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Ammonia as an active doping source gas of hydrogenated amorphous germanium films

I. Chambouleyron and R. Campomanes
Instituto de Fisica "Gleb Wataghin," Universidade Estadual de Campinas–UNICAMP, 13083-970 Campinas, São Paulo, Brazil

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In this work the electrical properties of nitrogen-doped hydrogenated amorphous germanium films (*a*-Ge:H) using ammonia (NH_3) as a gaseous doping source are reported. The results are compared with those of N-doped *a*-Ge:H films using N_2 as a source gas. The doping mechanisms appear to be similar in both cases. However, the doping efficiency of NH_3 is smaller than that of N_2. The use of NH_3 also induces a very large topological disorder. The present results give support to the view that active N doping in *a*-Ge:H originates from overcoordinated nitrogen atoms (N_4^+) without the need of one or more hydrogen neighbors. [S0163-1829(96)05020-5]

I. INTRODUCTION

Nitrogen as an impurity in column-IV elemental semiconductors takes a peculiar place because it introduces deep states in the crystalline Si lattice,[1] the situation regarding N in *c*-Ge still being a matter of debate.[2] The problems associated with the inclusion of N in tetrahedrally coordinated semiconductors are partially overcome in amorphous networks. Hydrogenated amorphous silicon (*a*-Si:H) or germanium (*a*-Ge:H) films are obtained from the fast condensation of the vapor phase, which allows the incorporation of atomic species or molecular fragments dissociated by a plasma.[3] Moreover, Spear and LeComber established that the doping properties of elements of columns III and V are similar in crystalline and amorphous group-IV semiconductors.[4] The doping mechanisms, however, are different in an amorphous semiconductor compared with a crystal.[5]

It has been argued theoretically that overcoordination of N is impeded in the *a*-Si network by its small size, and is probably only possible if one or more of its neighbors is hydrogen.[6] Indeed, nitrogen is a poor dopant in *a*-Si:H.[7,8] On the contrary, nitrogen appears to be a very efficient dopant in *a*-Ge:H.[9] The reasons for a different activity of N in *a*-Ge:H as compared to *a*-Si:H are not yet clear, given the similar valence structure and atomic size of both elemental semiconductors.

The active doping properties of nitrogen in rf-sputtered *a*-Ge:H films using N_2 as a doping source were independently established at Campinas[10,11] and Kaiserslautern.[12] The present paper deals with the transport properties of rf-sputtered N-doped *a*-Ge:H films using NH_3 as a doping source. These are compared with N-doped *a*-Ge:H films using N_2 as a doping source.[11] The study aims at the understanding of the likely role of hydrogen in the doping process by comparing precursor N-dopant species with and without bonded hydrogen. The comparison adds relevant information to the debate concerning the origin of the active N-donor site in *a*-Ge:H, i.e., overcoordinated nitrogen[11] or N-H complexes.[12]

The present data show that the doping efficiency of NH_3 is smaller than that of N_2 and that the use of NH_3 induces a very large topological disorder, which in turn affects the transport properties of *a*-Ge:H at moderate and high doping levels. These experimental findings give support to the view that the active doping configuration is overcoordinated N_4^+.[11] We suggest that the increased topological disorder found with the use of NH_3 is due to the incorporation of NH and NH_2 fragments into the network. These fragments, in which nitrogen retains its trigonal coordination, passivate Ge dangling bonds.

II. EXPERIMENT AND RESULTS

Nonintentionally doped and N-doped *a*-Ge:H films were prepared by rf sputtering a crystalline Ge target (99.9995 at. %) in a gas mixture of Ar (99.997 at. %)+H_2 (99.999 at. %) and of H_2+Ar+NH_3 (99.999 at. %), respectively. Details on optoelectronic characterization and deposition conditions can be found in Ref. 11. The total nitrogen concentration in the solid phase was determined with the $^{14}N(d,p)^{15}N$ deuteron-induced nuclear reaction.[13]

