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OPTICAL CHARACTERISATION OF SPUTTERED HYDROGENATED AMORPHOUS SILICON THIN FILMS

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Abstract

The present work is devoted to the study of some optical properties of hydrogenated amorphous silicon (a-Si:H) thin films prepared by radio-frequency cathodic sputtering technique. It is essentially focused on investigating separately the effects of increasing partial hydrogen pressure during the deposition stage, and the effects of post deposition thermal annealing on the main optical parameters of the deposited layers (refraction index, optical gap Urbach energy, etc.). We show that low hydrogen pressures allow a saturation of the dangling bonds in the material, while high pressures lead to the creation of new defects. We also show that thermal annealing under moderate temperatures allows a good improvement of the structural quality of deposited films.

I- INTRODUCTION

Research on hydrogenated amorphous silicon (a-Si:H) is increasing, not only for the fundamental study of its physical characteristics but also for its numberless possible applications in microelectronic and photovoltaic technologies. So much interest has been shown in this material because of its relatively simple preparation mode and its optical characteristics, which are particularly interesting. Indeed, the material is distinguished by an optical gap located in the required range for optimal photovoltaic performance [1]. It also presents a strong optical absorption within the maximum of solar spectrum. So, a large part of solar energy is absorbed in a small thickness of the material allowing to make structures in the form of thin layers. All these particularities are of great importance for the elaboration of cheap photocells with a high photovoltaic performance. Nevertheless, the optical properties that distinguish a-Si:H material depend closely on the manufacturing techniques involved, the experimental conditions of its preparation and, above all, the quantity of hydrogen it contains.

In the present work, we first prepare thin films of a-Si:H by radio frequency cathodic sputtering technique. Next, we study how optical characteristics of these films change with increasing hydrogen pressure during the deposition stage as well as with classical post deposition annealing.

II- EXPERIMENTAL PROCEDURE

Starting from a silicon polycrystalline target under reactive ions of argon and hydrogen plasma, a-Si:H thin films of about 0.5 µm thick, and 1cm^2 area are deposited by radio frequency cathodic sputtering technique [2]. The experimental set-up we have used is a full computerised system, model SCM 451, from Alcatel. It consists of a sputtering enclosure

(fig.1) which allows depositions at different temperatures, a pumping system allowing to reach a vacuum of about 10^{-7} mbar, and a radio-frequency source with a 0 – 500 W power range. The substrates we have used are made of corning glass C7059. Before each deposition, both the sputtering enclosure and substrates are submitted to an appropriate cleaning to prevent the eventual contamination of silicon films.

Many a-Si:H thin films have been deposited by sputtering the polycrystalline silicon target under a constant pressure of 2.10^{-2} mbar and 250W radio frequency power. The temperature of the substrate and the distance target-substrate are respectively 25 °C and 6 cm. The partial pressure of the hydrogen introduced in the enclosure being the parameter that we intend to study the effect, it was then ranged from 0 to 75% of the total pressure.

The optical characteristics of the deposited layers were determined by using a Shimadzu UV-3101 PC spectrophotometer operating with a double beam in a wide spectral range: from ultraviolet to near infrared light. Transmission measurements were taken by means of the differential method [3].

III- EXPERIMENTAL ANALYSIS AND RESULTS

III-1- Effects of hydrogen pressure during deposition

In figure.2, we have superposed different transmission spectra obtained for the whole a-Si:H samples prepared under various partial pressures of hydrogen (P_H). The spectra are normalised to the substrate. They all present two clearly distinct slopes [4]. The first one, in which interference fringes (oscillations) are seen, is commonly named transparency zone or zone of weak absorption. In the second one, which is well known as zone of high absorption, the signal is strongly reduced.

Starting from these different spectra, and using the mathematical expressions reported in reference [5], we were able to determine the main optical characteristics of our samples: layer thickness, surface roughness, refraction index, optical gap (E_g) and energy of Urbach (E_u) [6]. It should be interesting to remember that the latter draws light on the density of the energy states localised in the tail of the valence band, which are generally attributed to the structural disorder in the material [7].

