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Boron Incorporation and Its Effect on Electronic Properties of Ge:H Films Deposited by LF Plasma

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ABSTRACT

Previously the deposition conditions that provided low absorption related to both band tail and deep localized states have been found. In this work boron doping of Ge:H films have been systematically investigated. The films were deposited by low frequency plasma under such conditions that resulted in a low density of localized states. The boron incorporation in solid phase was observed to increase linearly with the increase of the doping in the gas phase. The hydrogen concentration in the films was determined from FTIR and SIMS measurements. In the entire region of boron concentrations here studied, the hydrogen content changed non-monotonously by a factor of 1.5 as it was determined from both stretching mode absorption at $k \approx 1870 \text{ cm}^{-1}$ and SIMS data. The activation energy of conductivity increased in the range of $[B]_{\text{sol}} = 0$ to 0.05% suggesting a compensation of electron conductivity, reaching maximum value $E_a = 0.5 \text{ eV}$ (corresponding approximately to $E_g/2$) at $[B]_{\text{sol}} = 0.05\%$. Then with further incorporation of boron reduced the value of the activation energy to a minimum value $E_a = 0.27 \text{ eV}$ (corresponding Fermi energy $E_F(\text{RT}) = 0.15 \text{ eV}$ at $[B]_{\text{sol}} = 0.12 \%$). After this point, a behaviour showing a trend to saturation with further boron increase is observed. This behaviour is related to the change of charge transport from electron to intrinsic at $[B]_{\text{sol}} = 0.05\%$ and beyond this point to hole transport. A significant reduction of both band tail and deep localized states were observed at $[B]_{\text{sol}} = 0.004\%$. The latter is presumably related to the improvement of the lattice structure.

INTRODUCTION

Hydrogenated Germanium film (Ge:H) deposited by plasma are of much interest because of its possible applications in devices such as low band gap solar cells (or the long wavelength part of the tandem of a photovoltaic structure), photo-detectors, which are well suited for fibre optic communications, thermo-photovoltaic devices, etc. A Ge:H p-i-n detector has been reported [1], but with the p-n layers made of silicon films. Usually, the plasma deposited Ge:H films demonstrate worse electronic properties in comparison with those of silicon films. The deposition conditions providing the best electronic properties for silicon films did not allow to prepare good quality Ge:H films. Dalal et al [2] have reported the important role of ion bombardment during growth in the plasma deposition of high quality Ge:H films. In this respect low frequency (LF) PECVD with its inherent higher ion bombardment than standard RF plasma is very attractive. In our previous studies [3], we have demonstrated a LF PECVD fabrication of Ge:H films with both low tail and low deep localized states absorption. Boron doping of plasma

deposited silicon films have been widely studied and applied in many devices, while only a few papers have been reported on B-doping of Ge:H films [4-6].

This work is devoted to the study of boron incorporation and its effect on the electronic properties of Ge:H films deposited by LF PECVD.

EXPERIMENT

The films were obtained by low frequency (LF) plasma enhanced chemical vapour deposition (PECVD) from a mixture of $\text{GeH}_4 + \text{B}_2\text{H}_6$ diluted with hydrogen. The deposition parameters were as follows: substrate temperature $T_s = 300^\circ\text{C}$, the discharge frequency $f = 110$ kHz, pressure $P = 0.6$ Torr, power $W = 300$ W, germane flow $Q_{\text{GeH}_4} = 50$ sccm, hydrogen flow $Q_{\text{H}_2} = 3500$ sccm. The Diborane (B_2H_6) flow was varied in the range of $Q_{\text{B}_2\text{H}_6} = 0$ to 20 sccm providing boron concentration in gas phase in the range of $[\text{B}]_{\text{gas}} = 0$ to 4%. The composition of the films was determined by SIMS profiling. Hydrogen bonding was studied by FTIR. The measurement -in a vacuum thermostat- of the temperature dependence of conductivity in DC regime was employed to study carrier transport. From transmittance and reflectance measurements were determined the optical gap, sub-gap absorption and refraction index of the deposited films.

