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Effect of substrate temperature and deposition rate on the photoconductivity of sputtered a-Si : H

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Résumé. — La variation de la photoconductivité en fonction de l'énergie des photons a été étudiée pour des échantillons produits à 150 °C, 190 °C et 250 °C à faible (30 Å/min.) et grande (~ 150 Å/min.) vitesse de dépôt. De plus, les densités de spins ont été étudiées. Prenant en considération la concentration et la distribution de l'hydrogène, nous proposons un modèle selon lequel la photoconductivité est principalement limitée par la densité et la profondeur de pièges peu profonds provenant de défauts matrice non compensés par l'hydrogène.

Abstract. — The variation of the photoconductivity *versus* photon energy is reported for samples deposited at 150 °C, 190 °C and 250 °C at low (30 Å/min.) and high (~ 150 Å/min.) deposition rates. The spin densities of the same samples are also reported. Taking into account the hydrogen concentration and distribution in these samples, a model according to the photoconductivity is mainly limited by the density and depth of shallow traps originating from hydrogen independent matrix defects is proposed.

From the variation of the photoconductivity *versus* photon energy and spin density of sputtered a-Si : H films deposited at low (30 Å/min.) and high (~ 120 Å/min.) deposition rate (v) at various deposition temperature (150, 190, 250 °C), we want to deduce some information about the nature and the depth of the localized states in these materials.

For *glow discharge* films, Spear and coworkers [1], deduced densities of localized states *versus* energy from field effect measurement. They report a decrease of the localized states density when the deposition temperature increases. They tentatively ascribed the E_x and E_y structures in the density of states to the distorted bonds of the reconstructed divacancy. With a somewhat similar type of preparation, Knights and coworkers [12], find an increase of dangling bonds spins when the number of $(\text{SiH}_2)_n$ radicals increases. They assumed that both occur on the internal surfaces of microvoids in their samples.

In our *sputtered* samples, the SiH_2 concentration can be increased or decreased without significant variation of the spin density [3], so that this last assumption cannot be retained. However, we find an increase of photoconductivity when the SiH_2 concen-

tration decreases [3]. We ascribed it to an increase of the trap depth corresponding to the *back* bonds of this radical when we go from distorted Si-Si bonds or from SiH to SiH_2 [3]. We also show [4] that according to the deposition rate of the films, the native Si matrix defects can be saturated (low v) or unsaturated (other v) by hydrogen, thus leaving an increasing number of (without spin) pure Si matrix defects [4, 5] as v increases. When the deposition or annealing temperature increases, we expect that their number decreases while their energy depth increases [6]. The variation of the optical gap with the deposition [7] or annealing [4] temperature in unsaturated material are mainly attributed to these effects.

We want here to derive information about the pure Si matrix defects left in the a-Si : H and their evolution with the deposition temperature from the comparison of the photoconductivity with the optical absorption and the spin density of these films.

Schematically, photoconductivity results from photon absorption giving electron-hole pairs, followed by majority carrier transport towards electrodes. The first step depends on the optical absorption coefficient, while the second one depends on the $\mu\tau$ (mobility-lifetime) product for the majority carriers [8]. μ and τ are expected to be primarily dependent respectively on the trap and recombination centres densities.

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From the variation of the photoconductivity *versus* doping in *glow discharge* a-Si:H, Anderson and Spear [9], assuming a density of localized states independent of doping, concluded that $\mu\tau$ is mainly limited by the lifetime of the electrons, i.e. by the density of recombination centres.

For *sputtered* undoped a-Si:H, we showed that the variations of photoconductivity with v and post-hydrogenation are mainly controlled by the changes in the trap density [3] through the concentrations of hydrogen dependent defects.

We want here to investigate the pure Si matrix defect behaviour when the deposition temperature is varied.

The films are prepared by cathodic sputtering of a Si target in a 20 % H_2 /80 % Ar reactive gas. We vary the deposition rate v and the deposition temperature T_s .

The total hydrogen content (nuclear reaction) and its distribution among the various sites (IR) depends primarily on the deposition rate v and weakly on the deposition temperature [7].

The D.C. photoconductivity is measured *versus* photon energy under 330 V/cm at 300 K with a Keithley 616 with low photons fluxes $\sim 10^{15}$ photons/cm²/s.

The spin density is measured at 300 K with a THN 51 spectrometer at various RF power from 2 to 100 mW.

The total hydrogen concentration decreases monotonically from ~ 21 % at ~ 30 Å/min. down to ~ 13 % at $v \sim 120$ Å/min. [7]. As at 190 °C [3], the spin density increases monotonically as v increases for $T_s = 150$ and 250 °C. The figure 1 shows the spin density N_s *versus* the deposition temperature for $v \sim 150$ Å/min. (upper curve) and $v \sim 30$ Å/min. (lower curve). In both cases, N_s decreases as T_s increases, but its variation with T_s is weak when compared with its variation

Fig. 1. — Spin density *versus* deposition temperature : upper curve : high v (~ 150 Å/min.) (unsaturated material); lower curve : low v (~ 30 Å/min.) (saturated material).

with v [3]. N_s remains in the 10^{17} /cm³ range for the high v and $\leq 10^{15}$ range for the low v .

Our maximum spin density for high deposition rate $\sim 10^{17}$ is of the same order of magnitude than the values reported for other undoped sputtered a-Si:H [10] and our minimum value of the same order of magnitude of the lower values reported for the glow discharge material [2, 10]. A decrease in the spin density with increasing deposition temperature and decreasing RF power (our v increases with the RF power) was reported by Knights *et al.* [2] on glow discharge material. However, it was correlated with the decrease of the 2090 I-R absorption line and a microvoid model which does not hold here [3]. Slight decrease of the spin density with increasing deposition temperature and decreasing deposition rate was reported by Thomas *et al.* [11] on ultra high vacuum evaporated Si.