Figure 1 shows the dark conductivity $\sigma(T)$ as a function of inverse temperature for some selected samples of the series. Sample 1 is a nonintentionally doped *a*-Ge:H sample. At and above room temperature (RT) the dark conductivity of all samples is thermally activated, i.e.,

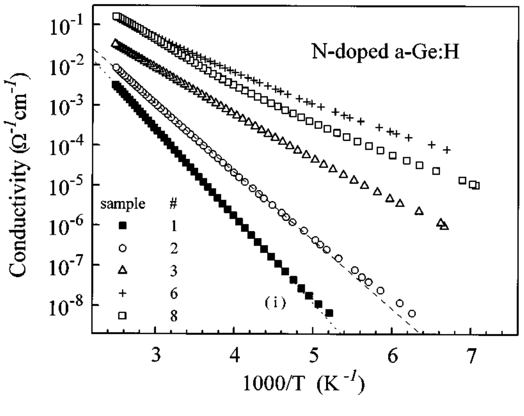

FIG. 1. Dark conductivity vs inverse temperature for N-doped *a*-Ge:H films deposited under different NH_3 partial pressures. The nonintentionally doped sample displays a thermally activated conduction down to low temperatures. Note the conductivity changes induced by increasing NH_3 pressures.

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TABLE I. Deposition conditions, composition, and optoelectronic properties of the present samples. P_{NH_3} is the NH_3 partial pressure during deposition; C_N and C_H are nitrogen and hydrogen content, respectively; σ_{RT} and E_a are room-temperature conductivity and activation energy, respectively; E_{04} is photon energy corresponding to an absorption coefficient of 10^4 cm^{-1}; E_0 is Urbach's edge energy.

Sample	P_{NH_3} (mbar)	$C_N(\pm 10^{19})$ (cm^{-3})	C_H ($\pm$0.5%)	σ_{RT} $(\Omega\ cm)^{-1}$	E_a (eV)	E_{04} (eV)	E_0 (meV)
1			5.8	5.3×10^{-5}	0.43	1.21	60
2	$<10^{-6}$	NA	5.3	2.6×10^{-4}	0.34	1.22	80
3	1.6×10^{-6}	$1.4\times 10^{19(a)}$	5.3	3.4×10^{-3}	0.23	1.23	90
4	3.7×10^{-6}	$2.8\times 10^{19(a)}$	5.7	1.1×10^{-2}	0.18	1.21	113
5	8.1×10^{-6}	$5.5\times 10^{19\ a}$	6.0	2.4×10^{-2}	0.15	1.22	117
6	2.1×10^{-5}	1.4×10^{20}	6.2	2.4×10^{-2}	0.18	1.21	126
7	4.0×10^{-5}	2.7×10^{20}	6.0	2.6×10^{-2}	0.19	1.21	137
8	5.8×10^{-5}	3.7×10^{20}	6.5	2.8×10^{-2}	0.19	1.20	155

[a] Extrapolated from higher nitrogen concentrations.

$$\sigma(T)=\sigma_0 \exp[-E_a/k_B T]. \tag{1}$$

Figure 1 indicates that an increasing P_{NH_3} in the reaction chamber during growth produces large changes in both the room-temperature conductivity σ_{RT} and the activation energy E_a. The hydrogen (C_H) and nitrogen (C_N) concentration of the samples, as well as some relevant properties, are shown in Table I. Note that: (i) C_H stays approximately constant in all samples (5.5–6 at. %), an indication that conductivity changes do not originate from a different hydrogenation but from impurity activity (in fact a slight increase of C_H is measured as P_{NH_3} is increased); (ii) the optical gap E_{04} does not change in the series (see Table I), as expected in samples in which the nitrogen concentration stays within doping levels, i.e., $C_N \leqslant 1\%$ (no detectable Ge-N alloying effects); (iii) the characteristic energy of the Urbach tail (E_0) increases noticeably with nitrogen incorporation. This behavior is different from that of N-doped a-Ge:H sample series using N_2 as a source gas.[11]

The present N-doped a-Ge:H samples may be meaningfully compared with those of Ref. 11 because they have been deposited in the *same* rf sputtering system under *similar* deposition conditions, the only difference between the two series being the use of a different dopant gas source. N_2 and NH_3 have different dissociation energies. The active species in the plasma and their chemical interaction with the growing film are also different. As a result a factor 2 larger incorporation of nitrogen in the a-Ge:H network when NH_3 is used has been measured. For similar nitrogen concentrations, however, the Urbach energy (indicative of topological disorder) is much larger in the case of NH_3.

