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Indium and gallium p-type doping of hydrogenated amorphous germanium thin films

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Hydrogenated amorphous germanium films have been p-type doped with indium and gallium. The room-temperature dark dc conductivity of the films has been found to change by several orders of magnitude within the studied dopant atomic concentration range ($\sim 3 \times 10^{-5}$ to $\sim 1 \times 10^{-2}$). The conductivity change from n to p type for the more heavily doped materials indicates effective p-type doping. The hydrogen content and the optical gap of the doped films, on the other hand, remain essentially unchanged with respect to the undoped material. For the most doped samples, signs of metallic segregation have been detected in the case of gallium doping. Metallic segregation is not apparent for indium-doped samples.

Hydrogenated amorphous germanium (a-Ge:H) is a natural candidate to be used for the development of tandem solar cells based on hydrogenated amorphous silicon (a-Si:H).[1] However, such device applications rely in part on the ability of controlling the transport properties of the material via electronic doping. Most of the doping studies in a-Ge:H and a-Si:H have traditionally employed phosphorus and arsenic (group V) and boron (group III) as n- and p-type dopants, respectively. The dopant source gases are hydrides of the elements fed into the reaction chamber during the glow discharge or rf-sputtering deposition of the films.[2,3] On the contrary, solid dopant sources have received little attention in the literature. Our research group reported recently the doping effects of Al in a-Ge:H.[4] Today, it is amply recognized[1] that, in order to gain a deeper understanding of the doping mechanism in both a-Si:H and a-Ge:H, and to improve device performance, it is of importance to explore other potential p- and n-type dopants of tetrahedrally coordinated amorphous semiconductors.

An alternative doping method involves the use of solid sources in a rf-sputtering deposition chamber, in which both host and dopant elements are plasma cosputtered from solid targets and deposited onto the substrate. This method avoids the use of toxic gases and opens the possibility of studying a broad range of dopant elements which are not readily available from gas sources. In this letter we use the cosputtering technique to study the effects of In and Ga doping on the optoelectronic properties of rf-sputtered a-Ge:H films. The In and Ga atomic contents in the a-Ge:H films are true doping concentrations, ranging from $\sim 3 \times 10^{-5}$ to a maximum of $\sim 1 \times 10^{-2}$. It has been found that the room-temperature conductivity of the doped samples changes by three–four orders of magnitude in the studied concentration range, the conduction changing from n type (the undoped and lightly doped a-Ge:H) to p type as the dopant concentration increases. These results are a clear indication that effective p-type doping of rf-sputtered a-Ge:H can be achieved with the use of In or Ga solid sources.

The a-Ge:H films were prepared in a conventional rf sputtering system in an Ar (99.997%) plus H_2 (99.9995%) atmosphere. A 3-in.-diam c-Ge (99.9995%) target was used.

The residual pressure of the chamber was 1×10^{-6} mbar and the substrates were held at 220 °C during deposition. Hydrogen and argon partial pressures of 1.5 and 14.7×10^{-3} mbar, respectively, were used in all deposition runs. The above deposition conditions produce intrinsic a-Ge:H films having a total density of states (DOS) of $\sim 3 \times 10^{17}$ cm^{-3}, higher than the value found in state of the art high quality a-Ge:H.[5] For the deposition of doped samples, the Ge target was partially covered with small pieces of solid In or Ga of varied sizes. The Ga and In pieces exhibited a spherical shape after the deposition run, indicating that melting of the pieces had occurred. The In content in the doped films was measured, in samples having In concentrations higher than 7×10^{-4}, by Rutherford backscattering (RBS). The measured In concentration was found to linearly scale with the area of the sputtered In piece measured after each deposition. Since it is known that partial crystallization of amorphous germanium can be induced by heavy In or Ga incorporation,[6] Raman spectra of the a-Ge:H samples having the highest In and Ga concentrations were taken. No evidence for microcrystallization was found in any sample. Dark dc conductivity measurements were performed on samples deposited on Corning 7059 glass substrates, using two coplanar rf-sputtered ohmic Cr contacts 1 mm apart. The temperature dependence of the conductivity was measured in an evacuated chamber. A controlled rate of 3 K/min was used during the cooling and heating of the samples. No differences were observed between conductivity data obtained during the cooling and heating processes. The content of bonded hydrogen was estimated from the integrated absorption of the Ge-H wagging vibration mode[7] at 565 cm^{-1}.

