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Abstract. — The electronic properties of some binary hydrogenated amorphous silicon-germanium alloys a-Si$_{x}$Ge$_{1-x}$ : H in the silicon rich region (x > 0.6) are investigated. Experimental evidence is presented of photoinduced effects similar to those described in a-Si:H (Staebler-Wronski effect). The electronic properties are then studied from the dual point of view of the germanium content dependence and of the photo and thermal histories of the films. The dark conductivity changes between the annealed state and the light-soaked state are interpreted in terms of the variation of the temperature coefficient of the Fermi level. The photoconductivity efficiency is shown to remain close to that of a-Si:H for 1 > x ≥ 0.9 and to strongly decrease when the germanium content is further increased : the photoresponse of the Si$_{0.62}$Ge$_{0.38}$ alloy is 10$^4$ times smaller than that of a-Si:H. This deterioration of the photoconductive properties is explained in terms of the increase of the density of gap states following Ge substitution. This conclusion is based on the study of the width of the exponential absorption edge and on the results of photoconductivity time response studies. The latter data are interpreted by means of the model of Rose of trapping and recombination kinetics and it is found that for x ≥ 0.6 the density of states at 0.4-0.5 eV below the mobility edge is 7 × 10$^{17}$ eV$^{-1}$ cm$^{-3}$ as compared to 2.4 × 10$^{16}$ eV$^{-1}$ cm$^{-3}$ for x = 0.97.

1. Introduction.

In recent years many papers have been devoted to the structural, optical and electronic properties of hydrogenated amorphous silicon (a-Si:H) prepared by glow discharge (GD) decomposition of silane. The subject has been stimulated by the discovery of substitutional doping from the gas phase [1] and promising applications in the field of solar cells [2]. It has been recognized that the quality of this material is due to incorporation of hydrogen in the network leading to a strong decrease of the density of defect-related states in the pseudogap [3]. In contrast hydro-
generated amorphous germanium (a-Ge:H) has a large overall density of states in the pseudogap and both its doping sensitivity and photoconductivity efficiency are reduced [4]. Indeed ESR and field effect studies have shown that the spin density and the density of gap states are about two orders of magnitude larger in a-Ge:H than in a-Si:H. Alloying C or Ge into Si in amorphous binary alloys is thought of as a way of adjusting the gap, a most desirable effect for solar cell applications. A linear decrease of the optical gap \( E_g \) has been observed for Si\(_{1-x}\)Ge\(_x\):H alloys in the whole range of composition [5]. But it has been clearly demonstrated that alloying Ge into Si reduces the effectiveness of hydrogenation [6, 7]. Infrared absorption and hydrogen evolution studies have shown that hydrogen preferentially attaches to Si so that the defects connected to Ge may be left uncompensated [6].

As a consequence the electronic properties of a-Si\(_{1-x}\)Ge\(_x\):H alloys are greatly changed when \( x \) decreases. This has been observed in both sputtered [8] and GD [9] alloys. In particular a decrease of the photoconductivity efficiency by four orders of magnitude has been measured when \( x \) is decreased from 1 to 0.1 [9]. On the other hand a considerable change in the electronic and photoluminescence properties has been noted when the Ge content is in the 25-40 at % range [8, 9].

In this paper we report on the electronic and optical properties of GD a-Si\(_{1-x}\)Ge\(_x\):H alloys in the silicon-rich region (\( x \geq 0.6 \)). A basic reason for re-investigating this class of alloys was to study the evolution of the physical properties as a function of \( x \) and of photo-induced effects such as those discovered by Staebler and Wronski for intrinsic and doped a-Si:H [10]. Conductivity data are discussed in terms of various proposed models [10-12], and the photoconductivity efficiency is measured in the annealed and «light-soaked» states of SW. Response time data are also described. From this set of results and other measurements including optical data the gradual change in the density of states in the pseudogap upon incorporation of Ge is qualitatively described.

2. Experimental.

The films were prepared by GD decomposition of SiH\(_4\) + GeH\(_4\) mixtures in the presence of hydrogen. Our first purpose was a systematic study of the dependence of the photoconductivity efficiency (measured by the \( \eta \) product, see § 3.3) upon the alloy composition \( x \) and the deposition temperature \( T_D \). So \( x \) was varied between 1 and 0.62 and \( T_D \) between 70 and 280 °C. It has to be noted that \( T_D \) is only approximate; indeed in our apparatus geometry (Fig. 1) the growing film is cooled down by the gas flow so that a temperature gradient \( \approx 70 \) °C is created between the film and the substrate holder where the temperature is measured. In the following we take \( T_D = \) substrate holder temperature \( -70 \) °C. The other deposition parameters were kept constant at the following values:

- RF power = 60 W;
- pressure = 22 mTorr;
- target bias = \(-400\) V.

