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On the doping efficiency of nitrogen in hydrogenated amorphous germanium

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This letter reports on the doping efficiency of nitrogen in *a*-Ge:H films of electronic quality. It has been found that nitrogen is an effective dopant in the *a*-Ge:H network, its doping efficiency being similar to the one corresponding to phosphorus in *a*-Si:H. The concentration of active nitrogen atoms decreases with impurity content following a square root dependence on total nitrogen. This behavior is similar to the one determined for column V dopants in *a*-Si:H films of electronic quality.

Since the pioneering work of Spear and LeComber¹ efforts have been directed toward the understanding of the conductivity variations produced by the incorporation of minute amounts of impurities in the network of tetrahedrally bonded amorphous semiconductors. It is at present universally accepted that the doping process is different in an amorphous network than in a crystal lattice. In the former, the minimization of free energy may be attained, either by the impurity atom having a first coordination number equal to its chemical valence, or by coordinating with the symmetry of the network in a substitutional site. Both types of sites coexist in amorphous networks and their relative stability results from the combined short-range chemical contributions and the lattice strain term, for it is known that tetrahedrally coordinated networks are topologically constrained.² Street³ suggested that: (a) the substitutional doping falls within a modified 8-*N* rule,⁴ including the possibility of charged states at the time of deposition (P_4^+ for example), and (b) the position of the Fermi energy plays a fundamental role in determining the relative density of each type of site, in the sense that the active doping efficiency is a function of the impurity concentration. E_F is not allowed to move up to the donor level during deposition because the occupied donor states (P_4^0) are in violation of the 8-*N* rule. At equilibrium the active dopant (fourfold) concentration n is balanced by an equal concentration of defects D . The reaction in n -type material is then $P_3^0 \leftrightarrow P_4^+ + D^-$. In the case of a low doping efficiency (η), Street³ obtains $\eta = n/N_0 = \text{const.}/N_0^{1/2}$, where N_0 is the total impurity concentration. The results being reported here on the doping efficiency of nitrogen atoms in amorphous germanium films confirm such assumptions:

Nitrogen appears to be distinctly different from the other group V elements and its electrical activity in the crystalline lattice of silicon and germanium is still a matter of debate. It has been argued⁵ that nitrogen should have a very low doping efficiency in *a*-Si:H because of the low stability of tetravalent N sites. A similar difficulty in forming tetravalent sites is expected to occur in *a*-Ge:H, although the presence of a hydrogen bonded to N may contribute in overcoming the difficulty.⁶ In any case, the doping efficiency should be much smaller than the one shown by phosphorus, for example. In a recent publication,⁷ the present authors showed that nitrogen is an effective

dopant in *a*-Ge:H films of electronic quality. Large conductivity variations, as well as a shift of nearly 400 meV in the activation energy of the dark conductivity, are measured as the partial pressure of N_2 is varied in the chamber during deposition. It has been found that a donorlike level, located around 50 meV below the conduction band edge, is responsible for the measured changes in electronic transport. The present letter discusses the efficiency of such a doping process, the main result being that the overall behavior is similar to the one found in the case of phosphorus and boron doping of *a*-Si:H films of electronic quality.

The *a*-Ge:H samples being studied here were prepared by the rf-sputtering method onto substrates held at $\approx 220^\circ\text{C}$. Electronic quality nitrogen gas was used as a dopant agent, and fed into the chamber during film deposition. Details on the deposition method and conditions are given in Ref. 7. Table I shows the deposition conditions, the composition, and the transport and electronic properties of the N-doped samples being reported. Note the low DOS and the small band tail characteristic energy E_0 of the intrinsic *a*-Ge:H sample. It may be seen that all samples are equally hydrogenated (bonded hydrogen content determined from IR transmission data⁸). As a consequence, no optical-gap (E_{04}) variations are measured. The total nitrogen content of the samples was determined with the $^{14}\text{N}(d,p)^{15}\text{N}$ deuteron induced nuclear reaction.⁹ The activation energy of the dark conductivity varies with nitrogen content. At a total N content of $4.3 \times 10^{19} \text{ cm}^{-3}$ (0.1 at. %) the Fermi energy shifts up, to around 0.1 eV from the conduction band edge, a shift of nearly 0.4 eV with respect to the intrinsic case. The concomitant increase of the DOS and the widening of the Urbach tail indicate that additional defects are being created while doping.¹⁰ Figure 1 shows the nitrogen concentration in the solid phase as a function of the N_2 partial pressure in the chamber. A linear dependence between nitrogen in the films and gas pressure is obtained. This is also the case of unhydrogenated *a*-Ge:N material, shown in Fig. 1 for comparison. Note that the maximum impurity content in the present *a*-Ge:H samples stays below 0.5 at. %.

