Photoconductivity of amorphous GaAs

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Abstract

The spectral response of photoconductivity has been measured in samples of amorphous gallium arsenide deposited by rf sputtering of monocrystalline GaAs targets with and without hydrogen. The maximum of the normalized spectral photoconductivity \( (h\nu \approx 2.0 \text{ eV}) \) as a function of hydrogen pressure, \( p_{H_2} \), increases when \( p_{H_2} \leq 0.1 \text{ Pa} \) and then tends to a constant value. The values of the Tauc optical gap, \( E_g \), and those of the photoconductive threshold, \( E_{\text{ph}} \), are similar. Their difference for the same sample tends to decrease with increasing \( p_{H_2} \). The same trend is shown by the difference between the Urbach energy computed either by photothermal deflection spectroscopy, \( E_\sigma \), or by photoconductivity absorption coefficient data, \( E_{\text{ph}} \). These results and the dependence of other quantities, such as the activation energy of the conductivity, \( E_{\alpha} \), on \( p_{H_2} \), are interpreted in terms of the possible effects that hydrogenation can induce in a compound semiconductor. They are: a less disordered network reducing the band tail depth; decrease of the bond-angle fluctuation and ineffectiveness of hydrogen on the density of wrong bonds. The first two contributions are strictly linked to the deposition conditions of the films which determine, for example, the deposition rate of the film.

1. Introduction

Papers can be found in the literature on photoconductive properties of amorphous silicon [1]. The metastable defects and the Staebler–Wronski effects control the photoconductivity of samples of a-Si [2–4]. Few results, to our knowledge, can be found on photoconductive properties of III–V amorphous materials [5–8]. The purpose of this work is to measure the dependence of the photoconductivity of films of a-GaAs on their deposition conditions with particular emphasis on hydrogenation.

2. Experimental

Films of GaAs were prepared by rf sputtering using a water cooled monocrystalline target (5 cm in diameter). The wafer, \( (1,0,0) \) oriented, was cut from an ingot grown by the liquid encapsulation Czochralski method. The target was undoped low resistivity GaAs (\( \rho = 0.1 \text{ } \Omega \text{ cm}, \mu = 4000 \text{ } cm^2 \text{ V}^{-1} \text{ s}^{-1} \) and \( n = 10^{16} \text{ } cm^{-3} \) at room temperature). The vacuum base pressure was less than \( 10^{-4} \text{ Pa} \).