Microprobe analysis showed that the film has a larger Ge content than the gas phase composition when the gas ratio GeH\(_4\)/SiH\(_4\) \( \approx 0.2 \), as already observed [5, 9]. We found that in the silicon-rich region, at \( T_D \approx 280 \) °C, the SiGe alloys have a maximum photoconductivity efficiency which is close to that of a-Si:H. A series of films with 0.62 \( \leq x \leq 1 \) was then prepared under the above conditions. The hydrogen atomic percentage was measured by nuclear analysis on a few samples (see Table I) and found to be \( \approx 10\% \), in agreement with Paul et al.’s data on sputtered silicon-rich SiGe alloys prepared at 100 or 250 °C.

The substrate used in these studies is a 1 mm thick glass-covered alumina CGE standard. Aluminium electrodes 2 mm apart were vacuum-evaporated in a coplanar arrangement. It has been checked that the contacts are ohmic up to 2.5 kV cm\(^{-1}\). Conductivity and photoconductivity measurements were carried out in a \( \approx 10^{-5} \) Torr vacuum, the current being measured by means of a Keithley 610 C electrometer under an electric field of 500 V cm\(^{-1}\). Photoconductivity was measured by irradiating with a 450 W xenon lamp and H25 Jobin-Yvon monochromator assembly. The photon flux was monitored by means of a 88XL photodyne radiometer fitted with a silicon head so that photoconductivity spectra were recorded under a constant flux of \( 5 \times 10^{14} \) photons cm\(^{-2}\) s\(^{-1}\). Photo-induced effects were studied by illuminating the films with a 800 W quartz-iodine lamp through a MTO 600-900 nm band-pass filter, the incident power being \( \approx 15 \) mW cm\(^{-2}\).

For optical measurements the films were deposited onto silica substrates. Transmission and reflection spectra were recorded by means of a Beckman Acta IV spectrophotometer. The experimentally determined reflectivity has been taken into account to calculate the film absorption coefficient.
### Table I. — Photo-induced changes in the conductivity of Si-rich SiGe alloys.

<table>
<thead>
<tr>
<th>Film</th>
<th>x</th>
<th>H at %</th>
<th>State A</th>
<th>State B</th>
<th>Band bending model(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$E_g^A$ (eV)</td>
<td>$\sigma_0^A$</td>
<td>$E_g^B$ (eV)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>11.5</td>
<td>0.59</td>
<td>265</td>
<td>0.60</td>
</tr>
<tr>
<td>2</td>
<td>0.97 ± 0.02</td>
<td>10.6</td>
<td>0.58</td>
<td>119</td>
<td>0.63</td>
</tr>
<tr>
<td>3</td>
<td>0.92 ± 0.03</td>
<td>—</td>
<td>0.53</td>
<td>44</td>
<td>0.58</td>
</tr>
<tr>
<td>4</td>
<td>0.90 ± 0.03</td>
<td>—</td>
<td>0.63</td>
<td>1 645</td>
<td>0.67</td>
</tr>
<tr>
<td>5</td>
<td>0.84 ± 0.05</td>
<td>12</td>
<td>0.65</td>
<td>500</td>
<td>0.75</td>
</tr>
<tr>
<td>6</td>
<td>0.71 ± 0.05</td>
<td>—</td>
<td>0.56</td>
<td>0.6</td>
<td>0.61</td>
</tr>
<tr>
<td>7</td>
<td>0.62 ± 0.05</td>
<td>9.3</td>
<td>0.57</td>
<td>8</td>
<td>No reversible effect</td>
</tr>
</tbody>
</table>

(*) From reference [12].

3. Results.

3.1 Optical Gap. — In figure 2 is shown the composition dependence of the optical gap $E_g$ at 293 K. $E_g$ was measured by plotting $(aE)^{1/2}$ as a function of the photon energy $E$, $a$ being the film absorption coefficient. As previously reported by Onton et al. [5a] and Chevallier et al. [5b] a linear decrease of $E_g$ is observed, when the germanium content increases but the rate is slower : $E_g = 1.32 + 0.44 \times x$.