In figure 3, we reproduce the dependence of deposited thin films refraction index (n) with the wavelength (λ) for all P_H used. The values of n were adjusted with the dispersion law of Sellmeiere [8]. It is clear that, when P_H increases, $n(\lambda)$ curve shifts towards higher n values. This is in good agreement with the results published by Swanpoel and Swart [9].

Figure 4 shows the evolution of E_g and that of E_u as function of P_H pressure. E_g values were determined from the Tauc formula [10], and those of E_u from Urbach law [6]. We notice that E_g and E_u evolve into strictly opposing directions: when one increases the other decreases, and when the first culminates, the second reaches its minimum. This clearly confirms the very close relationship existing between these two parameters, because of the presence of a more or less important density of dangling bonds in the material.

For weak P_H, we observe an important and fast increase of E_g which quickly reaches its maximum at a P_H value of 3.10^{-3} mbar. Beyond this threshold, E_g starts decreasing exponentially before saturating at a value slightly higher than that of the control. Co-jointly, E_u perfectly develops in the opposite direction. From these results, we can say that for low P_H, hydrogen incorporation saturates dangling bonds in the deposited layers [11]. This leads to a clear improvement of E_g and E_u. With a P_H value of 3.10^{-3} mbar, the density of dangling bonds is minimal and, hence, the optical performances of the layers are optimal (E_g culminates

and E_u is minimal). When P_H becomes higher than its optimal value, excessive presence of hydrogen in the material generates new structural defects, the concentration and the complexity of which increase with the density of the incorporated hydrogen species. This has negative repercussions on the optical performances of the layers, and leads to a re-diminution of E_g, accompanied by an increase of E_u as we can see on fig. 4.

III-2- Effects of post deposition thermal annealing

After examining the effects of partial hydrogen pressure on the optical characteristics of the samples, we focused on the changes that would affect these characteristics after annealing. It is essential to bear in mind that stability of photovoltaic a-Si:H compounds depends on their normal functioning temperature and on the thermal solicitations to which they are sometimes compelled to be submitted. This is why many studies hold on this extremely important aspect of the problem [12, 13].

In order to conduct this part of the work, we have prepared three a-Si:H samples under experimental conditions similar to those mentioned above, using a P_H value of $1,5.10^{-2}$ mbar. One of these samples is kept as a control. The other two were each submitted to a thermal annealing in a vacuum of 10^{-6} mbar for 45 min. Annealing temperature (T_a) was chosen to be the variable parameter of which we try to determine the effect. T_a was fixed at 350°C for the first annealing, and at 600°C for the second one.

Fig.5 shows the spectral scattering of the refraction index n for each of the three examined samples. We notice that thermal annealing induces a clear n increasing in the whole-explored spectral range. This increase is obviously slight for T_a = 350 °C but, when T_a reaches 600 °C, it becomes so important that, for high λ, n reaches typical values usually measured on silicon crystals [14]. In regard to this result, we can already say that thermal

annealing at 600°C allows a partial crystallisation of the deposited layer. Thus, we meet literature data [13] which show that amorphous silicon crystallises at a critical temperature between 550 °C and 700 °C during annealing processing.

In fig.6, the variations of E_g and those of E_u with the annealing temperature T_a were both reported on the same graph. The first remark is the close relationship that links these two parameters making their evolution curves quite symmetric. Furthermore, these curves present an important similarity with those found in the literature [15]. Examination of these curves allows noting the following points :

i) For the reference sample (control), E_g and E_u present values practically equal to those measured above on the sample that was prepared in the same experimental conditions (fig.4). This proves that our results are reproducible. In other words, the structural quality of the deposited layers is practically influenced only by deposition experimental conditions which are entirely under control.

ii) The first annealing at 350 °C simultaneously leads to a decrease in E_g and to a proportional increase in E_u. On the basic of literature data [15, 16], we attribute this to a partial out-diffusion of hydrogen resulting from a break of the less stable bonds of SiH_2 and SiH_3 that have been formed in the material during the deposition.

