

Transport properties of nitrogen-doped hydrogenated amorphous germanium films

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This paper discusses experimental data referring to the electronic properties of N-doped hydrogenated amorphous germanium films (*a*-Ge:H). The *a*-Ge:H films, prepared by rf sputtering, possess a low density of electronic states in the pseudogap (in the low 10^{16} cm⁻³ range) and exhibit a temperature-activated dark conductivity down to below 200 K. It is shown that N atoms incorporated into the *a*-Ge:H films produce large changes of both the room-temperature dark conductivity and the activation energy. The results of the present work are consistent with the overall picture of the active doping mechanism of group-V elements in tetrahedrally coordinated amorphous semiconductors. The donor level introduced by fourfold-coordinated nitrogen in *a*-Ge:H is found to be around 50 meV below the conduction-band edge.

I. INTRODUCTION

Solid-state electronics relies on the possibility of altering the electric properties of intrinsic semiconductors via doping with chemical impurities. As a consequence, the subject has received enormous attention in the past decades, in particular, the study of the electrical activity of the elements of groups III and V of the Periodic Table in the crystalline lattice of semiconductors such as Si and Ge. With the exception of N, these impurities are known to produce shallow levels in the band-gap donor levels for group-V and acceptor levels for group-III elements. The simple model corresponding to these cases assumes that four electrons are needed to fill the bonding orbitals of the tetrahedral neighbors. The extra electron (donor case) is bound to the impurity by a Coulomb-like attractive potential produced by the extra opposite charge of the impurity atom. The attractive force is modified by the dielectric constant of the crystal, the lattice potential being taken into account through the use of an appropriate effective mass.¹ A similar argument may be used to give account of the electronic levels of shallow acceptor states. Nitrogen appears to be distinctly different from the other group-V elements, and its electrical activity in the crystalline lattice of Si and Ge is still a matter of debate.

The existing literature exhibits some degree of uncertainty on the electrical activity of substitutional N in elemental semiconductors. The difficulty partly derives from the rather high dissociation energy of the N₂ molecule (9.8 eV) which prevents the normal mechanisms of atomic diffusion, and to the fact that the N₂ molecule may enter in the tetrahedral interstice of both Si and Ge. Moreover, by cooling melted Si or Ge in the atmosphere of pure N or NH₃ the reaction with the liquid phase forms the corresponding nitride phase (Si₃N₄ or Ge₃N₄), with planar bonded N and tetrahedral bonded Si (Ge). Thus, the manifestation of donor properties of substitutional N in Si and Ge may be determined only if it is introduced in the atomic state at relatively low doses. Ion

implantation has been used for such a purpose.²⁻⁴ Zorin, Pavlov, and Tetel'baum² found a N donor state in *c*-Si at 45 meV below the conduction-band edge, while Brower³ observed a deep level in laser-annealed ion-implanted *c*-Si. Campbell *et al.*⁴ conclude that N atoms do not possess donor properties in Ge. The debate around these experimental findings involves the subtleties of the annealing processes, always necessary to relax the radiation damages produced by the ion bombardment. Electron resonance experiments indicate that substitutional N in Si (as in diamond) presents a (111) axial distortion,³ which is probably due to nitrogen's tendency to form only three bonds and leave two electrons in a lone pair. However, the same authors failed to find a similar deep donor in N-implanted Ge crystals.

The problem of N as a substitutional impurity in elemental semiconductors has also been addressed theoretically.^{5,6} Traditionally, the structure of defects in these materials have been treated from two different points of view: perturbation methods which start with the perfect crystal one-electron wave functions, and cluster methods which stress the local environment of the defect. Atomic relaxations around the defect and electronic correlation are seldom considered. As both can influence the calculated energy levels by a factor as large as the band gap, the present methods are unable to reliably locate the electronic energy with respect to the band edges.

The problems related to the inclusion of substitutional N atoms in the crystalline Si and Ge lattices may be partially overcome in amorphous networks. The deposition conditions (fast condensation from the vapor phase) allow the incorporation of atomic components or radicals of complex molecules dissociated by an rf plasma. Moreover, Spear and LeComber⁷ established that, in tetrahedrally bonded amorphous semiconductors, the doping properties of group-III and -V elements are similar to those found in the crystalline semiconductor parents.