The deposition was carried out maintaining the pressure of the sputtering gas (argon) at \( p_{Ar} = 2.5 \text{ Pa} \) with a deposition power, \( P = 200 \text{ W} \), constant for all samples, and the substrate temperature, \( T_s \), constant at 20°C (Table 1). The hydrogen pressure varied in the range from 0.045 to 0.48 Pa. The percentage
Table 1
Summary of the deposition parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>( P_{H_2} ) (Pa)</th>
<th>( P_{Ar} ) (Pa)</th>
<th>( d ) (( \mu )m)</th>
<th>( \sigma_{\text{dark}} ) (( \Omega \text{ cm} )) (^{-1} )</th>
<th>( \sigma_{\text{ph}} ) (( \Omega \text{ cm} )) (^{-1} )</th>
<th>( \frac{\sigma_{\text{ph}}}{\sigma_{\text{dark}}} )</th>
<th>( E_g ) (eV)</th>
<th>( E_{\gamma,\text{ph}} ) (eV)</th>
<th>( E_0 ) (meV)</th>
<th>( E_{0,\text{ph}} ) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>-</td>
<td>2.5</td>
<td>0.95</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.85-0.90</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>48</td>
<td>0.045</td>
<td>2.2</td>
<td>1.10</td>
<td>( 1.5 \times 10^{-9} )</td>
<td>( 8.9 \times 10^{-9} )</td>
<td>-</td>
<td>1.30</td>
<td>1.17</td>
<td>103</td>
<td>90</td>
</tr>
<tr>
<td>46</td>
<td>0.091</td>
<td>2.4</td>
<td>0.90</td>
<td>( 1.7 \times 10^{-10} )</td>
<td>( 3.4 \times 10^{-9} )</td>
<td>-</td>
<td>20</td>
<td>1.35</td>
<td>1.32</td>
<td>89</td>
</tr>
<tr>
<td>47</td>
<td>0.11</td>
<td>2.2</td>
<td>0.90</td>
<td>( 4.8 \times 10^{-10} )</td>
<td>( 7.1 \times 10^{-9} )</td>
<td>-</td>
<td>15</td>
<td>1.39</td>
<td>1.4</td>
<td>75</td>
</tr>
<tr>
<td>95</td>
<td>0.21</td>
<td>1.8</td>
<td>1.00</td>
<td>( 1.1 \times 10^{-9} )</td>
<td>( 3.1 \times 10^{-8} )</td>
<td>-</td>
<td>28.5</td>
<td>1.47</td>
<td>1.46</td>
<td>75</td>
</tr>
<tr>
<td>73</td>
<td>0.26</td>
<td>2.2</td>
<td>0.55</td>
<td>( 3.0 \times 10^{-11} )</td>
<td>( 6.2 \times 10^{-9} )</td>
<td>-</td>
<td>204</td>
<td>1.46</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>21</td>
<td>-</td>
<td>1.1</td>
<td>0.90</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.85-0.90</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>57</td>
<td>0.39</td>
<td>1.0</td>
<td>0.50</td>
<td>( 1.1 \times 10^{-10} )</td>
<td>( 1.2 \times 10^{-8} )</td>
<td>-</td>
<td>105</td>
<td>1.40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>73</td>
<td>0.48</td>
<td>1.0</td>
<td>1.00</td>
<td>( 1.35 \times 10^{-10} )</td>
<td>( 7.7 \times 10^{-9} )</td>
<td>-</td>
<td>57</td>
<td>1.50</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\( P_{H_2} \), hydrogen pressure; \( P_{Ar} \), pressure of the sputtering gas (argon); \( d \), film thickness.

\( \sigma_{\text{dark}} \), dark conductivity; \( \sigma_{\text{ph}} \), photoconductivity; \( E_g \), Tauc optical gap; \( E_{\gamma,\text{ph}} \), photoconductivity optical gap; \( E_0 \), Urbach energy from PDS measurements; \( E_{0,\text{ph}} \), Urbach energy from photoconductivity curves.

error on \( T_e \) is about \( \pm 5\% \). The error on the rf power, \( P \), can be estimated to be about \( \pm 5\% \), while that of the pressure, \( p \), was less than \( \pm 1\% \), since pressure was controlled by flowmeters. Two unhydrogenated samples were deposited under the same deposition conditions and used for comparison with the results obtained on the hydrogenated ones. The substrates were Corning glass 7059 in all cases. The film thicknesses, \( d \), were measured using a mechanical stylus in a range between 0.55 and 1.1 \( \mu \)m. For the film thickness measurements, the accuracy of the calibrated profilometer was \( \pm 5\% \).

The photoconductivity measurements were carried out on specimens equipped with two coplanar thermally evaporated Au contacts. They lay on the outer surface of the specimens and were 1.5 mm apart. The ohmic properties of the contacts were determined with a curve tracer under a maximum applied field of about \( 10^3 \) V cm\(^{-1} \).

DC photocurrents were measured by an electrometer, while photoconductivity spectra were obtained by means of a lock-in amplifier, chopping the monochromatic light with a frequency \( f = 30 \) Hz. A Xenon lamp and a Rank Hilger D 330 monochromator equipped with a 1200 lines/mm grating, blazed to 0.5 \( \mu \)m, and a resolution factor equal to 95\%, were used. The percentage error on dark- and photoconductivity (\( \sigma_{\text{dark}} \) and \( \sigma_{\text{ph}} \), respectively) measurements was estimated to be less than \( \pm 5\% \). The incident photon flux (\( 10^{13}-10^{17} \) photons/cm\(^2 \) s) was measured by means of a pyroelectric radiation detector.