Figure 2 compares the activation energy E_a of N-doped a-Ge:H as a function of total nitrogen content for both series of samples. It is clear from Fig. 2 that, although the doping effects look very similar with the use of the two gases, equal amounts of nitrogen in the network do not induce equal activation energies and conductivity changes. When NH_3 is used the whole E_a versus C_N curve flattens and shifts toward larger N concentrations. This is an indication that the N-active doping efficiency is smaller for NH_3 than for N_2.

III. DISCUSSION

Let us summarize the electronic transport of N-doped a-Ge:H films using N_2 as a doping source.[11] *Intrinsic and lightly N-doped samples* ($C_N \leqslant 10^{19}$ cm^{-3}) possess a thermally activated conductivity in the 170–400-K range. The dark conductivity of the *most conductive N-doped sample* ($C_N \approx 5\times 10^{19}$ cm^{-3}) possesses a high-temperature activation energy of $E_{a(HT)}=0.12$ eV and a low-temperature activated behavior $E_{a(LT)}=10$ meV. The $E_{a(LT)}$ value is consistent with a thermally activated nearest-neighbor hopping at the Fermi energy E_F. *Heavily N-doped a-Ge:H samples* ($C_N \geqslant 10^{20}$ cm^{-3}) display two activation energies. $E_{a(HT)}$ corresponds to the promotion of carriers to extended states near the conduction-band mobility edge. $E_{a(LT)}$ corresponds to the excitation of electrons to a shallow impurity band, located at around 50–60 meV below the mobility edge. Note that the N-doped (from N_2) a-Ge:H samples always possess a low defect density ($N_{DOS}<10^{18}$ cm^{-3}). For similar nitrogen concentrations the present samples possess, on the contrary, a one order of magnitude larger N_{DOS} where DOS denotes the density of states.

Tsu, Lucovsky, and Mantini[14] studied the structure of glow discharge silicon nitride films prepared from SiH_4+N_2

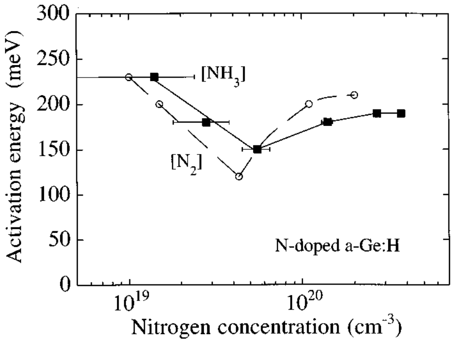

FIG. 2. High-temperature ($T>300$ K) activation energy of the conductivity vs nitrogen concentration in N-doped a-Ge:H films using N_2 (circles) and NH_3 (squares) as a doping source. Both doping sources induce similar changes of the activation energy. Note, however, the flattening of the curve and its shift to larger N concentrations for samples doped from NH_3.