iii) After an annealing at 600 °C, E_g decreases considerably reaching a value of 1,57 eV. Simultaneously, E_u increases to reach an average value of 138 meV. Logically, and in the same way as in the first annealing operated at 350 °C, these variations can also be attributed to the out diffusion of a higher quantity of hydrogen as a result of the break in the more stable bonds of SiH [15, 17]. Nevertheless, this interpretation is not sufficient to well explain the

changes we observed, even if we assume that all the quantity of hydrogen incorporated in the material during deposition has out diffused. Indeed, after an annealing at 600 °C, E_g and E_u values are very different from those measured on the sample which was deposited in the same experimental conditions, under no hydrogen pressure (fig.4). This proves that, even if the out diffusion of hydrogen is total, it cannot explain only by itself the observed results. Taking into consideration the values of E_g and E_u that we found, the most plausible interpretation of our results should combine hydrogen out diffusion to an efficient process of crystallisation of the layers, which is well favoured by the high values of T_a [18 - 22]. However, the creation of new structural defects in the material, due to thermal constraints and heating, is not excluded [23].

IV- CONCLUSION

In the present work, we have studied the effect of partial hydrogen pressure P_H, and that of the classical annealing on the optical characteristics of a-Si:H thin films prepared by radio frequency cathodic sputtering. The obtained results show that each of the optical gap E_g and the Urbach energy E_u allow a very good control of the optical characteristics of the deposited layers. For low P_H, hydrogen saturates most of dangling bonds existing in these layers. This is shown through the clear improvement of E_g and E_u. This improvement itself is optimal when $P_H = 3.10^{-3}$ mbar. For higher P_H, hydrogen begins to create its own defects and the optical performances of the layers start decreasing. After a first annealing at 350 °C, a high quantity of hydrogen incorporated in the layers out-diffuses. After a second annealing at 600 °C, hydrogen out diffusion is higher but it is accompanied by partial re-crystallisation of the layers. This is why structural quality of the latter shows a clear improvement.

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FIGURE CAPTIONS

Figure 1:
Diagram of the used sputtering apparatus. It allows performing a-Si:H thin film deposition at various temperatures:
1) Water circulation, 2) Handle for moving substrate holder, 3) Substrate holder, 4) Electric oven, 5) Substrate cover, 6) Target holder, 7) Guard ring, 8) Target cover, 9) Porthole, 10) pumping system, 11) micro-leakage vanes, 12) Water circulation, 13) Towards RF generator, 14) Towards power supply.

Figure 2:
Transmission spectra obtained on the prepared a-Si:H samples at different partial pressures of hydrogen (P_H). The spectra are normalised to the substrate. The hydrogen pressure is varying from 0 to 1,5 10^{-2} mbar.

Figure 3:
Experimental curves showing the evolution of the refraction index (n) of the prepared layers as function of the wavelength (λ) for various P_H values. Experimental data points were fitted to the Sellmeiere formula [8].
1) $P_H = 0$; 2) $P_H = 2.10^{-3}$ mbar; 3) $P_H = 3.\ 10^{-3}$ mbar; 4) $P_H = 4.10^{-3}$ mbar; 5) $P_H = 6.10^{-3}$ mbar; 6) $P_H = 8.10^{-3}$ mbar; 7) $P_H = 10^{-2}$ mbar; 8) $P_H = 1,5.10^{-2}$ mbar.

Figure 4:
Evolution of the optical gap (E_g) and of the Urbach energy (E_u) measured on deposited layers as function of P_H values. E_g was determined from the Tauc formula [10] and E_u from Urbach law [6]. We show that both E_g and E_u exhibit strictly opposed evolution trends.

Figure 5:
Spectral scattering of the refraction index (n) and its evolution with the annealing temperature T_a.
1) $T_a = 25$ °C; 2) $T_a = 350$ °C; 3) $T_a = 600$ °C.

Figure 6:
Variations of the optical gap (E_g) and the Urbach energy (E_u) as function of the annealing temperature. The strong co-relation linking these two parameters makes their curves completely symmetrical.