3. Results

The spectral responses of photoconductivity at room temperature for three of the measured samples are shown in Fig. 1. The hydrogen pressure, \( P_{H_2} \),

![Fig. 1. Normalized photocconductivity as a function of the photon energy for three samples of Table 1. Lines are drawn as guides for the eye.](image)
Fig. 2. Sensitivity to white light expressed through the ratio \( \sigma_{ph} / \sigma_{dark} \) as a function of the hydrogen pressure, \( p_{H_2} \).

Fig. 3. Sensitivity to white light expressed through the ratio \( \sigma_{ph} / \sigma_{dark} \) as a function of the hydrogen pressure, \( p_{H_2} \).

increases from sample 48 to sample 95. The ordinate is the normalized photoconductivity, \( i_{ph,n} = i_{ph}/(eN(1 - R)) \). This quantity represents the number of charge carriers flowing around the circuit for each photon absorbed in the specimen, being \( N(1 - R) \) the number of photons per second impinging on the sample and corrected for surface reflection. \( R \) was assumed constant and equal to 0.3 [9]. It must be noted that \( i_{ph,n} \) increases with \( p_{H_2} \), attaining about \( 10^{-8} \) in sample 95 (Fig. 1), the maximum value found in the measured samples at photon energy around 2.0 eV. This photon energy is the value for which all samples have their highest photocurrent.

The sensitivity of the samples to the illumination was measured using white light. The behaviour of the ratio \( \sigma_{ph} / \sigma_{dark} \) as a function of \( p_{H_2} \) is presented in Fig. 2 for air mass AM 1.5. The air mass indicates the thickness of atmosphere travelled by solar radiation under different incidence angles: by definition, AM 0 = 0.1353 W cm\(^{-2}\) corresponds to the total solar power flux density for a cloudless day with the sun directly overhead on the zenith, while AM 1.5 = 0.0832 W cm\(^{-2}\)[10].

4. Discussion

The increase of the normalized photoconductivity with photon energy (Fig. 1) corresponds to the usual assumption of an increase of the absorption coefficient and to an increase of the transition probability of photoexcited carriers.

Fig. 3 presents the peak values \( (h \nu = 2.0 \text{ eV}) \) of the normalized spectral photoconductivity, \( i_{ph,n} \), plotted as a function of the hydrogen pressure, \( p_{H_2} \). The photoconductivity reaches the maximum value for \( p_{H_2} \approx 0.21 \text{ Pa} \) (sample 95) and then tends to remain constant, \( \approx 8 \times 10^{-9} \). In Fig. 3, two values of \( i_{ph,n} \) (triangles) measured in samples 57 and 73 (Table 1), in which the pressure of the argon sputtering gas differ from the other ones, are given. As one can see, argon pressure, in the range used here, does not affect the photoconductivity of the samples. This fact seems to correspond to results of structural and morphological measurements performed on similar samples [11,12]. We found that the variation in \( p_{Ar} \) mainly affects the deposition rate, \( r_D \), while the microcrystalline mean dimension, \( D \), is invariant with \( p_{Ar} \). The data for \( D \) and the procedure to its measurement by TEM micrographs are given in Refs. [11,12].

The photocurrent reaches the maximum value for \( p_{H_2} \approx 0.21 \text{ Pa} \) and then remains constant within errors of measurement. The photocurrent is given by

\[
 i_{ph} = eGE\mu\tau, \tag{1}
\]

where \( \mu \) is the free carrier mobility, \( \tau \) is the recombination lifetime, \( E \) is the electric field and

\[
 G = (\eta N(1 - R)[1 - \exp(-\alpha d)]/d \tag{2}
\]