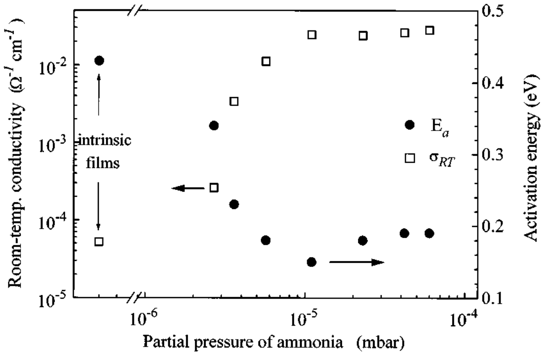

FIG. 3. Room-temperature conductivity and activation energy of N-doped a-Ge:H samples as a function of the partial pressure of NH_3 during deposition. Two different behaviors are apparent for P_{NH_3} lower and higher than 10^{-5} mbar, respectively.

or SiH_4+NH_3. In the latter, they found evidence of the incorporation of NH and NH_2 groups into the films. Samples deposited using ND_3 instead of NH_3 indicate that the source of the H in the NH and NH_2 groups is ammonia and not silane. Similar experiments using ND_3 have not been done with Ge but the similar valence structure of Si and Ge and the identical bonding configuration of a-Si_3N_4 and a-Ge_3N_4 lead us to imagine that NH and NH_2 groups are also incorporated in a-Ge:H films. Indeed, a-Ge:N:H alloys deposited under high NH_3 pressures display absorption bands at photon energies corresponding to NH and NH_2 local vibrations.[15] We conclude then that the augmented disorder originates from NH and NH_2 fragments that incorporate as Ge dangling-bond terminators inducing a large strain in the network. Note that here N retains its trigonal coordination and is electrically inactive. The picture is consistent with the data of Fig. 2, which indicate that NH_3 is a less efficient dopant than N_2. As a consequence of the disorder induced by NH and NH_2 fragments it is expected that the N-doping efficiency should not only be smaller with the use of ammonia, but should also decrease faster with increasing N content. The flattening and shifting of the E_a curve in Fig. 2 indicate that this is the case.

Figure 3 shows σ_{RT} and $E_{a(HT)}$ versus the partial pressure of NH_3 during growth. Two distinct regions are apparent in Fig. 3. For $P_{NH_3} \leqslant 10^{-5}$ mbar there is a clear correlation between changes in conductivity and in $E_{a(HT)}$. In this low P_{NH_3} region $\ln[\sigma_{RT}]$ and E_a are specular images of each other. Within the simple model of electronic transport of hydrogenated amorphous semiconductors the conductivity is given by Eq. (1) where σ_0 is referred to as the minimum metallic conductivity: $\sigma_0 = n(E_C)e\mu_0 k_B T$, n being the free carrier density and μ_0 the mobility at E_C. The correlation found for $\ln \sigma_{RT}$ and E_a (Fig. 3) suggests that at low doping levels the changes in conductivity are associated to changes in the density of free carriers $n(E_C)$, μ_0 being essentially constant at the conduction-band edge (extended states in the model). For these moderately N-doped samples a prefactor $\sigma_0 \approx 100$–$300\ \Omega^{-1}\,\mathrm{cm}^{-1}$ is found, consistent with a free carrier mobility of a few $\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ as expected in extended states.[3]

The right-hand side of Fig. 3 corresponds to heavily doped samples. σ_{RT} stays approximately constant despite small but significant variations of the activation energy (see Fig. 2). The RT conductivity of the most N-doped a-Ge:H films (from NH_3) is one order of magnitude larger than in equivalent samples doped from N_2. The larger topological disorder of the former, and the concomitant large DOS, allows electron hopping between localized states at E_F that contribute to conduction. As expected, the low-temperature conductivity of these samples follows a $\sigma(T) \approx \sigma_H \exp[-(T_0/T)^{1/4}]$ law[16] as shown in Fig. 4. Note that this behavior is never found in N-doped a-Ge:H samples using N_2 as a dopant source in which the conductivity remains activated at low temperatures at all doping levels.[11] The picture is consistent with the incorporation of NH and NH_2 groups in which nitrogen retains its trigonal coordination. The presence of hydrogen in the dopant species does not appear to enhance the doping activity of N in the a-Ge:H network.