DISCUSSION

Before to starting the study of doping we have investigated various deposition regimes for intrinsic films, and have found some optimal conditions for the deposition of intrinsic films with the both the lowest deep and tail density of localized states (see ref. [3]). These depositing conditions were employed in this study for fabrication of both reference and doped films.

The deposition rate of the deposited films changed non-monotonously with the atomic concentration of boron (from diborane as a stock gas) in gas phase as shown in Figure 1. The variation of the deposition rate in the entire range of the boron concentrations here studied, was from $V_d = 3.3 \text{ \AA/s}$ to a minimum 2.5 \AA/s at $[\text{B}]_{\text{gas}} = 3\%$. Nevertheless, the deposition rate here obtained is higher than that of the typical in RF discharge ($V_d \approx 1 \text{ \AA/s}$).

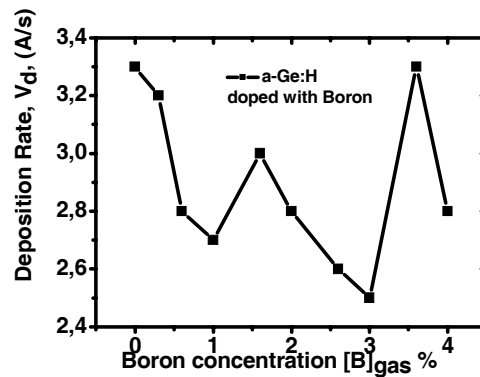


Figure 1. Deposition rate as function of boron doped in gas phase for a-Ge:H films.

The composition of the films and the boron incorporation were determined by SIMS. An example of a SIMS profile is shown in Figure 2 a). In order to analyze the boron incorporation and also to control such components as hydrogen and oxygen, the concentrations of the elements at approximately the middle part of sample thickness were considered. Figure 2 b) presents the boron concentration in solid phase versus that in gas phase. The solid line is the result of the best linear fit described as $[B]_{\text{sol}} \% \approx k [B]_{\text{gas}} \%$ ($k = 0.035 \pm 0.001$).

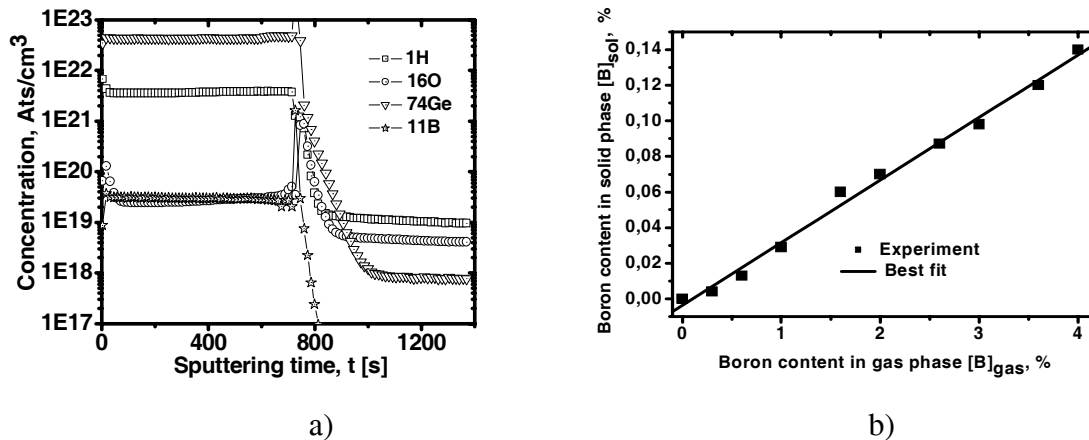


Figure 2. Composition SIMS profile of the sample # 595 (a) and boron gas into solid phase incorporation (b).