The doping process, however, is different in an amorphous semiconductor compared with a crystal^{8,9} in the

sense that in the crystal constraints of symmetry force an impurity atom of different valence to have the same coordination number as its host in a substitutional covalent site. In amorphous networks the local minimization of free energy may also be attained with the impurity atom having a first coordination number equal to its chemical valence (self-compensated site). In other words, the first coordination number is determined by purely chemical parameters and not by the impurity's environment.¹⁰ Both types of sites coexist in amorphous networks and their relative stability results from the combined short-range chemical contributions and the lattice strain. According to Street⁹ the position of the Fermi energy plays a fundamental role in determining the relative density of each type of site, from which the active doping efficiency is a function of the impurity concentration. The results of the present study confirm such an assumption.

The present work reports on the electrical properties of N-doped *a*-Ge:H samples (N concentration <0.5 at. %). It has been found that the introduction of N atoms in the *a*-Ge:H network produces large changes in the electronic transport of the films. The analysis of the data leads us to conclude that N shallow donorlike states localized near the bottom of the conduction band are responsible for the measured changes.

II. EXPERIMENT AND RESULTS

a-Ge:H and *a*-Ge:H(N) samples were deposited by RF sputtering a pure crystalline Ge target of 99.9995% nominal composition, in an argon (minimum purity: 99.997%) + nitrogen (99.999%) + hydrogen (99.9995%) atmosphere. A Leybold-Heraeus model Z-400 apparatus was used. Before each deposition run, the system was pumped down to a total pressure $P_T < 10^{-6}$ mbar for several hours and the residual gases analyzed with a mass spectrometer Edwards model EQ 80F. The most important residual-gas partial pressure corresponds to argon ($P_{Ar} \cong 5 \times 10^{-7}$ mbar), followed by nitrogen ($P_{N_2} \cong 10^{-7}$ mbar). All other contaminants, up to an atomic mass 80, display partial pressures below 10^{-7} mbar. The growth rate was adjusted before each deposition run and measured again after the end of the process. A growth rate of 1.1 Å/sec was adopted for the whole *a*-Ge:H series. Samples were, typically, 1 μm thick. RF-sputtered

chromium coplanar ohmic contacts were normally used to measure the dc conductivity.

Before each deposition run, the N₂ flow was adjusted to the desired N₂ partial pressure. With the exception of the N₂ partial pressure (P_{N_2}) in the chamber during growth, all other deposition conditions were kept constant in all runs. The nitrogen content of some selected samples was determined by the ¹⁴N(*d,p*)¹⁵N nuclear reaction,¹¹ with an incident deuterium beam of 610 keV. Table I displays the conditions under which all samples of the present work were prepared, as well as the typical partial pressures of residual gases before deposition runs.

The dark conductivity [(120–400)-K range] was measured in an evacuated chamber, using a Keithley model 617 digital electrometer connected to a microcomputer. Besides the acquisition of electric data and the corresponding sample temperature, the computer was used to program and to control the rate of temperature variation of the sample (3 K/min in the present work). Before these measurements, the samples were annealed during 20 min at 400 K. The experimental conductivity data (nearly 500 points/sample) were then computer processed in order to obtain the best fit to theoretical predictions.

Polished intrinsic *c*-Si wafers were used as substrates for IR optical transmission measurements in the (400–4000)-cm⁻¹ wave-number range. These measurements were performed either in dispersive or in interferometric Fourier-transform spectrophotometers. Optical measurements in the nir-vis region of the spectrum were made on films deposited onto Corning 7059 glass substrates. The optical properties of N-doped *a*-Ge:H films will not be discussed here. They are the subject of a coming publication.

The content of hydrogen atoms bonded to Ge was determined from the integrated absorption of the Ge-H wagging vibration mode in the midinfrared region.¹² The values are displayed in Table II. It may be seen that the deposition conditions used for the whole series lead to *a*-Ge:H films of similar composition. Table II shows that both the optical Tauc's gap¹³ and the E_{04} energy (photon energy corresponding to an absorption $\alpha = 10^4$ cm⁻¹) remain essentially constant in all samples. This is a consequence of a similar hydrogenation in all samples.

