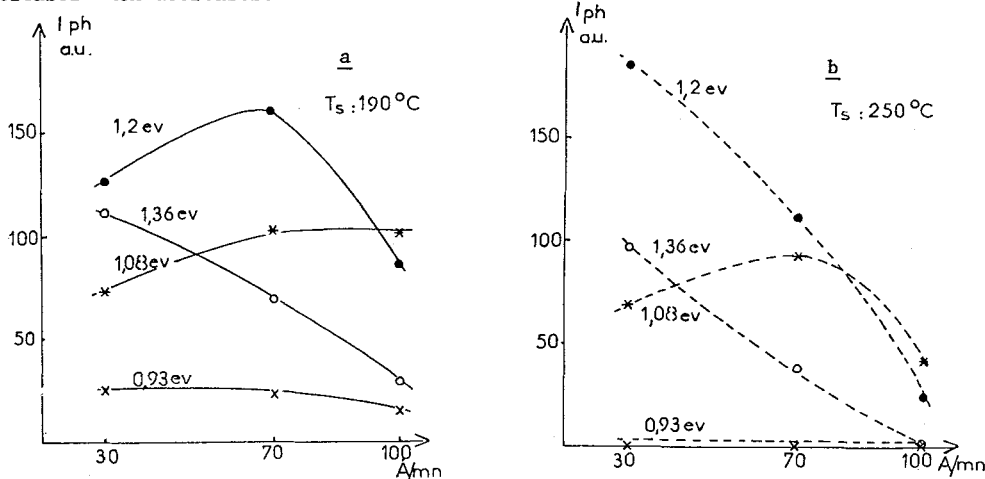


Fig. 2. Intensities of components of luminescence vs deposition rate.

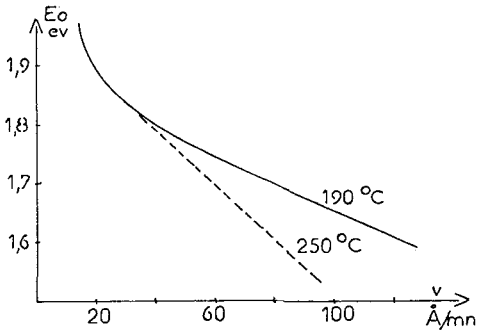


Fig. 2c : Variation of the optical gap with the deposition rate.  $T_s = 190^\circ\text{C}$  ;  $T_s = 250^\circ\text{C}$ .

The variation of the optical gap versus  $v$  at  $190^\circ\text{C}$  and  $250^\circ\text{C}$  are shown on Fig. 2c (8). The optical gap decreases as  $v$  increases and it decreases more rapidly as  $T_s$  increases. According to the basic two-phase model that we propose for a-Si:H, the absorption will take place mainly in the G.B.L. zone then the carriers will be transferred in the G.L. zone where luminescence takes place. In this case, the supply of carriers to the various levels will depend on the position of the mobility edge in the G.B.L. zone relative to the discrete like levels in the G.L. zone. The starting level of the 0.93 eV will be always below the mobility edge and so uniformly supplied with additional carriers. This will give a constant

intensity for the 0.9 eV peak as  $v$  or  $T_s$  increase. On the contrary, the higher starting level will have always poor carrier supply that will become poorer and poorer as the mobility gap narrows. As the gap narrows the 1.2 and 1.08 eV starting levels will change from the first to the second behaviour. This simple phenomenological picture agrees with all our experimental results.

b) Boron doped films

The energies of the lines decrease as the boron doping increases. The effect is larger and larger when the energy of the line decreases. Nearly the same energy values are obtained for high boron doping for any  $v$ . The variation of the luminescence intensities of the various components with increasing B doping is shown on Fig. 2a for  $v \sim 30 \text{ \AA/mn}$  and Fig. 4a for  $100 \text{ \AA/mn}$ . The corresponding variations of the mobility gaps are shown on Fig. 3b and 4b. For all components, at both  $v$ 's the luminescence intensity decreases rapidly as the doping level increases, much more rapidly than the decrease we have with  $v$  in the undoped material. However, the variation of the optical gap is quite different. At  $30 \text{ \AA/mn}$ , it goes through a maximum between  $10^{-5}$  and  $10^{-4}$  while it increases slowly with the doping level at  $v \sim 100 \text{ \AA/mn}$ . The hypothesis of nearly constant G.L. structure and luminescence intensity controlled by the transfer of carriers from the G.B.L. zone cannot be retained here. The simplest hypothesis is the occurrence of an increasing number of recombination centers in the G.L. zone when the doping increases. These additional defects may be induced for instance by non substitutional doping in the G.L. zone whose concentration will increase with doping.