Fig. 3. Peak values \( (h \nu = 2.0 \text{ eV}) \) of the normalized spectral photoconductivity (Fig. 1) as a function of the hydrogen pressure, \( p_{H_2} \). Triangles refer to two samples deposited at low \( p_{Ar} \) (Table 1).
is the electron–hole generation rate \[13\]. In Eq. (2), \( \eta \) is the quantum efficiency, \( \alpha \) is the absorption coefficient and \( d \) is the sample thickness. We have computed the quantity, \((\eta \mu \tau)\), at the photon energy 2.0 eV. The absorption coefficients were measured in our laboratory on co-deposited samples using Corning glass 7059 as substrate. These values were used in the computation of \((\eta \mu \tau)\) through Eqs. (1) and (2). Assuming \( \eta = 1 \) and \( \mu = 10^{-1} \text{ cm}^{-2} \text{ V}^{-1} \text{ s}^{-1} \) [14], we were able to estimate the recombination lifetime of specimens deposited at \( p_{\text{H}_2} \geq 0.21 \text{ Pa} \) and near the maximum of the photoresponse, as \( \tau \approx 10^{-9} \text{ s} \). This value cannot be compared with others for a-GaAs, due to lack of data. A comparison can be made with lifetime values measured in a-Si:H [1]. This value for a-GaAs is several orders of magnitude less.

The quantity,\
\[
\left[ \frac{hv}{i_{\text{ph},n}} \frac{\eta}{eN(1-R)} \right]^{1/2},
\]
was calculated in the low absorption region and plotted against the photon energy, \( h\nu \). This plot allows the determination [15,16] of the photoconductive threshold, \( E_{\text{t,ph}} \), extrapolating the straight line portion of the curve to intercept the energy axis. The computed values of \( E_{\text{t,ph}} \) are given in Table 1. Taking into account the experimental error (±5% both for \( E_g \) and \( E_{\text{t,ph}} \)), the values of the Tauc optical gap, \( E_g \), and those of \( E_{\text{t,ph}} \) are similar. A second important point is that the difference between these two quantities for the same sample tends to decrease with increase of \( p_{\text{H}_2} \). This last result also corresponds to the behaviour of the difference between the characteristic Urbach energies computed either by photothermal deflection spectroscopy (PDS) absorption data or by photoconductivity absorption coefficient data listed in Table 1, in which the two quantities are labelled \( E_0 \) and \( E_{0,\text{ph}} \), respectively. The error on \( E_0 \) and \( E_{0,\text{ph}} \) can be estimated to be about ±6%.

It is evident from the experimental results that hydrogen influences the properties of the material. From the values of \( E_g \) (Table 1), we note that the mobility gap is strongly dependent on the hydrogen content, \( C_{\text{H}_2} \), in the sputtering chamber. In fact, \( E_g \) is \( (0.85 \pm 0.05) \text{ eV} \) for the unhydrogenated samples 18 and 21, while it increases with hydrogen content up to \( (1.5 \pm 0.08) \text{ eV} \) when \( p_{\text{H}_2} \geq 0.11 \text{ Pa} \) (sample 47).

The hydrogenation of the material induces a possible rearrangement of the network, probably of the bond angles between Ga and As atoms with an influence on the depth of the valence band tail [17]. In fact, the characteristic energy of the Urbach tail, \( E_0 \), in the unhydrogenated sample is 130 meV with \( E_g \approx 0.85 \text{ eV} \) (Table 1). \( E_0 \) decreases to about 75 meV, with an increases of \( E_g \) in hydrogenated samples. The effectiveness of hydrogenation on the reduction of the density of states is supported by measurements of optical constant (\( E_g \), \( E_0 \) and \( \alpha \)) and relative defect density, \( N_s \), as a function of \( p_{\text{H}_2} \) in Fig. 4 [18]. These results show not only a dependence of all these quantities on the hydrogen content in the film but also their variations can be linked to the decrease of the deposition rate with increasing hydrogen content. So, the optical constants and \( N_s \) depend on structural properties of the material, on bond angle fluctuations and on wrong bonds, all quantities which depend on \( p_{\text{H}_2} \). N\text{ s} was evaluated using the PDS absorption coefficient data at photon energy less than 0.8 eV [18]. The integral of \( \alpha \) in that energy range has been directly related to the density of states associated with dangling bonds and other defects, localized in the mobility gap of a-GaAs. Following the procedure suggested by Amer and Jackson [19], the density of states, \( N_s \), can be
Fig. 5. Activation energy, $E_0$, of the conductivity plotted as a function of the hydrogen pressure, $p_{H_2}$.