Another important aspect to be noted is that the total concentration on nitrogen, as determined by a nuclear re-

TABLE I. Deposition conditions for all samples of the present work. SCCM denotes cubic centimeter per minute at STP.

Substrate temperat. (°C)	Total pressure (mbar)	H ₂ partial pressure (mbar)	H ₂ flow (SCCM)	Depos. rate (Å/sec)	Ar flow (SCCM)			
220±5	1.5×10^{-2}	1.3×10^{-3}	14	1.1	220			
Typical values of residual gas pressures before deposition runs								
Molecule	H ₂	He	H ₂ O	N ₂	O ₂	Ar	CO ₂	(N ₂ +CO)
Partial pressure (mbar)	5×10^{-8}	4×10^{-9}	4×10^{-8}	10^{-7}	2×10^{-8}	5×10^{-7}	3×10^{-8}	2×10^{-7}

TABLE II. Nitrogen partial pressures during deposition, hydrogenation, nitrogenation, and optoelectronic characteristics of N-doped *a*-Ge:H samples. NA, not available; BDT, below detectivity threshold. Note: sample thickness $\cong 10^{-4}$ cm. The activation energy E_a is the one corresponding to the high-temperature regime (electronic transport through extended states in the bands). The values given within parentheses correspond to thermally activated hopping through localized states near the band extrema (low-temperature regime). See Eq. (4).

Sample	N ₂ partial pressure (mbar)	Conduct. σ_{RT} ($\Omega \text{ cm}$) ⁻¹	E_a (eV)	Hydrogen C _H (IR) (%)	E_g (Tauc) (± 0.01) (eV)	E_{04}	Nitrogen C _N (nuclear) (cm ⁻³)
1	10 ⁻⁷	4 × 10 ⁻⁵	0.49	5.8	1.10	1.22	BDT
2	4 × 10 ⁻⁶	5.2 × 10 ⁻⁴	0.23	5.6	1.09	1.21	BDT
3	7 × 10 ⁻⁶	10 ⁻³	0.20	5.6	1.08	1.22	1.5 × 10 ¹⁹
4	1.5 × 10 ⁻⁵	3 × 10 ⁻³	0.11 (0.01)	5.6	1.09	1.22	NA
5	3 × 10 ⁻⁵	7 × 10 ⁻⁴	0.20 (0.17)	5.7	1.09	1.22	NA
6	7 × 10 ⁻⁵	1.4 × 10 ⁻³	0.21 (0.17)	5.3	1.09	1.21	2.0 × 10 ²⁰

action method, stays in all samples of the present work within a true doping range, i.e., $C_N < 0.5$ at. % (see Table II). We believe this to be a fundamental point because it is at these low contamination levels only that the active doping efficiency of nitrogen in tetrahedrally coordinated semiconductors can be determined. As a consequence no Ge-N stretching absorption bands are detected in the IR transmission spectra.

Nitrogen partial pressures higher than 10⁻⁴ mbar produce *a*-Ge:H films having a poorer hydrogenation and a smaller optical pseudogap. Absorption bands related to N-H vibration modes begin to appear in the IR transmission spectra. These "non-well-behaved" N-doped samples are not considered in the present work.

Figure 1 displays the logarithm of the dark conductivity of some N-doped *a*-Ge:H samples, as a function of inverse temperature. The behavior of the conductivity with temperature of an undoped *a*-Ge:H film prepared under identical conditions is also shown (sample 1).¹⁴ The

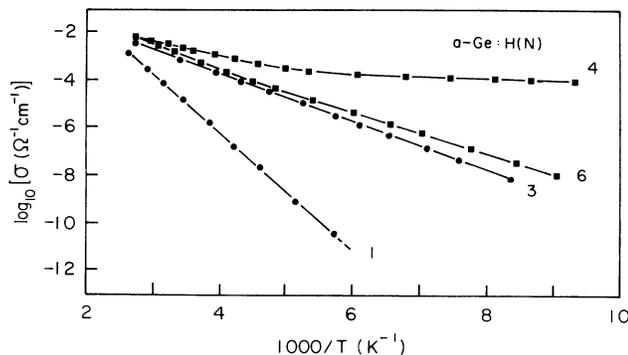


FIG. 1. Logarithm of the dark conductivity of N-doped *a*-Ge:H films as a function of inverse temperature. Intrinsic *a*-Ge:H and lightly N-doped samples possess a single activation regime down to low temperatures (solid circles). In heavier N-doped *a*-Ge:H films, thermally activated hopping through localized states near the conduction-band edge dominates the conductivity at low temperatures (solid squares).

characteristics of the complete *a*-Ge:H(N) sample series are shown in Table II.