The hydrogen incorporation was studied through FTIR and SIMS. In IR spectra two modes are attributed to Ge-H; deformation ($k \approx 560 \text{ cm}^{-1}$) and stretching ($k \approx 1870 \text{ cm}^{-1}$). The corresponding areas of each IR spectra of the absorption lines versus boron concentration in solid phase are shown in Figure 3. The hydrogen concentration obtained from SIMS measurements are also presented in this figure and there is observed a close correlation with the FTIR measurements.

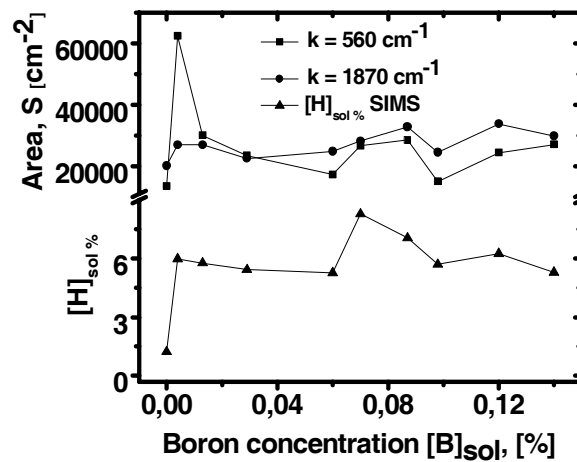


Figure 3. IR absorption related to Ge- H bonding versus boron concentration in the films.

In the entire region of boron concentrations here studied, the hydrogen content changed non-monotonously by a factor of 1.5 as it was determined from both stretching mode absorption at $k \approx 1870 \text{ cm}^{-1}$ and SIMS data. Absorption at $k \approx 560 \text{ cm}^{-1}$ demonstrated similar trend with the only exception at very low boron concentration $[B]_{\text{sol}} = 0.004\%$, where the hydrogen concentration showed a value 3 times larger than the other values.

From measurements of temperature dependence of conductivity $\sigma(T)$ for the different B concentrations in solid phase, have shown changes on electrical parameters such as, room temperature conductivity σ_{RT} , activation and Fermi energies E_a , $E_F(\text{RT})$ respectively, as shown in Figure 4. σ_{RT} reduces with $[B]_{\text{sol}}$ in the range of $[B]_{\text{sol}}$ from 0 to 0.03% and in a linear plot it practically remains constant. On the other hand, E_a increases from 0.25 eV at $[B]_{\text{sol}}=0$ to a maximum value of $E_a = 0.45 \text{ eV}$ for $[B]_{\text{sol}}=0.06\%$, then it reduces to minimum of 0.27 eV for $[B]_{\text{sol}}=0.12\%$, followed by a slight increase at $[B]_{\text{sol}}=0.13\%$. The behavior of $E_F(\text{RT}) = f([B]_{\text{sol}})$ is similar to that of $E_a([B]_{\text{sol}})$. The remarkable difference of E_a and $E_F(\text{RT})$ observed at $[B]_{\text{sol}} = 0.12\%$ suggests that these films have a less rigid lattice in comparison the rest of the deposited films.