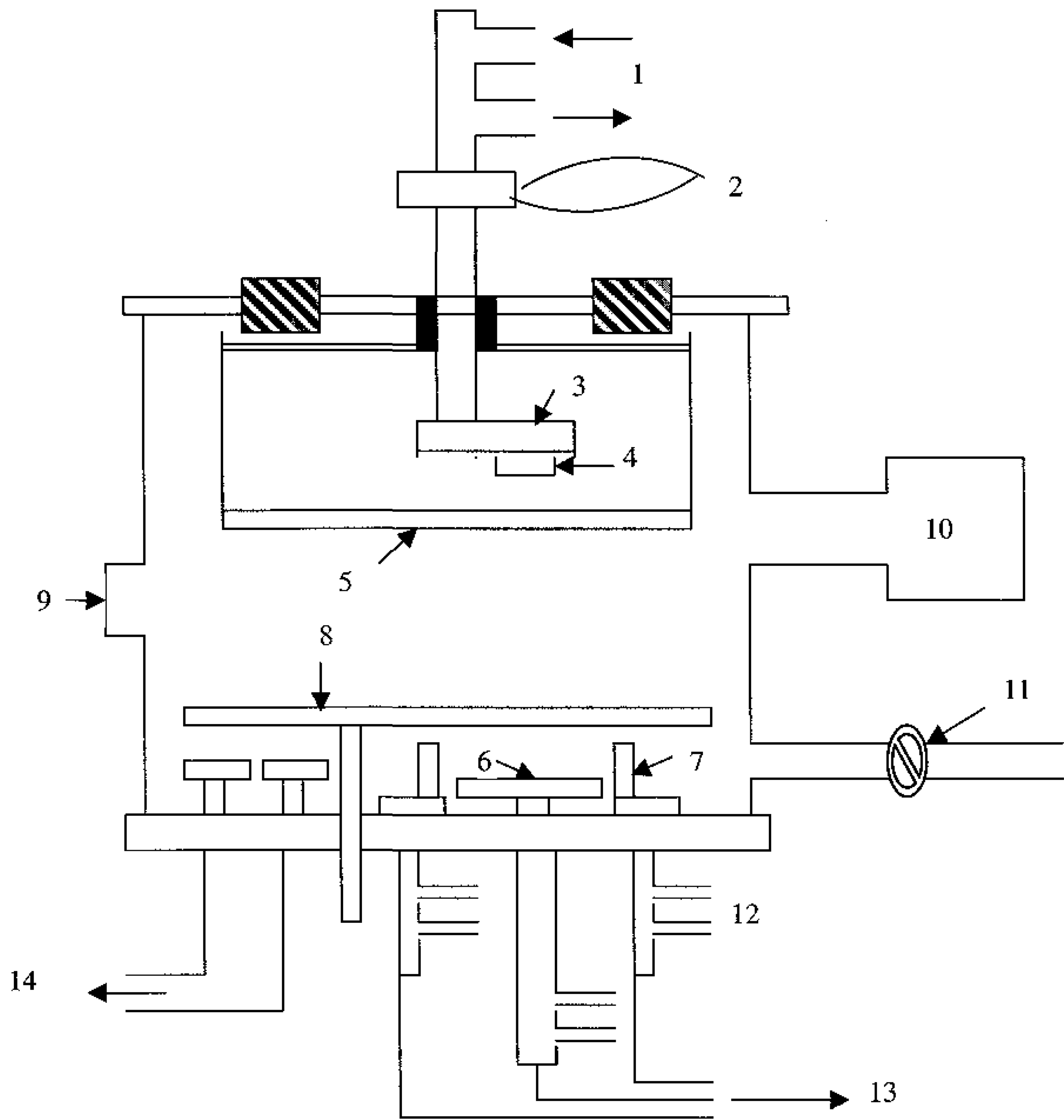

Figure 1