3.2 Dark Conductivity and Photo-induced Effects. — Large photo-induced effects on both the photoconductivity $\sigma_p$ and the dark conductivity $\sigma_D$ have been observed in intrinsic or doped a-Si : H films by Staebler and Wronski [10](SW). We soon got experimental evidence for the presence of identical effects in SiGe alloys and started to investigate in detail the influence of the optical and thermal histories upon the electronic properties. We recall that SW showed that when a-Si : H is submitted to long and intense light exposure both the activation energy $E_a$ and the pre-exponential factor $\sigma_0$ suffer large changes. Typical values are : $\Delta E_a = E_a^A - E_a^B \sim -0.3$ eV and $\sigma_0^A / \sigma_0^B \sim 0.04$. In a recent paper [12] we extended photo-induced effects studies to a number of GD a-Si : H films prepared under various conditions and showed that $\Delta E_a$ and $\sigma_0^A / \sigma_0^B$ can vary over wide ranges : $-0.3 \leq \Delta E_a \leq 0$ eV, $0.16 \leq \sigma_0^A / \sigma_0^B \leq 7.8$.

In Table I we give data on photo-induced effects in some a-Si$_{1-x}$Ge$_x$ : H alloys. For the sake of comparison we include data for an a-Si : H film ( # 1 ) prepared under exactly the same conditions (from ref. [12]). We emphasize that upon exposure to light this sample showed no change in the activation energy and a dark conductivity decrease by one order of magnitude only, as compared to a four orders of magnitude change in SW films. In contrast in SiGe alloys, for all compositions down to $x = 0.7$, $E_g$ was found to vary (Fig. 3).

and SW observed that when passing reversibly from the annealed state A to the light-soaked state B both the activation energy $E_a$ and the pre-exponential factor $\sigma_0$ suffer large changes. Typical values are : $\Delta E_a = E_a^A - E_a^B \sim -0.3$ eV and $\sigma_0^A / \sigma_0^B \sim 0.04$. In a recent paper [12] we extended photo-induced effects studies to a number of GD a-Si : H films prepared under various conditions and showed that $\Delta E_a$ and $\sigma_0^A / \sigma_0^B$ can vary over wide ranges : $-0.3 \leq \Delta E_a \leq 0$ eV, $0.16 \leq \sigma_0^A / \sigma_0^B \leq 7.8$.

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The alloy containing 38 Ge at % has an entirely different behaviour: starting from the as-received sample lying in an intermediate state for which \( E_g = 0.70 \) eV and \( \sigma_0 = 375 \ \Omega^{-1} \text{cm}^{-1} \), it was submitted to the usual annealing procedure at 200 °C. In the annealed state we measured \( E_g = 0.57 \) eV and \( \sigma_0 = 8 \ \Omega^{-1} \text{cm}^{-1} \). Any subsequent attempt to reach the light-soaked state by illuminating with 600-900 nm light turned out to be unsuccessful, the film remaining in state A. This behaviour change at this Ge composition is reminiscent of various observed variations of the electronic [8] and photoluminescence [9] properties of films prepared either by glow discharge or dc sputtering.

Recently we discussed [12] the use of Mott's minimum metallic conductivity theory [13] to rationalize \( \Delta E_g \) and \( \sigma_0^\beta / \sigma_0^\alpha \) data in terms of a significant physical material parameter namely the temperature coefficient of the Fermi level \( \beta \). Following Mott the dark conductivity can be written:

\[
\sigma_D = \sigma_{\text{min}} \exp(\beta/k) \exp[-(E_g - E_F)\beta/kT] \tag{2}
\]

where \( \sigma_{\text{min}} \) is the minimum metallic conductivity. Equation (2) is obtained under the assumption that, to first order,

\[
E_g - E_F = (E_g - E_{F0})\beta - \beta T \tag{3}
\]

where \( E_g - E_F \) is the Fermi level distance from the mobility edge, \( (E_g - E_{F0})\beta \) is the experimental activation energy and:

\[
\sigma_0 = \sigma_{\text{min}} \exp(\beta/k). \tag{4}
\]

When passing reversibly from state A to state B the dark conductivity change is given by:

\[
\frac{\sigma_D^B}{\sigma_D^A} = \exp[(\beta_A - \beta_B)/k] \exp(-\Delta E_g/kT) \tag{5}
\]

so that a plot of \( \ln(\sigma_D^B/\sigma_D^A) \) vs. \( 1/T \) gives a straight line whose intercept yields \( \Delta \beta = \beta_A - \beta_B \).