Takano *et al.*¹¹ reported conductivity variations in N-doped *a*-Ge films. However, the high density of states (DOS) in the pseudogap of the unhydrogenated films of Ref. 11, and the appearance of absorption bands in the IR

TABLE I. Deposition conditions, composition, and optical properties of N-doped *a*-Ge:H films. In all cases, the substrate temperature and the hydrogen partial pressure were: $T_S=220\pm 5^\circ\text{C}$ and 1.3×10^{-3} mbar, respectively.

Sample	N ₂ partial pressure (mbar)	Hydrogen C _H (IR) (%)	Nitrogen C _N (nuclear) (cm ⁻³)	E _a (σ _d) (eV)	E ₀₄ (eV)	E ₀ (Urbach) (meV)	N _S (PDS) (cm ⁻³)	Doping Effy.
01H	$< 5\times 10^{-7}$	5.8	...	0.49	1.22	52	5.0×10^{16}	...
02H	4×10^{-6}	5.6	1.0×10^{19a}	0.23	1.21	62	1.1×10^{17}	1.1×10^{-2}
03H	7×10^{-6}	5.6	1.5×10^{19}	0.20	1.22	73	1.4×10^{17}	9.3×10^{-3}
04H	1.5×10^{-5}	5.6	4.3×10^{19}	0.11	1.22	83	1.7×10^{17}	4.0×10^{-3}
05H	3×10^{-5}	5.7	1.1×10^{20}	0.20	1.22	88	2.0×10^{17}	1.8×10^{-3}
06H	7×10^{-5}	5.3	2.0×10^{20}	0.21	1.21	114	4.5×10^{17}	2.2×10^{-3}

^aSensitivity limit. Value extrapolated from higher N concentrations.

transmission spectra at energies associated to the Ge-O vibrations, lead us to think that the measured conductivity variations may have a different origin. The doping efficiency of phosphorus and boron in *a*-Ge:H films prepared by glow discharge has been studied by Stutzmann.¹² Contrary to the case of P doping in *a*-Si:H films of electronic quality, in which the impurity content is proportional to the dopant gas (PH₃) concentration,¹³ Stutzmann finds in *a*-Ge:H films a square root dependence of P content on phosphine partial pressure. It is important to note that the intrinsic *a*-Ge:H samples of Ref. 12 possess a DOS of approximately 10^{18} cm⁻³, a factor of 20 larger than the DOS of the rf sputtered *a*-Ge:H films being reported here. Jousse *et al.*¹⁴ studied the doping efficiency of As in rf-sputtered *a*-Si:H films. It was found that, in spite of a linear dependence of impurity incorporation on dopant gas pressure, similar to the one shown in Fig. 1, there is no a square-root dependence of active doping efficiency with either the gas or the solid-phase active dopant concentration. The authors of Ref. 14 interpret these results in terms of surface reactions produced by energetic particle bombardment typical of sputtering processes. Let us mention that the rf-sputtered *a*-Si:H films reported in Ref. 14 possess a high DOS in the pseudogap.

It useful at this point to discuss some aspects of substitutional doping in tetrahedrally coordinated amorphous semiconductors. Substitutional active doping in electronic

quality films is more involved than just conductivity variations, which may have a quite different origin, i.e., thermal treatments, particle bombardment, etc. The analysis becomes particularly relevant when the efficiency of the doping process is being quantified. There is an abundant literature reporting on the doping efficiencies of different group III and group V elements in group IV amorphous semiconductors. In many cases, however, a complete characterization of the samples is lacking. In our opinion, the determination of the active doping efficiency requires: (i) a starting intrinsic material having a very low DOS (this requirement has almost never been met in the case of *a*-Ge:H); (ii) a relatively low density of states (DOS) in the pseudogap in all doped samples (as a consequence, the dark conductivity must be thermally activated, at least, at room temperature and above); (iii) an overall impurity content corresponding to true doping levels (typically below 0.5 at. %), rather than higher foreign atom concentrations leading to the alloy phase; and (iv) the same degree of hydrogenation in all samples (many of the changes measured in the transport and in the optical properties of doped amorphous samples may be a consequence of a different degree of hydrogenation and not of impurity activity). Not all of the above requirements have been sufficiently considered in studies concerning doping effects in *a*-Ge:H films. In most cases the poor quality of the intrinsic material was a limiting factor for an appropriate determination of the doping efficiency.