The experimental data indicate that the temperature dependence of the dark conductivity of N-doped *a*-Ge:H samples may be well represented, in the considered temperature range, by either one exponential function, or by the sum of two exponential functions; i.e.,

$$\sigma(T) = \sigma_1 + \sigma_2, \quad (1)$$

$$\sigma(T) = \sigma_{01} \exp[-(E_a/k_B T)] + \sigma_{02} \exp[-(E_H/k_B T)], \quad (2)$$

where the following occur.

(i) E_a is an activation energy which dominates the electric transport of undoped and lightly doped *a*-Ge:H at all temperatures [(170–400)-K range] and corresponds, under the assumption of a linear temperature dependence of the pseudogap, to the energy difference at $T=0$ K between the Fermi level and the conduction-band (CB) mobility edge.

(ii) The second exponential appears in samples deposited under nitrogen partial pressures higher than 10⁻⁵ mbar. It dominates the electric transport at low temperatures and corresponds to electronic transport through localized states (hopping). In Table II the low-temperature activation energies E_H are indicated below the corresponding E_a values.

The dark conductivity of samples 1–3 displays an exponential-like dependence on $1/T$ over more than five orders of magnitude. A single activation energy in this temperature range indicates a negligible contribution of localized states to electronic transport in undoped and lightly N-doped *a*-Ge:H films. This experimental behavior is consistent with a low density of states in the pseudogap. Figure 2 shows the subgap absorption coefficient of samples 1, 2, and 3 as determined from photothermal deflection spectroscopy (PDS).¹⁵ Although an increase in the density of states (DOS) is measured as nitrogen enters the amorphous network, as expected, the overall density of states in the pseudogap remains low. A concomitant

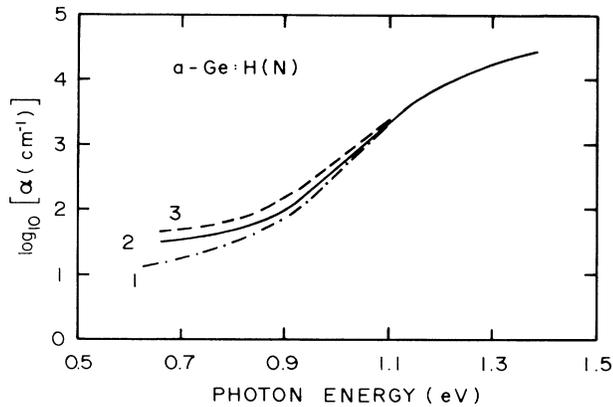


FIG. 2. Absorption coefficient vs photon energy for the undoped and lightly N-doped a -Ge:H samples. The DOS values given below were calculated from the area between the subgap absorption curve and the exponential absorption tail extrapolated to zero absorption, in a way similar to the case of a -Si:H (Ref. 15). The DOS and the characteristic energy of the Urbach tail are, respectively, 1: $5 \times 10^{16} \text{ cm}^{-3}$ and 54 meV; 2: $1.1 \times 10^{17} \text{ cm}^{-3}$ and 62 meV; 3: $1.4 \times 10^{17} \text{ cm}^{-3}$ and 73 meV.

increase of the characteristic energy of the Urbach tail is also measured (see the caption to Fig. 2), consistent with an increased topological disorder produced by foreign atoms of quite different size and valence structure. The large difference in activation energy between the undoped film and sample 2 clearly indicates the active doping role on N atoms which provoke a 0.26-eV shift of the Fermi energy.