The determination of \( \Delta \beta \) in various a-Si:H films allowed us to rationalize the random \( \Delta E_g \) and \( \sigma_0^\beta / \sigma_0^\alpha \) variations and reach the conclusion that films suffering large photo-induced effects are such that \( \Delta \beta \) is large and negative, e.g. SW films from reference [10] showed \( \Delta \beta \sim -6 \times 10^{-4} \) eV K\(^{-1}\). In contrast for films having a weak photo-induced sensitivity like #1, \( \Delta \beta = 1.7 \times 10^{-4} \) eV K\(^{-1}\).

In table I we give the \( \Delta \beta \) dependence on composition for the studied SiGe alloys. We see that, when the germanium content is increased, \( \Delta \beta \) shifts to more negative values. In spite of some scattering in the data this is better seen when \( \Delta \beta \) is plotted as a function of \( x \) (Fig. 4a). In spite of the lack of reversibility in film 7 we calculated \( \Delta \beta \) considering that the intermediate state is close to state B. Interestingly enough when plotting \( \Delta \beta \) as a function of \( \Delta E_g \) as suggested earlier [12] all the data for SiGe alloys fit the line found for a-Si:H films whose slope is 22.6 eV\(^{-1}\) (Fig. 4b). This plot is suggested by the empirical Meyer-Neldel rule applied to photo-induced effects [10b, 12].

Concerning the origin of the light-induced changes in SiGe alloys we are faced with the same problems as in a-Si:H. Whether these changes are a bulk or a surface effect is still a matter of debate. The Dersch et al. [14] recent ESR measurements, the Tanielian et al. [15] and Goodman [23] field effect data in a-Si:H point towards an increase of the density of gap states upon a long and intense exposure to light. The former authors have suggested that the primary act is the breaking of weak Si-Si bonds. Neighbouring hydrogen atoms then switch over to the arising bonds leaving new dangling bonds. If the temperature is high enough hydrogen exchange may occur and when the distance between the newly created dangling bonds is sufficient a metastable state (B) is created.

An alternative model proposed by Solomon et al. [11] explains these effects as being due to the presence of a density of charges \( Q \) at one of the surfaces of the film giving rise to a band bending \( V_0 \) at the surface. These authors have shown that for conductivity measurements in the planar configuration, with a conservative value for \( Q \) of \( 10^{10}-10^{11} \) elementary charges per cm\(^2\), the surface conductivity dominates the bulk conductivity by 3 to 6 orders of magnitude. The effect is controlled by the penetration depth \( \Lambda \), i.e. the « Debye length » of the material. The parameters are related through the following equations:

\[
\Lambda = \frac{1}{e} \sqrt{\frac{\varepsilon \varepsilon_0}{N(E_F)}} \tag{6}
\]

\[
V_0 = -\frac{Q}{e \sqrt{\varepsilon \varepsilon_0 N(E_F)}} \tag{7}
\]

where \( N(E_F) \) is the density of states near the Fermi
level and \(\varepsilon\) the dielectric constant of the material. When
the surface conductance is much larger than the bulk conductance:

\[
\sigma_0 \sim \sigma_0^B \frac{\delta}{d}
\]  

(8)

where the effective surface thickness \(\delta\) is related to \(\Delta\) through:

\[
\delta = \frac{\Delta}{\left| \frac{eV_0}{kT} \right| - 1}
\]  

(9)

with \(eV_0 = \Delta E_r\). Obviously this model applies if \(\Delta E_r \neq 0\) and \(\sigma_0^B > \sigma_0^A\). These two conditions are not fulfilled for films \# 1, 2 and 3. For films 4, 5 and 6 we calculated \(\Delta\) and \(N(E_F)\) (see Table I). Although no reversible effect was observed in film \# 7 we deduced \(\Delta\) and \(N(E_F)\) assuming that the as-received state \((E_a = 0.70 \text{ eV}, \sigma_0 = 375 \Omega^{-1} \text{ cm}^{-1})\) is close to state B. Thus we find an increase of the density of gap states near \(E_F\) from \(2 \times 10^{16} \text{ eV}^{-1} \text{ cm}^{-3}\) (\(x = 0.90\)) to \(6 \times 10^{17} \text{ eV}^{-1} \text{ cm}^{-3}\) (\(x = 0.62\)).

3.3 PHOTOCONDUCTIVITY. — In the following we give photoconductivity data as a function of the alloy composition in the two SW states. These include the high energy spectrum \((E > 1.77 \text{ eV})\) where the photoconductivity efficiency can be measured, the study of the exponential part of the absorption edge (Urbach tail) using photoconductivity data, and photoconductivity time response measurements. The low energy part of the spectrum and the determination of the absorption coefficient in this energy range is described in reference [22].