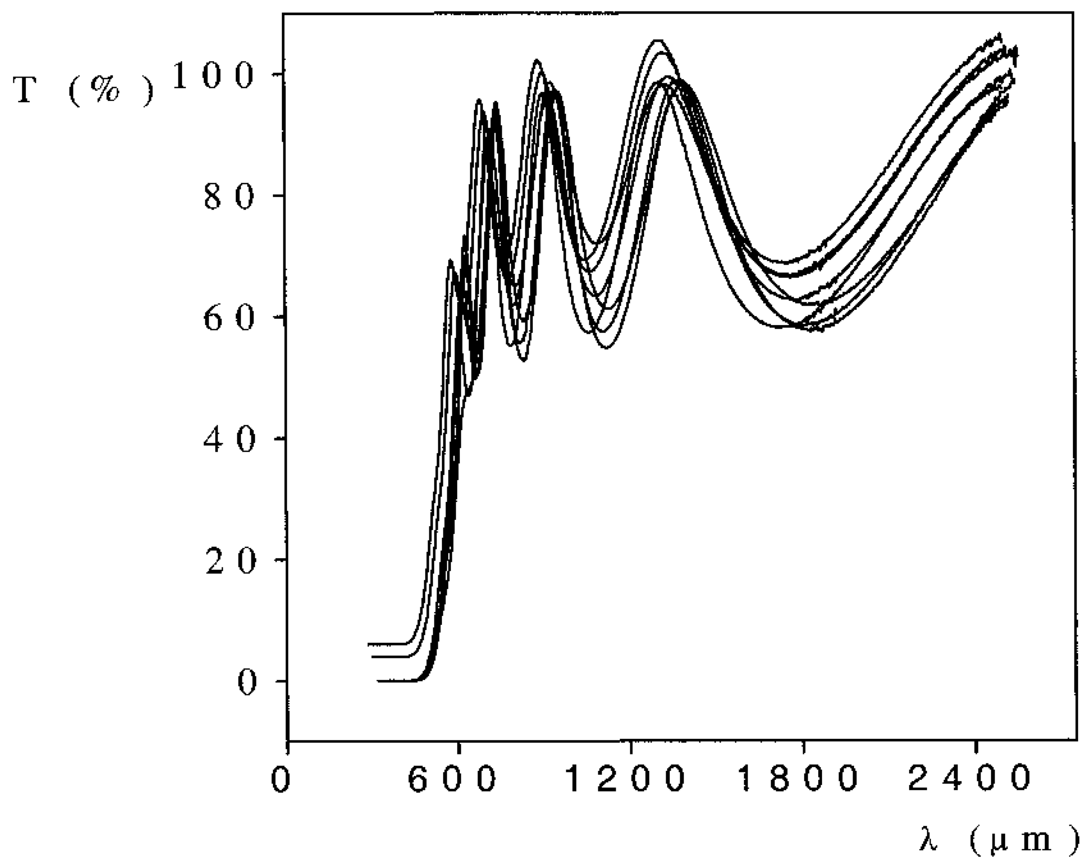

Figure 2