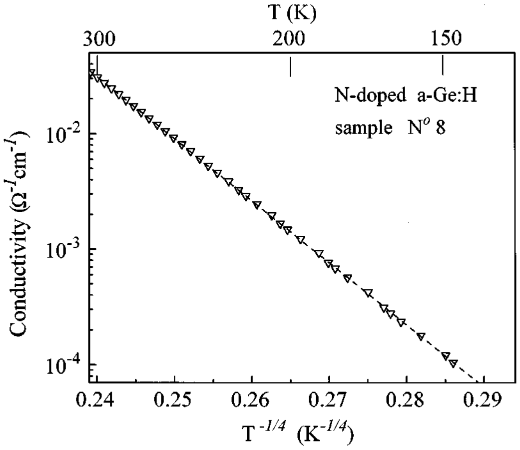

FIG. 4. Dark conductivity of sample 8 as a function $T^{1/4}$. Variable range hopping dominates electron conduction at $T<300$ K.

The question of the different activity of nitrogen in the Si and Ge amorphous networks remains to be answered. The present contribution indicates that NH_3 is, in the a-Ge network, a poorer dopant gas than N_2. This experimental finding, which supports the view that N_4^+ is the active configuration, suggests that atomic relaxation in a-Ge:H allows tetrahedral coordinated nitrogen.

IV. CONCLUSIONS

A factor of 2 larger amount of nitrogen is incorporated in N-doped a-Ge:H films when NH_3 is used as a dopant gas instead of N_2 (films deposited under similar conditions). The N-doping mechanism appears to be similar with both gases; the N-doping efficiency, however, is smaller for NH_3. Moreover, the use of NH_3 induces a large topological disorder in the network. It is suggested that it stems from the incorporation of NH and NH_2 groups as Ge dangling-bond terminators. The present results suggest that active N doping in a-Ge:H originates from overcoordinated nitrogen[11] (N_4^+) and not from nitrogen-hydrogen complexes as, for instance, Ge-NH_2-Ge.[12]

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[1] K. L. Brower, Phys. Rev. Lett. **44**, 1627 (1980); also Phys. Rev. B **26**, 6040 (1982).

[2] A. Campbell, J. B. Mitchell, J. Schewchun, and D. A. Thompson, Can. J. Phys. **53**, 303 (1975).

[3] See, for example, R. A. Street, *Hydrogenated Amorphous Silicon* (Cambridge Univ. Press, Cambridge, 1991).

[4] W. Spear and P. LeComber, Solid State Commun. **17**, 1193 (1975); Philos. Mag. **33**, 935 (1976).

[5] R. A. Street, Phys. Rev. Lett. **49**, 1187 (1982).

[6] J. Robertson, Philos. Mag. B **63**, 47 (1991).

[7] B. Dunnett, D. I. Jones, and A. D. Stewart, Philos. Mag. B **53**, 159 (1986).

[8] A. R. Zanatta and I. Chambouleyron, Braz. J. Phys. **24**, 434 (1994).

[9] I. Chambouleyron and A. R. Zanatta, Appl. Phys. Lett. **62**, 58 (1993).

[10] F. C. Marques and I. Chambouleyron, *Defects in Materials*, edited by P. D. Bristowe, J. E. Epperson, J. E. Griffith, and Z. Lilienthal-Weber, MRS Symposia Proceedings Vol. 209 (Materials Research Society, Pittsburgh, 1991), p. 555.

[11] A. R. Zanatta and I. Chambouleyron, Phys. Rev. B **46**, 2119 (1992).

[12] T. Drusedau, B. Schroeder, and H. Hoechsner, Solid State Commun. **79**, 799 (1991).

[13] The N content of the samples was determined by Professor F. L. Freire at the 4 MeV van der Graaff accelerator, Pontificia Universidade Catolica, Rio de Janeiro, RJ, Brazil.

[14] D. V. Tsu, G. Lucovsky, and M. J. Mantini, Phys. Rev. B **33**, 7069 (1986).

[15] F. C. Marques, I. Chambouleyron, and F. Evangelisti, J. Non-Cryst. Solids **114**, 561 (1989).

[16] See, for example, N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Semiconductors*, 2nd ed. (Clarendon, Oxford, 1979).