The figure 2 shows the photoconductivity *versus* the photon energy for a photon flux of 10^{15} photons/s cm². When the photon energy decreases, all the photoconductivities after a maximum first decrease slowly then almost exponentially and slowly at

Fig. 2. — Photoconductivity *versus* photon energy at various T_s and v : solid line : low v ; dotted line : high v .

lower energy. These $\sigma_{ph}(hv)$ curves are similar to those reported for glow discharge [12] and sputtered [13] a-Si:H. These variations are qualitatively similar to those of the optical absorption coefficient [7] α . However :

i) there is a maximum in photoconductivity (~ 0.3 eV) above the optical gap (defined by extrapolation to zero of $\sqrt{\alpha hv}$) while α still increases at higher energy. This may be as usually ascribed by the progressive dominance of surface recombination as the light absorption occurs closer and closer from the film surface when hv increases ;

ii) the relative magnitude of the various components of σ_{ph} depends strongly on the deposition rate v (larger exponential range for low v than for high v) and T_s .

On the contrary, excepted a parallel shift to higher energy of the whole $\alpha(h\nu)$ curve when v decreases [7], $\alpha(h\nu)$ depends weakly on v . So, here v and T_s act mainly on $\mu\tau$.

The figure 3 shows the maximum value (versus $h\nu$) of the photoconductivity versus the deposition temperature for low and high v .

Fig. 3. — Maximum photoconductivity versus deposition temperature : upper curve : low v ; lower curve : high v ; inset : photoconductivity versus spin density.

There is a maximum value of the photoconductivity at 190 °C for the low deposition rate, while there is a fast decrease between 150 and 190 °C then a slower variation between 190 and 250 °C for high deposition rate.

The inset shows the variation of the photoconductivity versus the spin density. The photoconductivity always decreases approximately linearly with the number of spins as in a monomolecular regime.

The photoconductivity was reported to increase as the deposition temperature increases [12] and as E_c-E_F decreases [9] in glow discharge material, at a large value of the hydrogen partial pressure in the reactive gas for sputtered material [13]. High P_{H_2} for preparation of sputtered a-Si:H was shown to produce similar conductivity and photoconductivity versus $1/T$ than doping in glow discharge material [14] so the increase in σ_{ph} probably occurs from the decrease in E_c-E_F . Higher deposition temperature was otherwise shown to decrease the density of localized states in

glow discharge material [1]. So higher σ_{ph} can originate from lower E_c-E_F or low density of localized states or from both effects as already discussed elsewhere [3].

At constant T_s , the photoconductivity decreases as the deposition rate increases, but E_c-E_F also decreases. So its variation is not the dominant effect. The photoconductivity varies almost linearly with the spin density so the variations in photoconductivity with v at constant T_s might be ascribed to an increase of the concentration of dangling bonds. However, they might also originate from the increase in electron traps (pure Si matrix defects) when the hydrogen concentration in the material is further and further from saturation [4].

At constant v , the photoconductivity exhibits a maximum at 190 °C for low v and a monotonic decrease at high v (Fig. 3) while spin concentration continuously decreases (Fig. 1). So in both cases, the variations of spin are not the dominant features. Similarly, with no spin density variation, posthydrogenation has shown previously that a relative increase of SiH_2 decreases the photoconductivity [3]. We have reported [7] that at low v , there is a minimum of the relative SiH_2 content at 190 °C, while at high v this value slightly increases with T_s . So the qualitative variation of the photoconductivity with T_s agrees with the evolution of the relative SiH_2 content of the films.

However [3], we find 1 1/2 order of magnitude of variation when the relative SiH_2 content varies from 1/3 to 2/3 at low v , or from 1/3 to 0 at high v by posthydrogenation, while the variations of the relative SiH_2 content are here lower (1/3 to 1/5 at low v , 1/4 to 3/5 at high v), so we think there are only additional components.

As pointed out from annealing [4] and posthydrogenation [5] measurements some pure Si matrix defects remains always in the material. Their density increases as v increases because the lower hydrogen content gives unsaturated material, but as usually decreases as T_s increases because the material is less imperfect. However, the variation of the optical gap with v and T_s [7], implies an increase of their depth as T_s increases [15]. This interpretation is also supported by these measurements. These pure Si matrix defects are expected to give recombination centres when they have spins, and trap centres when they have not spin. The traps centres will act primarily on the electron mobility, but through their energy depth as well as through their number. As T_s increases, their number decreases but their energy depth increases, these two features acting in opposite ways. According to their relative strength the photoconductivity may increase or decrease. This might explain the maximum of photoconductivity around 190 °C at low v , as well as its monotonic decrease at high v .

Finally, the comparison of $\sigma_{ph}(h\nu)$ and $\alpha(h\nu)$ shows two important points. First the constant value of $\mu\tau$ on some $h\nu$ ranges does not imply identical value for

every $h\nu$ and this property for other sample. $\mu\tau$ depends on the distribution of trap, so on the preparation and history of the sample. It will be independent of $h\nu$ only if there is instantaneous thermal equilibrium of the sample. This is not generally right.

Second-although the effect of these traps appears quite dominant in the transport properties, it is clearly quite small in the optical absorption. We may speculate either that their wave function extension is too small to give significant matrix element for absorp-

tion, but this appears improbable for shallow traps, or that they appear as trap only when they are occupied, i.e. they have a significant positive or negative correlation energy. We favour here the second explanation.

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