Table II shows that the activation energy E_a depends very strongly on the nitrogen partial pressure in the reaction chamber during film deposition. Very small N_2 partial pressures induce large changes in the activation energy and in the conductivity, an indication of a very efficient active doping process. As the Fermi energy approaches the conduction-band edge, however (note $E_a = 0.11 \text{ eV}$ in sample 4, Table II), the active doping process becomes less effective. The incorporation of threefold-coordinated N increases and the material undergoes a phase transition towards the Ge-N alloy phase. As a consequence, the conductivity drops and the activation energy increases again.

The small activation energies measured in sample 4 may lead one to think that an exponential-like dependence on $1/T$ may not be the only possibility for a good fitting of the conductivity data, and that other transport mechanisms, namely variable range hopping, may contribute to the electronic transport. Figure 3 shows the conductivity data of sample 4 in a $\log_{10}\sigma$ versus $T^{-1/4}$ representation. A visual inspection clearly indicates that a straight-line fit is far from possible. A similar picture occurs with samples 5 and 6. We conclude then that the sum of two exponential functions is the best representation of the dark-conductivity behavior of samples 4–6.

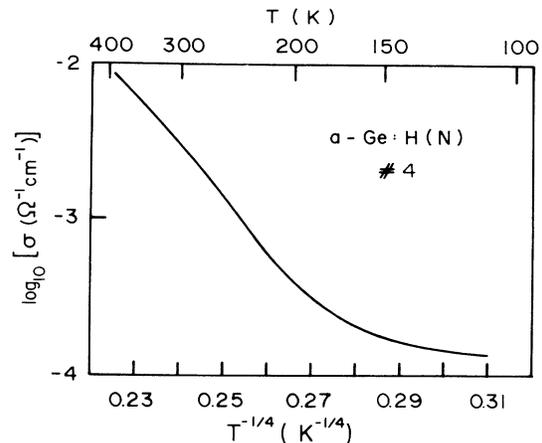


FIG. 3. Logarithm of the dark conductivity of sample 4 vs temperature to the power $-1/4$. Note the curvature at low temperatures, a behavior incompatible with variable range hopping electronic transport.

Before going into a detailed discussion of the electronic properties of the present a -Ge:H samples, it is important to stress that in all cases the concentration of hydrogen bonded to Ge atoms is *almost the same*. Consequently, the differences appearing in the electronic properties of the samples should not be attributed to hydrogenation. Figure 1 shows that the incorporation of N atoms produces large changes in the behavior of the dark conductivity with temperature. The undoped a -Ge:H film (sample 1) exhibits a classical activated conduction regime down to the smallest current measurable under the present experimental conditions which occurs at $T \cong 165 \text{ K}$. Activation energies varying between 0.48 and 0.52 eV are normally found in a -Ge:H films of electronic quality prepared either by the RF sputtering method¹⁴ or by the glow discharge decomposition of GeH_4 .¹⁶ An activated conduction process down to very low temperatures is an indication of a low density of states in the pseudogap (see Fig. 2). This is consistent with the fact that the optoelectronic properties of undoped a -Ge:H samples prepared under the present deposition conditions degrade when exposed to visible light¹⁷ with a light-induced degradation kinetics similar to the one displayed by a -Si:H films of electronic quality.¹⁸ *It is in fact the low density of states in the pseudogap which makes the present a -Ge:H films so sensitive to nitrogen doping.*

III. DISCUSSION

In the study of amorphous binary alloys it is important to refer to similar compounds of known properties. The natural choice for the present study is the a -Si:H:(N) system. The similarity of the electronic valence structure of Si and Ge suggests that the local coordination and chemical ordering of a -Si:N and a -Ge:N alloys should resemble each other.