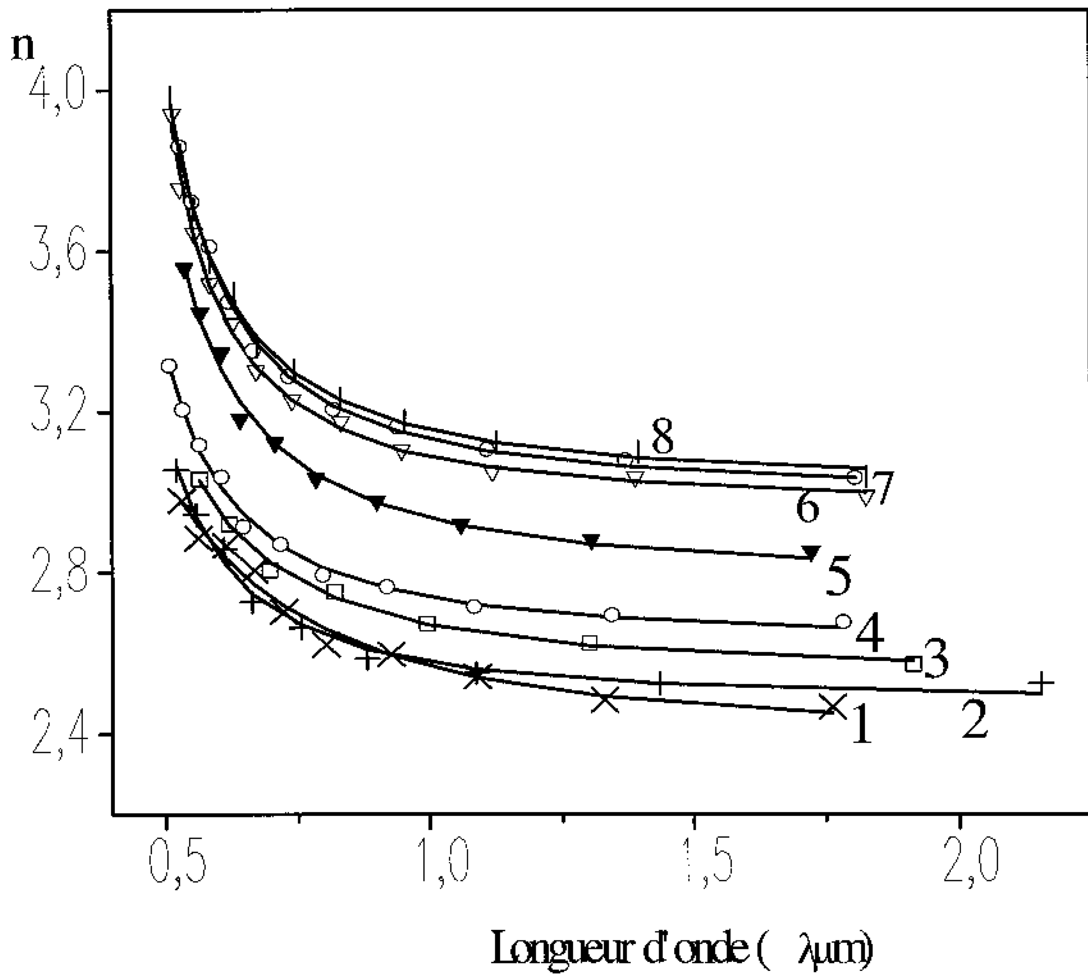

Figure 3

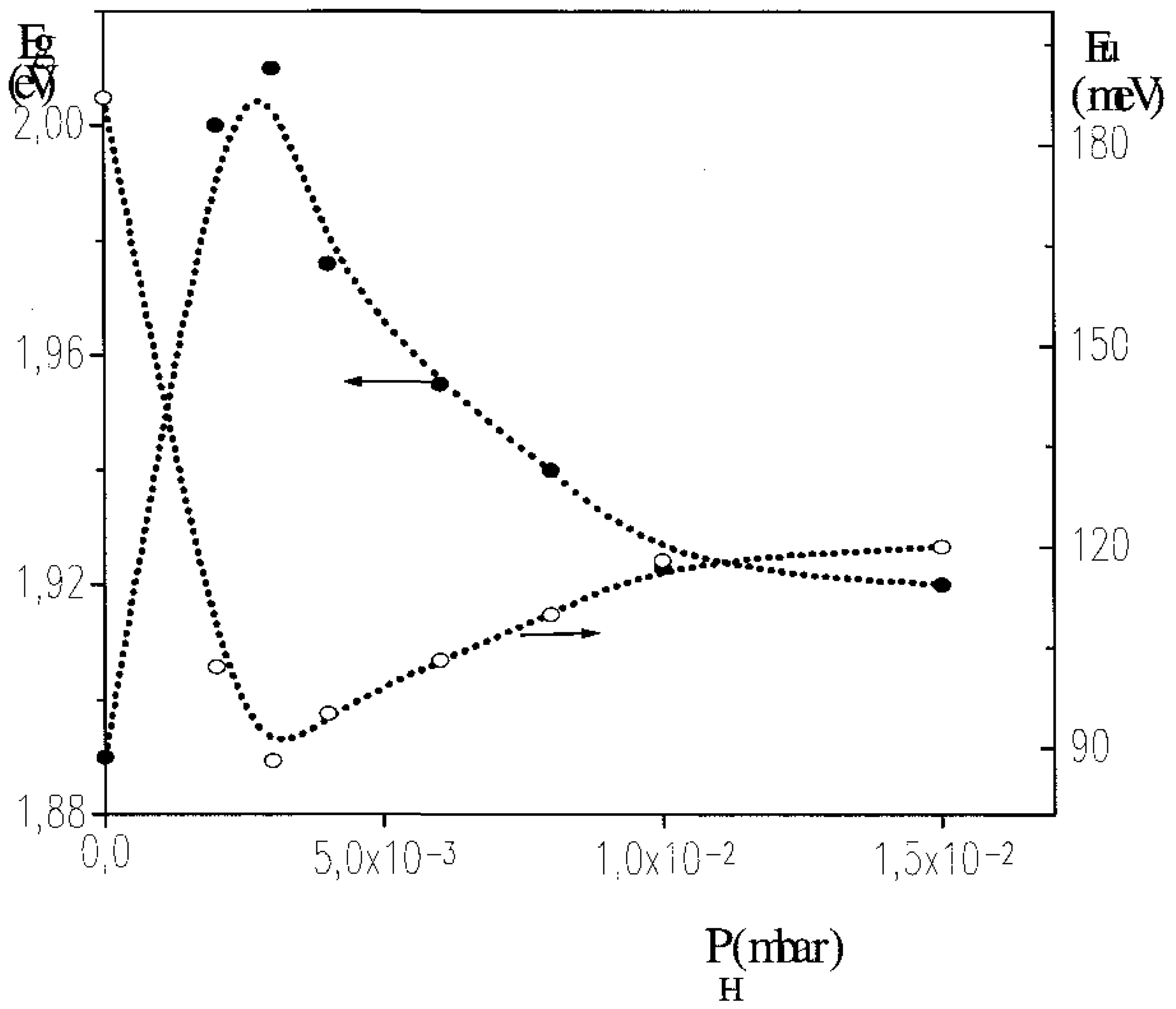