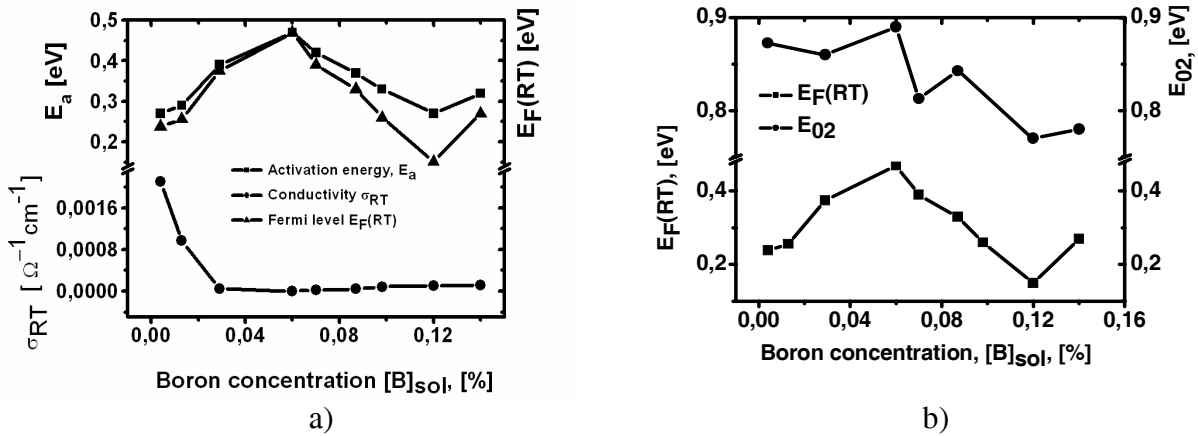


Figure 4. Room temperature conductivity, activation energy and RT Fermi level a) and energy E_{02} corresponding photon energy with observed absorption $\alpha = 10^2 \text{ cm}^{-1}$ b) versus boron concentration in the films.

The increase of E_a with $[B]_{\text{sol}}$ at low boron concentration is thought to be due to compensation of electronic conductivity with respect to the un-doped reference sample. In fact at $[B]_{\text{sol}} = 0.06\%$ we have compensated material with a Fermi energy near the center of the mobility gap. Further increase of boron concentration results in p-type material with further reduction on the activation energy. In Figure 4 b) the position of the Fermi level referred to the conductivity band edge is shown in comparison with energy E_{02} , this energy corresponds to the photon energy observed for the absorption value $\alpha = 10^2 \text{ cm}^{-1}$. The energy E_{02} practically does not change for $[B]_{\text{sol}}$ in the range of $[B]_{\text{sol}}$ from 0 to 0.05% and then decreases with further boron incorporation. This behavior in general agrees with the behavior of the Urbach energy and deep states versus boron content as is shown in Figure 5 b).

The Figure 5 a) shows the spectral dependence of the optical absorption $\alpha(h\nu)$ for the samples with different boron concentrations. It can be seen that the boron incorporation changes both the absorption related to band tail states and that related to deep defect states. The tail state absorption is characterized by the Urbach energy E_U . For a quantitative characterization of the

deep states, we have employed the absorption coefficient α_D measured at the photon energy $h\nu = 0.85$ eV. Both E_U and α_D are shown in Figure 5 b) as a function of the boron concentration in the films. It is interesting to note that the incorporation of a very small boron quantity reduced both tail and deep states (both E_U and α_D have minimum values at $[B]_{sol} = 0.004\%$).