Photoemission studies show¹⁹ that in a -SiN_x the

valence-band maximum, dominated by Si 3*p* states in *a*-Si, recedes linearly with *x*. For $x \geq 0.85$ the highest occupied states change to trigonally coordinated N 2*p*. In contrast to *a*-SiN_{*x*}, little experimental work has been done on the local order of Ge-N alloys. Boscherini *et al.*²⁰ studied by extended x-ray-absorption fine structure the short-range order in amorphous germanium nitrogen alloys. The study showed that the interatomic Ge-N and Ge-Ge distances are independent of N content, and equal to 1.83 and 2.44 Å, respectively. As in the case of *a*-Si:N alloys,²¹ the incorporation of nitrogen atoms in the Ge-N alloy phase is under trigonal coordination.²⁰

The above studies allow a reasonably clear understanding of the chemical behavior of the amorphous Ge-N phase (large fraction of N atoms in the network). Highly diluted N, however, may behave in a different way in a tetrahedral network. Besides the above-mentioned threefold self-compensated nitrogen, a possibility exists of N atoms going into a substitutional fourfold-coordinated site. As no phase separation occurs, it should be possible to increase the N content from a very high dilution to a point where further incorporation leads to clear structural modification and the material reverts to intrinsic behavior.

Street⁹ explains substitutional doping in an amorphous network applying a modified 8-*N* rule which includes the possibility of incorporating charged atoms at the time of deposition (N₄⁺ in the present case). According to the model, the final equilibrium between threefold- and fourfold-coordinated group-V elements is determined by the position of E_F in the pseudogap. E_F is not allowed to move up to the donor level because occupied donor states (N₄⁰) are in violation of the 8-*N* rule. As E_F approaches the donor level, group-V elements would coordinate according to their own valence structure. The model predicts an equilibrium between threefold- and fourfold-coordinated group-V impurities with the donors being compensated by an equal number of dangling bonds. These assumptions lead to an active doping efficiency law $\eta \cong \text{const}/N_0^{1/2}$, where N_0 is the total impurity density. This square-root dependence has been experimentally found in P-doped *a*-Si:H, as well as in B- and P-doped *a*-GeH.²²⁻²⁴

The conductivity variations found in the N-doped *a*-Ge:H films being reported here indicate that N is an active dopant in the network. The presence of small quantities of nitrogen in the reaction chamber induces room-temperature conductivity variations of more than 2 orders of magnitude in *a*-Ge:H and the Fermi level experiences an upward shift up to 0.1 eV from the CB mobility edge, scanning an energy range of almost 0.4 eV (see Table II). Similar effects have been measured in N-doped *a*-Si:H films.²⁵⁻²⁷ Baixeras, Mencaraglia, and Andro²⁵ found that N doping induces a Fermi-level shift up to within 0.1 eV of the conduction-band edge of *a*-Si:H, an indication that N is also an effective dopant in the *a*-Si network. The experimental data show that the donor level introduced by fourfold-coordinated N in *a*-Si is rather shallow, of the order of a few tens of meV below the CB mobility edge, a value similar to the level given by other charged group-V impurities, such as P₄⁺ (Ref. 7) or

As₄⁺.²⁸ These data appear at odds with some results concerning N-related defects in *c*-Si,³ where a deep defect has been found. They are also in contradiction with some theoretical predictions of a very unfavorable tetravalent nitrogen site in *a*-Si and *a*-Ge networks and a consequently very low active doping efficiency.²⁹ The energy difference may be accounted for, in the first case, considering the large influence that the atomic relaxation associated with bond-length and bond-angle variations play in the position of defect levels.⁶ Regarding the considerations leading to a very low N-doping efficiency,²⁹ it may be argued that they strictly apply to the alloy Si-N or Ge-N phase where, as the present results indicate, the incorporation of tetravalent nitrogen in the network is a highly inefficient process.

Table II shows that a P_{N_2} as low as 4.0×10^{-6} mbar (sample 2) produces an upward shift of the Fermi level of 260 meV. A single-exponential curve fits the $\log_{10}\sigma$ versus $1000/T$ behavior of samples prepared under P_{N_2} up to 10^{-5} mbar. In other words, conduction paths other than through extended states in the band are not important within the measured temperature range (120–400 K). This is an indication of the following in undoped and very lightly doped samples.

(i) The density of states at the Fermi level is sufficiently low to prevent any hoppinglike current contribution.

(ii) The density of localized states at the donor level (CB tail) is not yet sufficient to provide an alternative current path. Under these conditions the conductivity is given by

$$\sigma_d(T) = \sigma_{01} \exp[-(E_a/k_B T)], \quad (3)$$

where $E_a = (E_c - E_F)_0$ roughly represents the energy difference between the CB mobility edge and the Fermi level.