qualitatively estimated from this part of the absorption spectrum. Due to the lack of parameters to perform calculations in a-GaAs, parameters of a-Si:H were used. For this reason, relative defect values are given in Ref. 4, assuming the $N_s$ value of sample 18 is unity. The shaded area contains the $N_s$ values estimated for our unhydrogenated samples. Typical absolute values of $N_s$ for these samples are greater than $5 \times 10^{17}$ cm$^{-3}$.

A similar effect of increase of $E_0$ was found by Baker et al. [20] in unhydrogenated a-GaAs, grown with increasing deposition temperatures, $T_s$, and interpreted in terms of a stronger influence on the dangling-bond density by increasing $T_s$ rather than on the wrong-bond defect density.

In the hydrogenated specimens, because of the high resistivity, we could not measure conductivity at low temperatures. We conclude that the density of localized states in the mobility gap is strongly reduced by hydrogenation. Fig. 5 shows the activation energy of the conductivity, $E_0$, versus the hydrogen content. From this figure, the influence of hydrogenation on $E_0$ is evident. $E_0 \approx 0.26$ eV for the unhydrogenated samples; then it increases rapidly with $C_{H_2}$, saturates to about 0.80 eV for $C_{H_2} \approx 0.1$ and is then independent of $C_{H_2}$. Similar dependences are shown by $E_g$ and $C_{H_2}$ versus $p_{H_2}$. All these quantities have a rapid increase in a narrow range of $p_{H_2}$ when $p_{H_2} \leq 0.1$ Pa [21]. The conclusion is that a high content of hydrogen in the sputtering chamber is not necessary: in fact, the main variations on physical properties are obtained when $p_{H_2} \leq 0.1$ Pa.

Finally, we note that our results are in general agreement with the few data quoted in the literature on the effect of $H_2$ addition to a-GaAs [5,6]. We were not able to find results on photoconductivity measurement in a-GaAs. It is difficult to perform a detailed comparison between our results and the literature, due to a scarcity of data and to different deposition conditions of the films.

5. Conclusions

The optical properties of a-GaAs are strongly dependent on deposition conditions, in particular on the presence of hydrogen in the deposition chamber. Small quantities of hydrogen ($p_{H_2} = 1\% p_{Ar}$) induce changes of the network of the deposited films, giving rise to an increase of the photoconductivity of the material. The decrease of $E_0$ can be partially attributed to a less disordered network, reducing the tailing of the density of states [18]. This effect can be added to that of the decreasing bond-angle fluctuations [16], due to the introduction of hydrogen into the semiconductor network. On the other hand, the relatively high value of $E_0$ in hydrogenated films can be attributed partially to the presence of wrong bonds. These are typical defects of compound semiconductors, and they cannot be compensated for by hydrogen.

All these effects depend on the deposition parameter values and influence the photoconductive properties of the deposited films. All of our results show that the physical properties of a-GaAs films change with $p_{H_2} \leq 0.1$ Pa. This dependence is also true for $i_{ph,n}$ (Fig. 3), but its absolute value is less than the photocurrent obtained in samples of a-Si:H deposited under similar conditions [1].

All deposition parameters influence the photoconductive properties of the deposited films; hydrogenation alone is not able to give a significant improvement of the photoconductivity.

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References

[9] The value $R = 0.3$ was estimated from absorbance measurements and used to compute the absorption coefficient: A. Carbone, F. Demichelis, G. Kaniadakis, F. Gozzo, R. Murri, N. Pinto, L. Schiavulli, G. Della Mea, A. Drigo and F. Paccagnella, Nuovo Cim. D13 (1991) 571. See also Ref. [18].