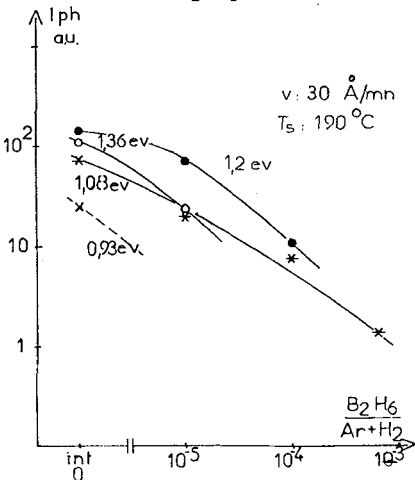


Fig. 3a. Intensities of components of luminescence vs boron doping.

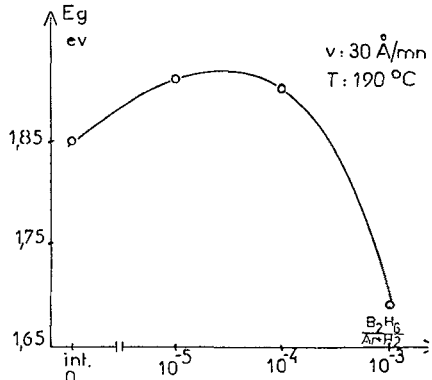


Fig. 3b : Variation of the optical gap of the corresponding films.

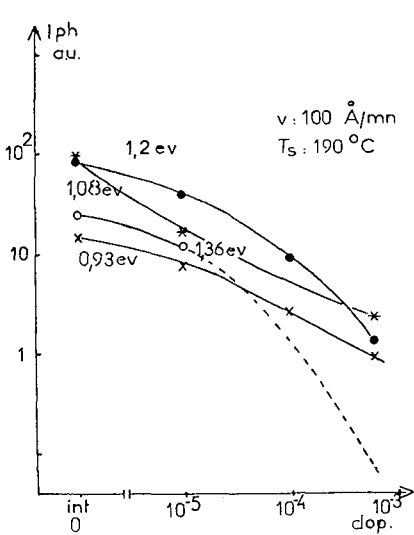


Fig. 4a : Variation of the intensities of the various components of the luminescence vs boron doping  $T_s = 190^\circ\text{C}$  ;  $v = 100 \text{ \AA/mn}$ .

place in the G.B.L. zone. For undoped a-Si:H, the efficiency of the carrier transfer to the G.L. zone where the luminescence takes place controls the intensity of the various peaks whose energy remains about constant reflecting the constancy of the G.L. structure. The situation is simpler in the case of B doping where the dominant feature is the increase of non radiative channel by the defects introduced by non substitutional doping in the grain like zone as well as the grain boundary like zone.

ACKNOWLEDGMENTS - We wish to thank B.K. Chakraverty for fruitful discussions, and M. Le Contellec, C.N.E.T. Lannion, for his help in luminescence measurements.

#### REFERENCES

- Engemann D. and Fisher R., Proc. XII Int. Conf. Phys. Semiconductors, Stuttgart, 1974, p. 1042.
- Nitta S., Shimakawa K., Tsutsumi Y., Endo T. and Morigaki K., Proc. XIV Int. Conf. Phys. Semiconductors, Edinburgh 1978, Ed. Wilson R.H., p. 1151.
- Street R.A., Phys. Rev. B 17, N° 10 (1978) 3984.
- Paesler M.A. and Paul W., Phil. Mag. B 41 (1980), 5775.
- Street R.A., Phys. Rev. B 21, n° 12 (1980) 5775.
- Deneuille A., Bruyère J.C., Hamdi H., These Proceedings.
- Knights J.C. and Lujan R.A., Appl. Phys. Lett. 35 (1979) 244 ; Reimer J.A., Vaughan R.W. and Knights J.C., Phys. Rev. Lett. 44 (1980) 193.
- Bruyère J.C., Deneuille A., Mini A., Fontenille J. and Danielou R., J. Appl. Phys. 51 (1980) 2199.
- Toulemonde M., Grob J.J., Bruyère J.C., Deneuille A., Hamdi H. and Siffert P., These Proceedings.

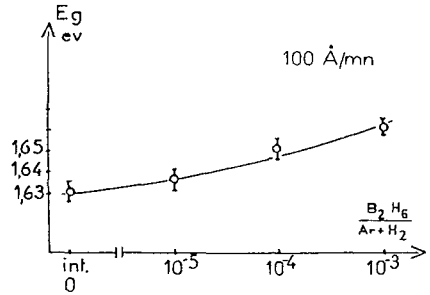


Fig. 4b : Variation of the optical gap of the corresponding films.

The shift of the peaks that we observe with B doping is consistent with this picture.

#### IV. CONCLUSION

We have shown that the grain like - grain boundary like model for a-Si:H with the corresponding model of two distributions of states in the material can give a good description of our luminescence results. Absorption of light which produces carriers, takes