Figures 1(a) and 1(b) show the dark conductivity (σ) as a function of the reciprocal temperature ($1/T$) of an undoped a-Ge:H film and of some selected In- and Ga-doped a-Ge:H samples. It can be seen from Fig. 1 that, for low In or Ga content, the dark conductivity decreases considerably relative to that of the undoped sample. A concomitant increase of the log σ vs $1/T$ slope is also observed. An increasing In or Ga content produces the opposite effect, i.e., the conductivity of the samples increases and, eventually, becomes larger than that of the undoped a-Ge:H sample. This behavior is indica-
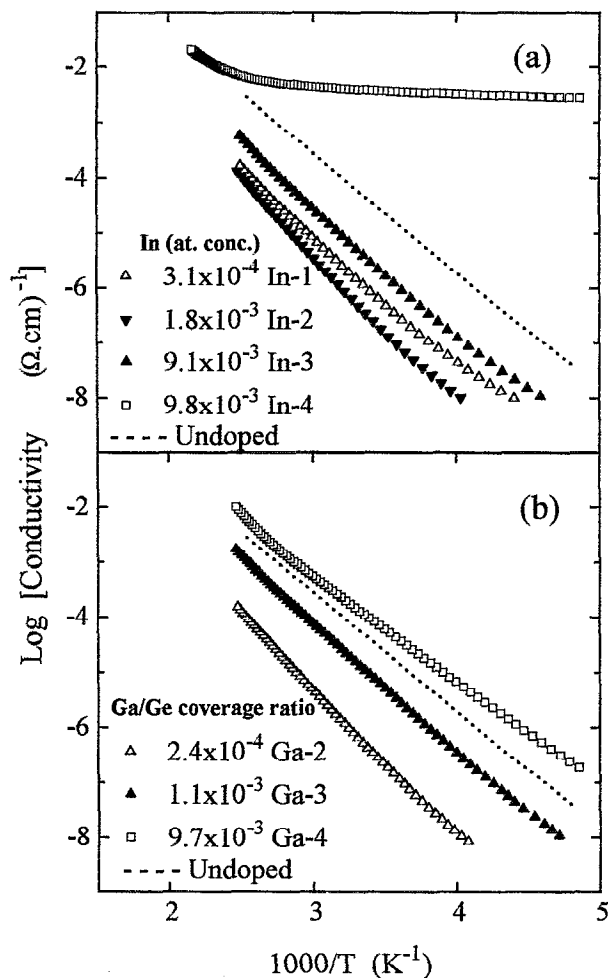
FIG. 1. Temperature dependence of the dc conductivity vs inverse temperature of some selected p-type doped a-Ge:H samples (a) In-doped, and (b) Ga-doped films. In atomic concentrations smaller than 7×10^{-4} were estimated from the In sputtered areas and from RBS measurements. For the case of Ga doping, the values shown in the legend correspond to Ga-to-Ge sputtered areas.

FIG. 2. Room-temperature conductivity (σ_{RT}) and activation energy (E_a) as a function of the In atomic concentration in a-Ge:H films. The change of conduction from n to p type corresponds to the change of the thermoelectric power sign (S).

tive of an effective p-type doping of the a-Ge:H films, and is corroborated by thermopower measurements. Note that all samples in Figs. 1(a) and 1(b) [except sample In-4 in Fig. 1(a)] exhibit a thermally activated behavior for at least four orders of magnitude conductivity change.

Figure 2 shows the room-temperature conductivity (σ_{RT}) and the corresponding activation energy of the dark conductivity (E_a), for In-doped a-Ge:H films. It can be seen in Fig. 2 that σ_{RT} decreases by about two orders of magnitude with increasing In concentration accompanied by a concomitant increase of E_a. This behavior indicates that compensation of the intrinsic n-type material is occurring, producing a minimum in σ_{RT} of nearly 3×10^{-7} (Ω cm).$^{-1}$ For In concentrations higher than 2×10^{-3} σ_{RT} increases and E_a decreases. For In concentrations approaching 1×10^{-2} an abrupt change in both σ_{RT} and E_a is measured. Please note that for these heavy doped samples [see sample In-4 in Fig. 1(a)] the conductivity measurements were performed up to a temperature of 465 K, for which E_a was estimated from the data in the
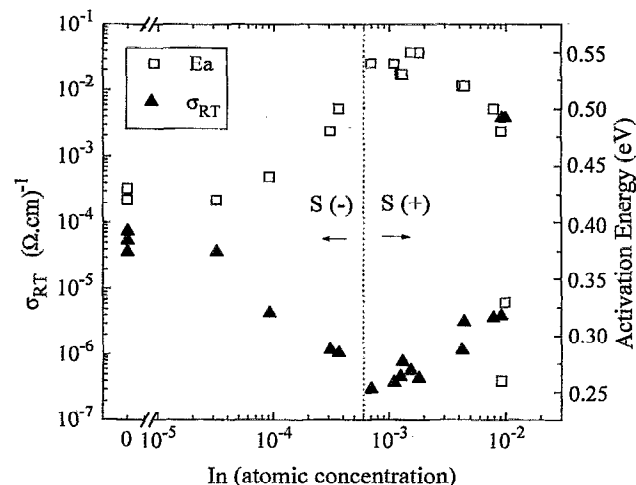
high temperature range. For temperatures lower than 380 K the activation energy of the conductivity for these samples is very small (12 meV), an indication of a near-neighbor hoppinglike conduction mechanism. The results depicted in Fig. 2 clearly indicate that the addition of In to a-Ge:H produces acceptorlike levels inducing a shift of the Fermi energy towards the valence band tail. Further evidence for the above is given by the sign of the thermoelectric power S. As shown in Fig. 2, S is found to change sign for samples having In concentrations close to that corresponding to the minimum conductivity. At this In concentration (approximately 6×10^{-4}) the conductivity of doped films changes from n to p type. Similar results to those shown in Fig. 2 for In-doped a-Ge:H samples were obtained for Ga-doped films, except for the highest dopant concentrations (see below).