According to the model proposed by Street,³ a reasonable measure of the fraction of fourfold coordinated column V impurities in the *a*-Ge:H network can be obtained by equating their number to the density of compensating defects, as measured for instance, by photothermal deflection spectroscopy. The results of this operation on the data of Table I are shown in Fig. 2, where the nitrogen doping efficiency versus the total nitrogen content in the solid phase has been plotted. It may be seen that the fraction of active dopant sites decreases as the square root of the total impurity concentration. In the same figure the doping efficiencies of phosphorus in *a*-Si:H¹² and *a*-Ge:H¹³ films have been plotted. The agreement between the doping efficiency of N in *a*-Ge:H and of P in *a*-Si:H is remarkably good. This is not the case for P-doped *a*-Ge:H films.¹³ It is interesting to note that Street's model is followed in cases where the starting DOS is low, either in GD or rf-sputtered

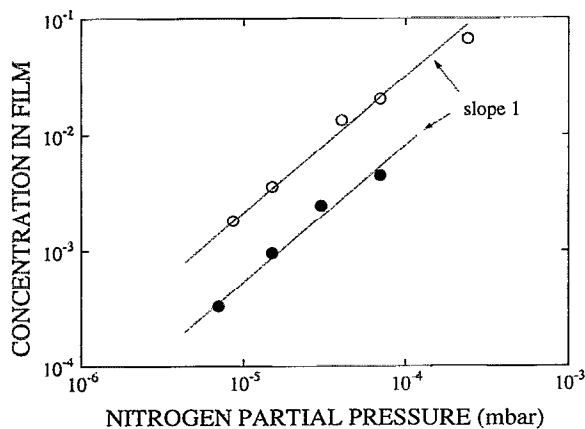


FIG. 1. Nitrogen concentration in the solid phase vs N₂ partial pressure of rf sputtered *a*-Ge films (open circles) and *a*-Ge:H samples (filled circles).

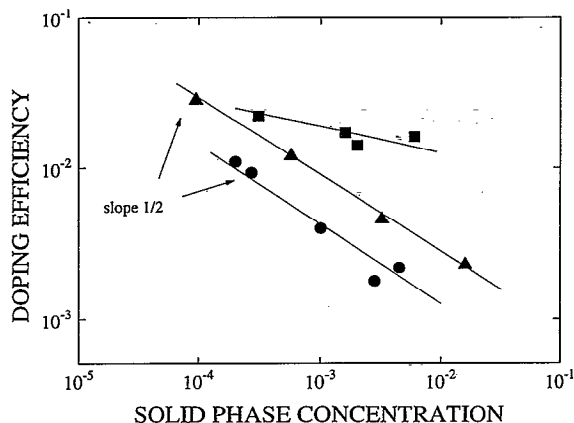


FIG. 2. The doping efficiency (η) vs the concentration in the solid phase for N-doped rf-sputtered a -Ge:H (circles), P-doped glow discharge a -Si:H (see Ref. 13) (triangles), and P-doped glow discharge a -Ge:H (see Ref. 12) (squares).

material. Let us remember that a departure from the square-root dependence of doping efficiency on impurity content, was also measured in rf sputtered As- and B-doped a -Si:H films of poor quality.¹⁴ The present results suggest then, that these departures may be a consequence of a large defect density and not of a different doping mechanism or preparation technique. More experimental work is underway to clarify the point.

It is the present authors' belief that substitutional doping by nitrogen of a -Ge:H by a similar mechanism to that of other group V elements in a -Si:H is a very significant result because: (1) N is an uncommon dopant and the

present work should stimulate research in other materials; (2) a -Ge:H is an increasingly important material for solar cell and sensor technology; (3) the availability of alternate dopants will help understanding the doping properties; and (4) a nontoxic dopant is quite appealing.

Summarizing, the results of the present work indicates that: (i) nitrogen is an efficient dopant in a -Ge:H films of electronic quality, its doping efficiency being comparable as to that measured in P-doped a -Si:H. (ii) the present experiment data agree with the predictions of Street's³ model of substitutional doping in tetrahedrally bonded amorphous semiconductors.

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¹⁰The authors are indebted to Dr. P. V. Santos, Xerox Parc, CA, for PDS measurements.

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