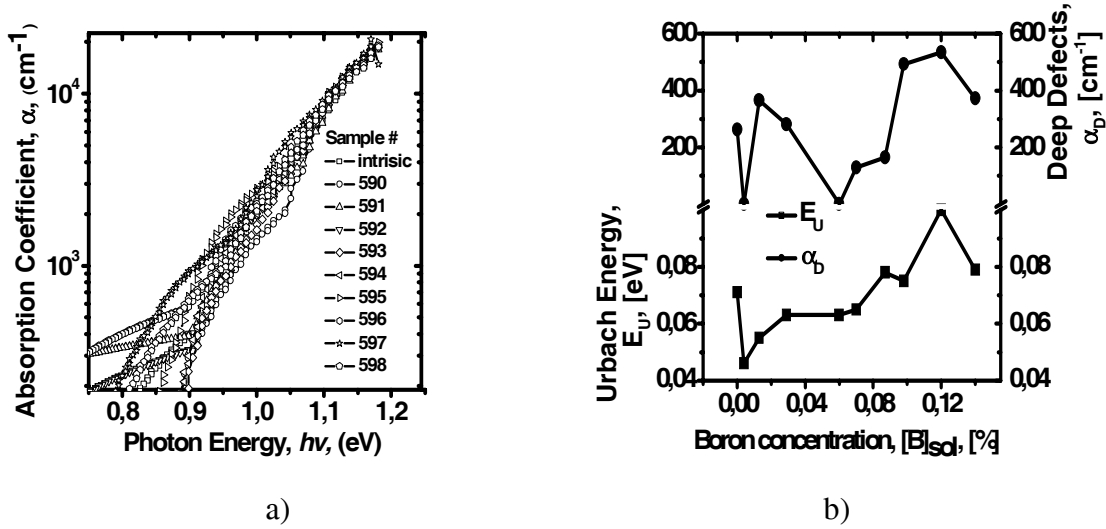


Figure 5. Spectral dependence of absorption coefficient $\alpha(h\nu)$ a), and Urbach energy E_U and deep defect absorption α_D b) in the films with different boron concentration.

Table I. Optical characteristics and electrical properties of the films with different boron concentration.

$[B/Ge]_{sol}$ %	σ_0 [Ω^{-1} cm^{-1}]	E_a [eV]	σ_{RT} , [Ω^{-1} cm^{-1}]	$\gamma \times 10^{-4}$ [eV/k]	E_F (RT) [eV]	E_{03} [eV]	E_{04} [eV]	ΔE [eV]	$n_{(\infty)}$	E_U [meV]	Defect absorption at $h\nu=0.85$ eV, [cm^{-1}]
0.0	17.6	.22	3.5E-3	-2.14	0.20	0.96	1.12	0.16	4.21	71	260
0.004	59.7	0.27	2.1E-3	-1.06	0.24	0.96	1.12	0.15	4.28	46	0
0.013	56.8	0.29	9.7E-4	-1.11	0.26	0.95	1.12	0.16	4.29	55	370
0.029	114.4	0.39	4.9E-5	-0.49	0.38	0.94	1.11	0.17	4.27	63	280
0.060	200.3	0.47	3.5E-6	-0.015	0.47	0.96	1.10	0.14	4.21	63	0
0.070	86.5	0.42	1.9E-5	-0.74	0.39	0.94	1.10	0.16	4.21	65	130
0.087	44.7	0.37	4.5E-5	-1.32	0.33	0.91	1.11	0.19	4.21	78	170
0.098	20.0	0.33	8.7E-5	-2.04	0.26	0.93	1.10	0.17	4.25	75	490
0.12	2.69	0.27	1.0E-4	-3.8	0.15	0.91	1.10	0.19	4.22	100	540
0.14	21.1	0.32	1.2E-4	-1.98	0.27	0.95	1.11	0.16	4.25	79	370

It is worth to note that a small amount of boron incorporation $[B]_{sol} = 0.004$ to 0.013% resulted in practically no change on the conductivity of the films, but it is evident that changes have occurred in the film structure i.e. a reduction in the Urbach energy E_U and an increase in the refraction index n_{∞} as is shown in Table I.

CONCLUSIONS

The LF PE CVD a-Ge:H(B) films doped with boron in the range of $[B]_{\text{sol}} = 0$ to 0.14% using the deposition conditions corresponding to the reference intrinsic film with the lowest density of localized states have been fabricated and studied. It was observed the following: a linear incorporation of boron from gas source into the solid phase; no significant effect of boron incorporation on the hydrogen concentration; a small boron amount in the film, significantly reduced the density of both band tail and deep localized states; the boron incorporation in the range of $[B]_{\text{sol}} = 0.004\%$ to 0.06% resulted in compensation of the electron conductivity in the intrinsic material; further boron incorporation increased the conductivity to $\sigma_{\text{RT}} = 10^{-4} \text{ Ohm}^{-1} \text{ cm}^{-1}$ and reduced the Fermi level to a minimum $E_{\text{F}}(\text{RT}) = 0.15 \text{ eV}$ at $[B]_{\text{sol}} = 0.12\%$; these films were deposited at deposition rate $V_{\text{d}} = 3.3 \text{ \AA/s}$ which is higher than that in a standard RF discharge.

ACKNOWLEDGMENTS

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