3.3.1 Photoconductivity efficiency. — This is measured by the product \(\eta \mu T\) of the quantum yield \(\eta\), the electron mobility \(\mu\) and the electron lifetime \(T\). At each photon energy \(\eta \mu T\) is given by:

\[
\eta \mu T = i_p L^2/eN_0 S(1 - R) \left[ 1 - \exp(-\alpha d) \right] V
\]  

(10)

where \(i_p\) is the measured photocurrent, \(L\) the interelectrode spacing, \(S\) the illuminated area, \(d\) the film thickness, \(R\) the reflectivity, \(N_0\) the photon flux and \(V\) the applied voltage.

Photoconductivity spectra were recorded for annealed and light-soaked films. No difference in the shape was found in the high-energy range \((> 1.8 \text{ eV})\). In contrast, in the low-energy range \(< 1.5 \text{ eV}\) we have shown that the photoconductivity spectrum changes with the alloy composition [22].

In figure 5 is shown the photon energy dependence of \(\eta \mu T\) for various germanium concentrations in states A and B. A red shift is observed when the germanium content increases and a decrease of the \(\eta \mu T\) product by about four orders of magnitude is observed between a-Si : H and a-Si_{0.62}Ge_{0.38} : H. In figure 6 is shown the composition dependence of \(\eta \mu T\) at \(h \nu = 1.9 \text{ eV}\) for the films in states A (●) and B (○). This figure clearly shows that the photoconductivity efficiency ratio in the two states \(R = \frac{(\eta \mu T)_B}{(\eta \mu T)_A}\) decreases when the germanium content is increased. Whereas for \(0.8 \leq x \leq 1\) \(R \sim 7-10\), for \(x < 0.8\) \(R\) steadily decreases and \(R = 1\) at \(x \approx 0.6\). Thus the photo-induced photoconductivity changes get smaller when the germanium atomic percentage is increased.

3.3.2 Exponential absorption edge. — It has been shown [16] that in a-Si : H films the optical absorption coefficient below the band gap energy has an exponential dependence (Urbach edge) on photon energy \(E\)
of the form
\[ \alpha \propto \exp(E/E_g). \]  

Below 1.5 eV the optical absorption was inferred from photoconductivity measurements either on Schottky diodes [17, 18] or coplanar electrodes structures [18]. The study of the optical absorption edge as a function of temperature and structural disorder allowed Cody et al. [19] to draw the conclusion that the thermal and structural disorder are additive and that the optical gap \( E_g \) is determined by the degree of disorder in the lattice rather than by the hydrogen content.

We used our photoconductivity data at photon energies below the band gap 1.4 \( \leq E \leq 1.7 \) eV for determining \( \alpha \). Provided that the photoconductivity efficiency \( \eta_{\text{photo}} \) and the reflectivity \( R \) of the film are independent of \( E \) one can write [20]:

\[ i_p \propto (\alpha N_0)^\gamma \]  

(12)

taking into account the dependence of the photo-current \( i_p \) on the incident light flux \( N_0 \):

\[ i_p \propto N_0^\gamma. \]  

(13)

Therefore in the exponential absorption edge:

\[ (i_p)^{1/\gamma} \propto \exp(E/E_g). \]  

(14)

For each film in the studied photon energy range and for \( 5 \times 10^{12} \leq N_0 \leq 10^{15} \) cm\(^{-2}\) s\(^{-1}\) we found a constant value of \( \gamma \). When the germanium content is varied small random variations of \( \gamma \) between 0.8 and 1 were found. The measurements were made for films both in the annealed and in the light-soaked states and no change in the value of \( \gamma \) was detected. A similar result was found by Abeles et al. [18] on GD a-Si: H films. For all SiGe alloys the \( \ln \left( \frac{(i_p)^{1/\gamma}}{N_0^\gamma} \right) \) vs. \( E \) plot was found to be linear, giving evidence for an exponential tail in a-Si\(_x\)Ge\(_{1-x}\):H alloys. In figure 7 is shown a typical example for \( x = 0.92 \). As seen the slope is the same whether the sample is in state A or in state B, and the same result applies to all films. \( E_0 \) was found to increase linearly when the germanium content increases (Fig. 8) from 80 meV \( (1 - x = 0.03) \) up to 110 meV \( (1 - x = 0.16) \). A sharp increase occurs around \( 1 - x = 0.3 \) and \( E_0 = 160 \) meV at \( 1 - x = 0.38 \). In figure 9 is shown a plot of \( E_0 \) as a function of the optical gap \( E_g \). Such a plot was suggested by Cody et al. [19] who noted the similarity between the temperature dependence of \( E_g \) and \( E_0 \) for a-Si:H films including heat treated samples from which \( H \) had partially evolved. They found a linear \( E_g \) vs. \( E_0 \) variation and concluded that this relationship can be explained in terms of the equivalence of structural and thermal disorder. As seen in figure 9 we find a linear relationship between \( E_0 \) and \( E_g \); here the parameter is the germanium content and not the temperature and we can tentatively draw the conclusion that disorder is the actual parameter.