Increasing the nitrogen partial pressure above 10^{-5} mbar during film growth induces, at low temperatures, the appearance of a second activated mechanism for electronic conduction. The dark conductivity for these more doped samples is given by

$$\sigma_d(T) = \sigma_{01} \exp[-(E_a/k_B T)] + \sigma_{02} \exp[-(E_H/k_B T)], \quad (4)$$

where the second exponential is associated to electronic transport involving tail states, in which the wave functions are localized and conduction can only occur by phonon-assisted hopping; i.e., $E_H = [(E_D - E_F)_0 + W]$ where W is a hopping energy (of the order of $k_B T$) and E_D is the energy corresponding to the centroid of the donor level distribution.³⁰

Note that in the most conductive sample the low-temperature activation energy is only $W = 10$ meV. This value is consistent with a thermally activated nearest-neighbor³¹ or "Miller-Abrahams" hopping at the Fermi level:

$$\sigma_4(T_{\text{low}}) = \left(\frac{1}{6}\right) e^2 R^2 \nu_{\text{ph}} N(E_F) \times \exp[-2\alpha R] \exp[-W/k_B T], \quad (5)$$

where R is the nearest-neighbor jumping distance, α

represents the rate of falloff of the localized wave function, ν_{ph} is an attempt frequency (in the 10^{13}-s^{-1} range), and $N(E_F)$ is the DOS at E_F . We conclude that the Fermi energy of sample 4 is located in high DOS energy region, most probably the CB tail (note the high-temperature activation energy of only 0.11 eV).

The whole picture is illustrated in Fig. 4, where the DOS of $a\text{-Ge:H(N)}$ has been sketched for two different doping concentrations. The solid line represents the DOS of undoped $a\text{-Ge:H}$. The CB and the valence-band (VB) tails, as well as the dangling-bond levels, are included in the figure. As the nitrogen content increases, the undoped $a\text{-Ge:H}$ DOS (solid line) evolves toward the dashed DOS (sample 5, for example). The shallow donor level E_D associated with N_4^+ is indicated below the CB edge. The Fermi energy, as well as the main conduction paths, have been drawn for samples 1, 3, 4, and 5. In the inset the up and down movement of the Fermi level has been indicated, as proposed by Street.⁹

Let us return to more nitrogenated samples. Table II indicate that the $\log_{10}\sigma$ versus $1000/T$ curve of samples 5 and 6 is well fitted with two straight lines. The high-temperature activation energy E_a is, in both samples, higher than that corresponding to the less-nitrogenated sample 4. There is no doubt that samples 5 and 6 contain more nitrogen than sample 4 (see C_N , from nuclear reac-

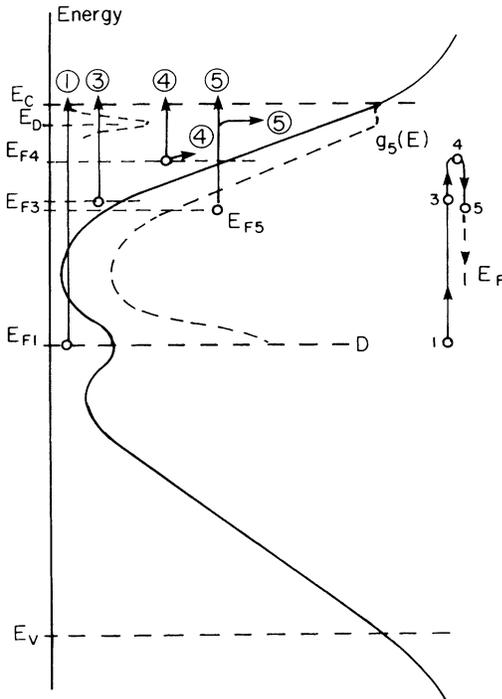


FIG. 4. Sketch of the density of states vs energy of undoped $a\text{-Ge:H}$ films (solid line) and N-doped sample 5 (dashed line). The symbols have their usual meaning. The Fermi energy position corresponding to different doping levels, as well as the likely activated process dominating the dark conductivity, have been indicated. Note the donor level E_D below the conduction-band edge which may eventually give rise to an increased DOS at the CB tail. The up and down movement of the Fermi level with N doping is indicated on the right-hand side of the figure.

tion methods, in Table II). The downward shift of the Fermi energy in samples 5 and 6 is due to the already discussed modified $8-N$ Mott's rule for incorporation of impurities in amorphous networks.⁹ As the Fermi energy approaches the donor level, more and more N atoms would incorporate in a threefold-coordinated configuration. Fourfold- and threefold-coordinated N atoms would coexist in the network but, as P_{N_2} increases, the material undergoes a transition towards the germanium nitride structure.