Figure 4

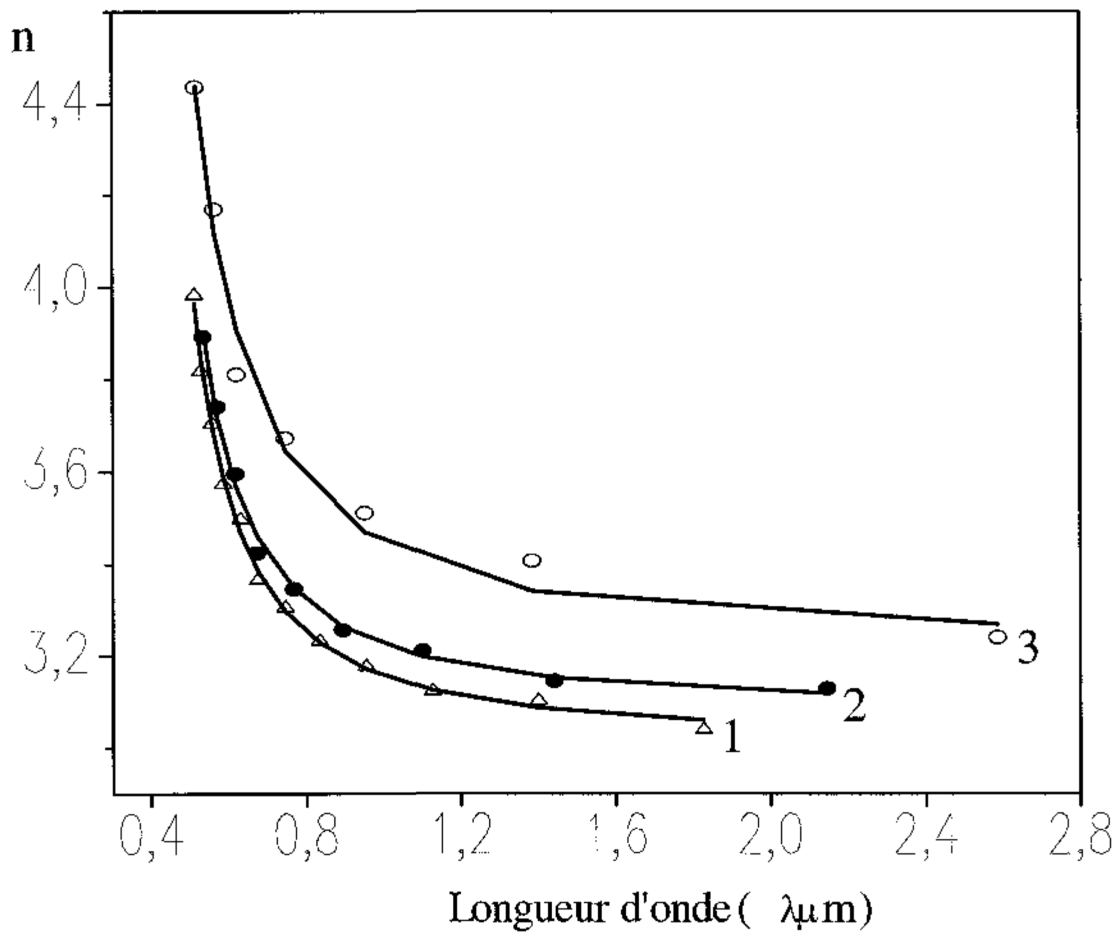