3.3.3 Photocurrent response time studies. — It is agreed that in a-Si:H over a wide temperature range the photoconductivity results are consistent with free-carrier transport in the extended states. Therefore the photoconductivity data may be considered in terms of electron trapping and recombination kinetics. This point has been extensively discussed by Rose [21] and recently Wronsiki and Daniel [10c] have studied electron trapping and recombination kinetics in GD undoped a-Si:H films. These authors applied the model of Rose to results of photocurrent response times for investigating in particular the densities, energies and carrier capture cross sections of gap states.

The steady state photoconductivity is given by:

\[ \sigma_p = e\mu_n n \]  

(15)
where \( n \) is the free electron density and \( \mu_n \) the microscopic mobility in the conduction band. On the other hand:

\[
n = f \tau_n
\]

\[
f = N_0 (1 - R) [1 - \exp(- \alpha d)]/d
\]

where \( f \) is the volume free-electron generation rate, assuming that the quantum efficiency is one. The decay of the steady-state photocurrent when the illumination is turned off can be related to \( n_t \), the density of trapped electrons emptied in a time \( \tau_0 \) by:

\[
\tau_0 = \left(1 + \frac{n_t}{n}\right) \tau_n
\]

\( \tau_0 \) is defined as the time taken for the photocurrent to decay to half the steady-state value. As \( n_t \gg n \)

\[
n_t = f \tau_0.
\]

If \( E_{F_n} \) is the quasi-Fermi level the density of states in the gap acting as traps \( N_t(E_{F_n}) \), is related to \( n_t \) through the equation:

\[
n_t = kT N_t(E_{F_n})
\]

and the free-electron density in the conduction band is given by:

\[
n = N_c \exp[-(E_e - E_{F_n})/kT]
\]

where \( N_c \) is the density of states at \( E_e \).

When the light intensity is increased \( E_{F_n} \) moves upwards and measurements of \( \tau_0 \) allow us to determine \( N_t(E_{F_n}) \) at various energies between \( E_F \) and \( E_e \).

The free-electron densities and lifetimes are obtained from equations (15) and (16) assuming \( \mu_n = 1 \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) as in a-Si:H. So far the microscopic mobility in the extended states has not been measured in binary SiGe alloys and the above value is only an approximation. Therefore the quasi-Fermi level positions, obtained from equation (22) may be shifted by some 0.05 eV from the actual position. We have also assumed that \( N_c = 10^{20} \) eV\(^{-1}\) cm\(^{-3}\) as in a-Si:H. It should be stressed that until \( \mu_n \) and \( N_c \) are measured the derivation of \( N_t(E_{F_n}) \) below, only allows a qualitative comparison of the evolution of the density of states when the germanium content is increased.

In figure 10 is shown a typical plot of the response time \( \tau_0 \), electron lifetime \( \tau_n \) and photocurrent intensity \( i_p \) versus the photogeneration rate \( f \). In these experiments the studied \( f \) range was upperbounded because we used a mechanical shutter to terminate the illumination. When \( f \) was \( \sim 5 \times 10^{16} \) photons cm\(^{-2}\) s\(^{-1}\) the response time \( \tau_0 \) turned out to be of the same order of magnitude as that of the shutter. So we could measure \( \tau_0 \) in the range 20-150 ms corresponding to \( f \)

changes by \( \sim 1.5 \) order of magnitude leading to a displacement of the quasi-Fermi level by \( \sim 0.10 \) eV upwards in an energy range between 0.35 and 0.55 eV below \( E_e \) depending upon the sample. The measurements were carried out on samples in both the annealed and the light-soaked states of SW. In contrast with the results obtained by Wronski and Daniel [10c] we found no systematic variation of \( \gamma \) and the same \( f \) dependence of \( i_p \) and \( \tau_0 \) in both states.

As shown in figure 10 the dependences of the photocurrent, response time and electron lifetime on intensity of illumination have the following forms:

\[
\gamma \propto f^\gamma
\]

\[
\tau_0 \propto f^{-\gamma}
\]

\[
\tau_n \propto f^{-(1-\gamma)}
\]

In table II we give the \( \gamma \) values for various films together with the density of states \( N_t(E_{F_n}) \) and the energy range \( E_e - E_{F_n} \) in which the measurements

Table II. — Response time data and density of states at the quasi-Fermi level.