Table I shows the hydrogen content C_H, the optical gap E_{04} (defined as the energy at which the optical absorption equals 10^4 cm^{-1}), the characteristic energy of the exponential absorption edge (Urbach energy, E_0 measured by photothermal deflection spectroscopy), and conductivity data for some selected In- and Ga-doped a-Ge:H samples. It can be seen from Table I that E_{04} remains essentially unchanged for low dopant concentrations whereas the transport properties are very much affected within this doping range. For higher dopant concentrations (i.e., higher than 2×10^{-3} in the case of In doping), a slight reduction of E_{04} is measured. The hydrogen content, on the other hand, does not change significantly with the inclusion of the dopants, even for the highest dopant concentrations. Hence, it can be concluded that the changes in the dark conductivity observed in Figs. 1 and 2 are due to substitutional doping effects and not to structural changes induced by modifications in the hydrogen content. In addition, it should be noted in Table I that, as expected, the Urbach energy increases with increasing In content, reflecting an increased doping-induced disorder. This is consistent with previous observations in doped a-Ge:H and a-Si:H films.[3–5]

                                                      Fajardo, Comedi, and Chambouleyron

TABLE I. Composition and optoelectronic properties of indium- and gallium-doped a-Ge:H films.

Sample	C_{dopant} (at. conc.) RBS	Hydrogen C_H (IR) (%)	E_{04} (eV)	σ_{RT} $(\Omega\,cm)^{-1}$	E_a (σ) (eV)	E_0 (Urbach) (meV)
Undoped	$\cdots$	5.8	1.20	5.3×10^{-5}	0.43	65
In-1	3.1×10^{-4a}	5.4	1.20	1.2×10^{-6}	0.48	73
In-2	1.8×10^{-3}	5.8	1.19	4.3×10^{-7}	0.55	92
In-3	9.1×10^{-3}	5.3	1.14	3.9×10^{-6}	0.48	145
In-4	9.8×10^{-3}	5.5	1.12	3.7×10^{-3}	0.33	155
Ga-1	2.4×10^{-5b}	5.6	1.20	6.0×10^{-6}	0.48	$\cdots$
Ga-2	2.4×10^{-4b}	5.8	1.20	4.9×10^{-7}	0.57	$\cdots$
Ga-3	1.1×10^{-3b}	6.0	1.19	1.3×10^{-5}	0.50	$\cdots$
Ga-4	9.7×10^{-3b}	5.7	1.12	1.2×10^{-4}	0.38	$\cdots$

[a]Extrapolated from the RBS data at higher concentrations.
[b]Ga/Ge target area ratio.

It is worth noting that, in the case of In-doped a-Ge:H films, an abrupt change in the magnitude of the conductivity, as well as in its dependence on temperature occurs when the In concentration varies from 9.1 to 9.8×10^{-3} [see samples In-3 and In-4 in Figs. 1(a) and Table I, and also Fig. 2]. This abrupt change is reproducible for samples made in different runs and not a measurement artifact. It may be related to an important shift of the Fermi energy trough an energy region of low DOS and a subsequent conduction through localized states (near neighbor hopping) in the valence band tail states.[8] Indeed, such a minimum in the DOS has been deduced from electron spin resonance experiments in p-type (B-doped) a-Ge:H.[9] It occurs in the energy region between the singly occupied dangling bond band and the valence band tail. Please, note that such behavior was not observed for the Ga-doped samples within the studied concentration range. For the case of the a-Ge:H having the highest Ga concentration, dots of metallic Ga were clearly seen on the surface of the films, indicating a tendency for Ga segregation. On the contrary, no signs of In segregation in the In-doped a-Ge:H films were detected. The reasons for the different behavior of indium and gallium as dopant elements in a-Ge:H are not yet completely understood. More work is under way to clarify the point.

In summary, rf-sputtered a-Ge:H films have been p-type doped using In and Ga solid sources. The conductivity at room temperature of both Ga- and In-doped materials is found to change by three–four orders of magnitude with doping. The conduction changes from n type (the undoped and lightly doped a-Ge:H) to p type in the more heavily doped films. For In dopant concentrations approaching 10^{-2}, an abrupt transition of the conductivity from a thermally activated behavior to a weakly activated hopping mechanism at temperatures below 380 K is observed. For the Ga doped samples such a behavior has not been observed. Metallic segregation is apparent on a-Ge:H films having the highest Ga content.

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