Figure 5

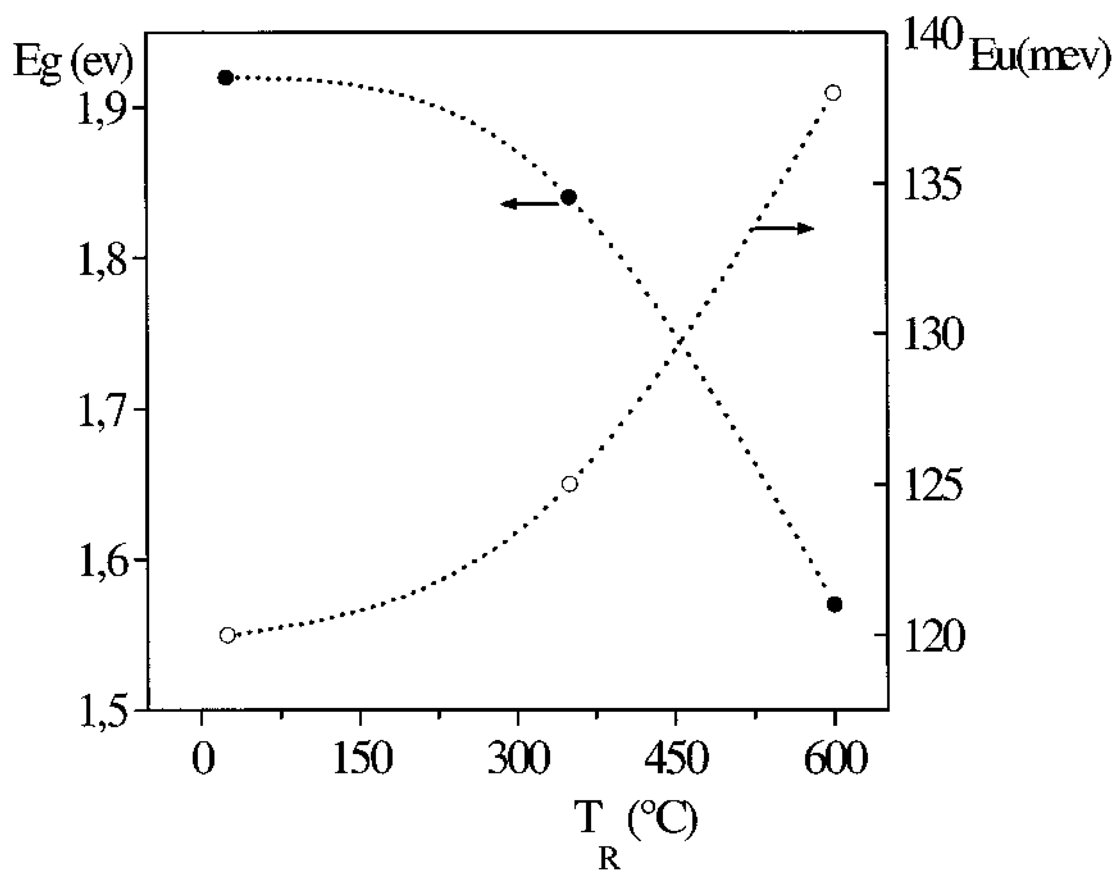

Figure 6