<table>
<thead>
<tr>
<th>Film</th>
<th>( x )</th>
<th>( \gamma ) State A</th>
<th>( \gamma ) State B</th>
<th>( N_t(E_{F_n}) ) ( \times 10^{16} ) eV(^{-1}) cm(^{-3})</th>
<th>Energy range ( E_e - E_{F_n} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.97</td>
<td>0.93</td>
<td>0.85</td>
<td>2.4 ± 0.5</td>
<td>0.43-0.51</td>
</tr>
<tr>
<td>3</td>
<td>0.92</td>
<td>0.90</td>
<td>1.00</td>
<td>4.0 ± 0.8</td>
<td>0.43-0.51</td>
</tr>
<tr>
<td>4</td>
<td>0.90</td>
<td>0.87</td>
<td>1.00</td>
<td>2.5 ± 0.5</td>
<td>0.39-0.49</td>
</tr>
<tr>
<td>6</td>
<td>0.84</td>
<td>0.91</td>
<td>0.91</td>
<td>7.5 ± 1.5</td>
<td>0.45-0.53</td>
</tr>
<tr>
<td>8</td>
<td>0.62</td>
<td>0.82</td>
<td>0.91</td>
<td>7.0 ± 14</td>
<td>0.49</td>
</tr>
</tbody>
</table>
were carried out. \( N(T(E_F)) \) was found to be the same whether the film is in state A or B. Our data clearly show an increase of the density of gap states at \( E_{F_a} \) when the germanium content in the binary alloys is increased.

4. Discussion and conclusion.

In the silicon-rich region \((x > 0.6)\) we find that a-Si\(_x\)Ge\(_{1-x}\):H alloys deposited at 280 °C contain the same hydrogen content \((\sim\ 9-12 \text{ at} \% )\) as a-Si:H. This is in agreement with the results obtained by Paul et al. who studied hydrogen evolution and infrared vibrational absorption in the whole range of germanium concentration: the hydrogen content keeps this value for \( x \gtrsim 0.7 \) and apparently takes higher values for \( x \sim 0.3 \). We may then infer that the alloys electronic properties do not depend upon the hydrogen amount but rather upon the preferential attachment to Si [6].

To our knowledge this report gives the first evidence of reversible photo-induced effects in binary amorphous Si-Ge alloys. As shown in Table I the change in the activation energy of the dark conductivity \( \Delta E_{p} \) between the annealed and the light-soaked states is increased when germanium is incorporated into a-Si:H. When the germanium content is further increased though accurate measurements of the small activation energy changes are difficult it seems that \( \Delta E_{p} \) increases slightly. In contrast the pre-exponential factor \( \sigma_{0} \) suffers random variations.

Though the physical origin of the Staebler-Wronski effect is not yet firmly established there are strong experimental evidences that in a-Si:H illumination with intense light in the 600-900 nm range results in an increase of the density of gap states as shown by Dersch et al.'s ESR studies [14] together with Goodman's field effect results [23]. On the other hand Hack and Madan [30] have recently demonstrated that upon illumination and subsequent annealing photo-electronic changes occur both in the bulk of a-Si:H and at the surface. Following these authors bulk effect represents a reversible conductivity change and surface effects can be attributed to a variable charge density at the surface as demonstrated by Solomon et al. [11].