The large density of fourfold-coordinated N in samples 5 and 6, however, creates an impurity band near the CB edge which adds, at low temperatures, an alternative hopping conduction path for electrons excited from E_F ,

$$\sigma_5(T_{low}) = e\mu_{hop}N(E_D)k_B T \exp\left[-\frac{E_D - E_F + W}{k_B T}\right], \quad (6)$$

where μ_{hop} is the hopping mobility, $N(E_D)$ is the density of states at the donor level E_D , and W is a hopping energy (of the order of $k_B T$) between neighboring states. The above considerations and the figures of Table II locate the centroid of the donor level band at approximately 50 meV below the CB mobility edge.

It is worth comparing the present results on N-doped $a\text{-Ge:H}$ films with those obtained by Jones and co-workers³² on the electronic transport of P-doped $a\text{-Ge:H}$ samples prepared by glow discharge. The overall behavior of P and N as dopants is similar. The only differences between the present results on N doping and those of Ref. 32 are (i) Jones *et al.*³² found that $a\text{-Ge:H}$ is less sensitive to P doping than $a\text{-Si:H}$. We believe that the above finding is a direct consequence of a higher DOS at E_F in the samples of Jones *et al.* This higher DOS prevented any measurable E_F shift for dopant gas (PH_3) concentrations less than 100 (volume paths per million).³² At larger phosphine concentrations, however, the room-temperature activation energy decreased and eventually saturated at 0.24 eV. This minimum activation energy for P-doped $a\text{-Ge:H}$ is higher than the one displayed by the present N-doped samples ($E_{a\min} = 0.11$ eV). In spite of this difference, which may originate from the material's quality, we conclude that both elements, phosphorus and nitrogen, act as shallow donors in the $a\text{-Ge:H}$ network.

Summarizing, the transport properties of hydrogenated amorphous Ge samples indicate that nitrogen atoms enter the network with two different bonding configurations. At low N concentrations the host network imposes its own symmetry and fourfold-coordinated N atoms go substitutionally into Ge. Under these conditions nitrogen acts as an active n -type dopant and produces a shallow donor level. Increasing amounts of nitrogen induces threefold-coordinated N and the material undergoes a phase transition to intrinsic behavior.

IV. CONCLUSIONS

This paper reports the doping effects of nitrogen in the $a\text{-Ge:H}$ network. The study discusses the changes produced by minute amounts of N ($C_N < 0.5$ at. %) on the

electronic properties of the material. The main conclusions of the work follow.

(A) Nitrogen atoms enter into the a -Ge:H network with two different bonding configurations: tetrahedral (active dopant) and trigonal (self-compensated site, Ge-N alloy phase). The relative concentration of each depends on the total nitrogen incorporated in the film.

(B) The transport properties of a -Ge:H samples are substantially affected by nitrogen doping. The conductivity of intrinsic and lightly N-doped a -Ge:H samples show a single activation energy in the (120–400)-K range. At temperatures below 250-K heavier N doping induces a second conduction path through localized states near the conduction-band edge. Other transport mechanisms appear to be incompatible with the experimental data.

(C) Highly diluted nitrogen coordinates mainly with the symmetry of the host network (tetrahedral). In a active dopant configuration, nitrogen produce a shallow donor level located at around 50 meV below the

conduction-band edge. The activation energy of N-doped a -Ge:H layers varies from 0.50 eV (undoped material) to around 0.10 eV (highest effective doping).

(D) The concentration of nitrogen atoms in self-compensated sites (trigonal coordination) increases as the Fermi energy approaches the band-tail region. The material undergoes then a transition toward the nitride phase (a -GeN_x).

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