Our a-Si:H film (1, in Table I), deposited in the same conditions as the alloy films, does not have a typical Staebler-Wronski behaviour: the \( \sigma_{0} \) activation energy change is zero when passing reversibly from state A to state B. This can be interpreted as being due to a bulk effect: the Fermi level \( E_{F} \) does not shift in the process and a likely explanation is that the gap density of states grows symmetrically around \( E_{F} \) during illumination. Already when a small amount of Ge is incorporated (3 % film \# 2) the density of states grows differently, \( E_{F} \) is shifted towards midgap and \( \Delta E_{F} \gtrsim 0 \). Film \# 7 deserves attention because at this germanium percentage (38 %) new properties are observed. In particular we noted that the as-received sample i.e. lying in an intermediate state, once annealed at 200 °C, did not show any reversible effect upon illumination. From the work of Paul et al. [6] it is known that hydrogen evolution upon warming depends on the alloy composition. Whereas H evolves from Ge near 150 °C, the evolution from Si occurs above 400 °C. Alloy behaviour is intermediate and it is possible that hydrogen exodiffusion starts around 200 °C so that a high density of defects is created resulting in an increase of the gap states density, the Fermi level is pinned and the film becomes insensitive to illumination. This idea is substantiated by the large values of the width of the exponential absorption edge (Fig. 8) and of the density of states \((\sim 7 \times 10^{17} \text{ eV}^{-1} \text{ cm}^{-2})\) measured at \( E_{c} - E_{F_0} = 0.5 \text{ eV} \) by photoconductivity time response studies. As far as a quantitative interpretation of \( \Delta E_{p} \) and \( \sigma_{0} \) changes are concerned, the use made of Mott's theory of minimum metallic conductivity allowed us to measure the variations \( \Delta \beta = \beta_{a} - \beta_{s} \) of the temperature coefficient of the Fermi level when the annealed alloy is illuminated. This interpretation applies only to photo-electronic changes due to bulk effects and rests upon two assumptions: i) \( E_{c} - E_{F} \) depends linearly upon the temperature (equation (3)) and ii) \( \sigma_{min} \) in equation (2) does not change with from state A to B. Undoubtedly, in the case of the a-Si:H film (\# 1) for which \( \Delta E_{b} = 0 \) we are dealing with a bulk effect, since in the framework of Solomon et al.'s model \( \Delta E_{b} = 0 \) implies a zero surface potential i.e. no band bending. The tentative approach we made for SiGe alloys led us to reach the conclusion that \( \Delta \beta \) decreases from positive to negative values when the germanium atomic percentage is increased.

Next we find that the alloy photoconductivity efficiency remains high and close to that of a-Si:H \((5 \times 10^{-5} < \eta_{F} < 8 \times 10^{-5} \text{ cm}^{2} \text{ V}^{-1})\) in the annealed state at a photon energy of 1.9 eV) as long as the germanium content is kept below \( \sim 10 \% \). Beyond this concentration \( \eta_{F} \) strongly decreases and at \( x = 0.62 \eta_{F} = 7 \times 10^{-9} \text{ cm}^{2} \text{ V}^{-1} \) (Fig. 6). Obviously this inferior photoresponse of the SiGe alloys as compared to a-Si:H is due to the increase of the density of states in the gap: the width of the exponential absorption edge (Fig. 8) and the density of states at \( E_{c} - E_{F_0} \sim 0.4-0.5 \text{ eV} \) (Table II) steadily grow when the germanium content is increased. Recent studies of the optical absorption edge of GD SiGe alloys [22] allowed us to draw the same conclusion. The absorption coefficient was determined from 10\(^5\) down to \( \sim 1 \text{ cm}^{-1} \) by a combination of optical and photoconductivity measurements. A shoulder located between 1.2 and 1.4 eV observed in a-Si:H by several authors [20, 24-29] remains roughly at the same energies for Si-rich alloys and its magnitude increase with the germanium content. This shoulder must correspond to a local maximum in the density of localized states in the gap located \( \sim 0.5 \text{ eV} \) above the valence band. Thus it is seen that, upon increasing incorporation of Ge, more defects acting as recombination centres are introduced. The very low photoresponse
observed in the annealed film containing 38 % Ge is due to the same phenomenon but in addition, as suggested above, hydrogen evolution upon warming at 200 °C might further increase the density of dangling bonds.

It has been suggested by Paul et al. [6] that in SiGe alloys hydrogen is preferentially bound to Si. These authors deduced from infrared absorption spectra a measure of the preference $P$ for H to bond to Si rather than to Ge:

$$P = \frac{\text{integrated Si-H absorption}}{\text{integrated Ge-H absorption}} \times R$$

the ratio $R$ taking into account the Si and Ge content and Si-H and Ge-H matrix elements. Whatever the alloy composition $P \sim 10$. This result has a great significance in connection with transport and photoconductive properties since dangling bonds on Ge atoms may be left uncompensated creating efficient recombination centres for photocreated carriers.

In conclusion though the optical gap is decreased in a-SiGe alloys as required for practical applications in the field of solar cells we find a decrease of the photoreponse whatever the alloy composition. Only in the 0-10 % Ge range can interesting alloys be found with a moderate optical gap decrease. At least in the energy range we have investigated the density of states for these alloys $\sim 2 - 4 \times 10^{16} \text{eV}^{-1} \text{cm}^{-1}$ i.e. close to that measured for a-Si:H. More studies are necessary to improve the electronic properties in particular by varying the deposition parameters and by trying to compensate the dangling bonds with atoms more firmly bound to Ge.

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References