Nitrogen Doping in Amorphous Semiconductors

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In this work experimental data referring to the electronic properties of Nitrogen-doped hydrogenated amorphous germanium and silicon tliin films (a-Ge:H and a-Si:H, respectively) are presented and discussed. The results agree with tlie overall picture of active doping process of Group V elements in tetrahedrally coorclinated amorphous semiconductors. It is shown that low nitrogen doses in tlie amorphous structure produce large changes of both, the room temperature dark conductivity and the activation energy. The influence of the starting material's quality on the processes of N incorporation and doping is also discussed.

I. Introduction

Among tlie elements of the nitrogen sub-Group in the Periodic Table nitrogen itself as an impurity in germanium and silicon takes a. peculiar place whereas phosphorus, arsenic., antimony aiid bismutli are typical shallow donors in Si aiid Ge. Attempts to use nitrogen as an active donor in the crystal lattice of elemental semiconductors have given ainbiguous results. Nitrogen implanted into crystalline silicon, for example, can produce either a sliallow or a deep donor level (activation energy ranging from few tens to several hundred meV) depending on the implantation energy and temperature, as well as on the subtleties of annealing techniques and temperatures[1]. Reference 1 briefly reviews all tlie existing reports referring to nitrogen implantation in silicon, the conclusion being that tlie electrical behavior of N in c-Si is not yet coinpletely understood. However, the subject deserves attention because nitrogen lias some clear advantages over tlie otlier Group V impurities. First, nitrogen is the only Group V element which is naturally in tlie gaseous state. Second, it is available, inexpensive aiid non-toxic. Finally, depending on N content, nitrogen combines the possibility of active doping with tlie deposition of dielectric films, such as Si_3N_4 and Ge_3N_4, an interesting perspective for electronic technology.

The constraints on bond leiigtli and bond angles iinposed by the Si and Ge lattices may be partly relieved by atomic relaxation in the ainorplious networks. Moreover, the deposition conditions of a-Si:H and a-Ge:H (fast condensation from tlie vapor pliase) allow the incorporation in tlie growing film of atoms, ions or radicals of complex molecules. In amorphous networks tlie first coordination number is mainly deterinined by purely chemical parameters and not by the impurity's environment[2]. As a consequence, threefold coordinated nitrogen atoms may coexist in amorphous Si aiid Ge networks, their relative stability resulting from tlie combined short range chemical contributions and tlie network strain.

The present work reports on the electrical properties of N-doped a-Ge:H and a-Si:H samples deposited by the rf sputtering technique. It has been found that the iiitroduction of N atoms in the above semiconductors produces important changes in the electronic transport.

II. Experimental

All tlie intrinsic and N-doped a-Ge:H and a-Si:H sarnples studied in this work were prepared by the rf sputtering technique using semiconductor grade targets and 6N nominal purity argon, hydrogen, and nitrogen. The standard characterization of the films include: dark conductivity as a function of temperature, optical transmission spectroscopy in the near infrared-visible (NIR-VIS) and mid-IR energy ranges, and photothermal deflection spectroscopy (PDS). The absolute nitrogen content of the N-doped a-Ge:H samples was deterinined by a deuteron induced nuclear reaction $[N^{14}(d,p)^{15}N]$[3], whereas in N-doped a-Si:H samples tlie impurity concentration was estimated from IR absorption data[4]. In both alloys the hydrogen content was deterriined from the integrated absorption of the

Si-H (Ge-H) wagging mode[5]. The dark coiiductivity as a function of temperature was measured (300-470 K range) in an evacuated chainber using a computer data acquisition system. The activation energies appearing in Figs. 1 ai-d 3 correspond to this temperature range, the maximum relative error being estimated to ±2%. The sample thickness (d), the index of refraction (n), and the optical gap (E_g) of the alloys were determined froin optical data. Information on the electronic structure, such as the characteristic energy of the Urbach tail (E,), ai d the defect density [$g(E)$] in thc pseudo gap were ob;ained from PDÇ measurements[6].

III. Results and discussion

Until two decades ago it was believed that a-semiconductors could not be actively doped. This belief was based on the assumption that, due to the absence of crystal constraints the coordination of the impurity would be determined by the number of its valence electrons, and not by the host network (Mott's $8 - N$ rule[7]). A series of unsuccessful attempts seemed to confirm such assumption. In 1975, however, Spear and LeComber established that, in tetrahedrally coordinated amorphous semiconductors, the doping properties of Group-III and -V elements are similar to those found in the crystalline semiconductor parents[8].

To explain these unexpected results, Street proposed a modified $S - N$ rule[9]. The new formulation considers the possibility of including charged species during film deposition. In the specific case of an active donor atom, phosphorus for example, a positive impurity containing four valence electrons (P_4^+) will accomodate in a substitutional site, satisfying, the four hybrid bonds of tlie tetrahedral network. In an amorphous material of electronic quality the density of electronic states in the pseudo-gap (dangling honcls) is extremely small. Acccrding to Street phosphorus will exist in the host a-semiconductor with two different coorclinations, given by thr reaction:

$$P_3^0 \Longleftrightarrow P_4^+ + D^- \tag{1}$$
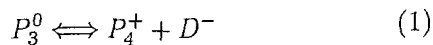
The threefold coordinated P_3^0 corresponds to tlie low energy state determined by tlie $S - N$ rule for neutral phospl.orus atoms. Hence, most phosphorus is in this configiiration, with only a small concentration of active donor states P_4^+. According to the model, the final equilibrium between threefold and fourfold coordinated phosphorus is determined by tlie position of
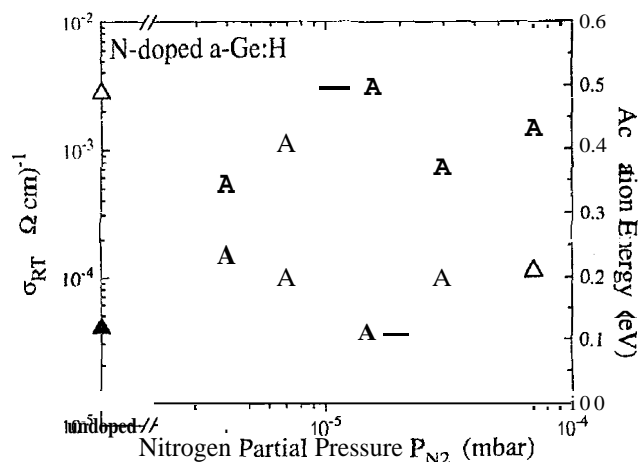

Figure 1: Dark conductivity at room temperature (σ_{RT}) and activation energy (E,) of N-doped a-Ge:H films as a function of nitrogen partial pressure (P_{N2}) during deposition.

the Fermi level (E_F) in the pseudo gap. As E_F approaches the donor level (increasing impurity concentration N_d), Group V impurities would coordinate with their own valence structure. Besides the availability of active dopant species, the effectiveness of substitutional doping in a-semiconductors depends on the density of deep defects [$g(E)$][10]. If E_F lies in an energy range where $g(E)$ is small and almost constant, the changes in the Fermi energy position produced by doping can be approximately given by:

$$\Delta E_F \approx N_d/g(E) \tag{2}$$

It is clear from equation (2) that, for a given N_d, the most effective doping will be achieved in materials having a small $g(E)$. Thus, the first and most essential requirement is a material having a very low overall density of gap states. With these ideas in mind a research effort to establish the doping properties of N in a-Si:H and a-Ge:H was undertaken.

The main results referring to N-doping of a-Ge:H are summarized in Fig. 1. A complete and detailed discussion of these results, as well as on measurement techniques, can be found in Ref 11. It is worth stressing that all the investigated a-Ge:H samples possess the sarne hydrogen content and the same optical gap ($C[H] \approx 6\%$ and $E_g \approx 1.1$ eV, respectively). A large Fermi energy shift was obtained on doping, partly due to the very low defect density of the intrinsic starting material [typically $g(E) \approx 5 \times 10^{16}$ cm^{-3}]. A shallow donor level produced by N active doping was found in a-Ge:H at $E_D = E_C - 50$ meV[11]

Our efforts to produce an rf-sputtered a-Si:H film having a low DOS were not very successful. In spite of this, N-doped a-Si:H films exhibit several interesting properties. The first oiie, not related to doping! is tlie increased facility for hydrogen incorporation: tlie same deposition conditions lead, in a-Si:H, to hydrogen concentrations several times those found in a-Ge:H. The same easiness of incorporation was found witli nitrogen. Fig. 2 shows that similar deposition conditions lead to very different nitrogen contents in a-Ge:H and a-Si:H films, thc incorporation rntc being roughly one order of magnitude higher in a-Si:H.

It is useful at this point to discuss some aspects of doping iii tetrahedrally coordinated amorphous semiconductors. In addition to active doping, conductivity variations in amorphous semiconductor films of electronic quality may originate from different causes! i.e., thermal treatments, particle bombardment, different hydrogenation, etc. In order to proceed to meaningfull comparisons, N-doping in a-Si:H films was only considered in samples having tlie same degrec of hydrogenation and a.nitrogen content smaller than N 1% (see Fig. 2).

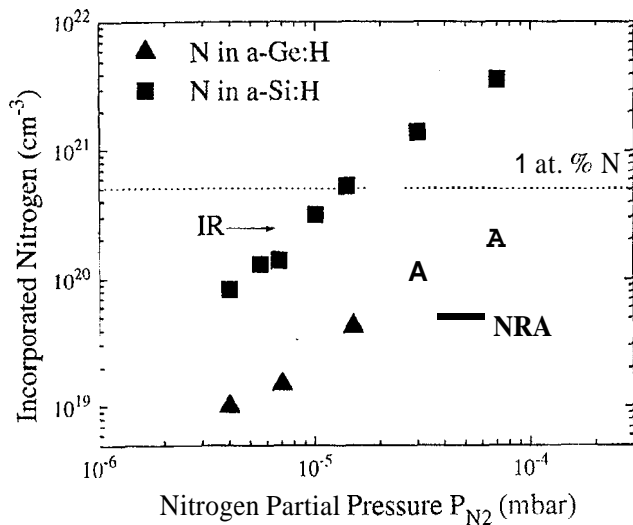Figure 2: Nitrogen incorporation in a-Si:H and a-Ge:H thin filins as a function of nitrogeii partial pressure (P_{N2}) in tlie reaction cliamber during deposition. The nitrogen concentration in N-dopetl a-Si:H filins mas determined fiom IR absorption data, whereas the impurity content in a-Ge:H was measured by nuclear reaction methods (see text for details).

As expected (see Fig. 3), at low N_2 partial pressures in tlie cliamber the enerpy difference between the Fermi energy and the conduction band edge, given by tlie ac-
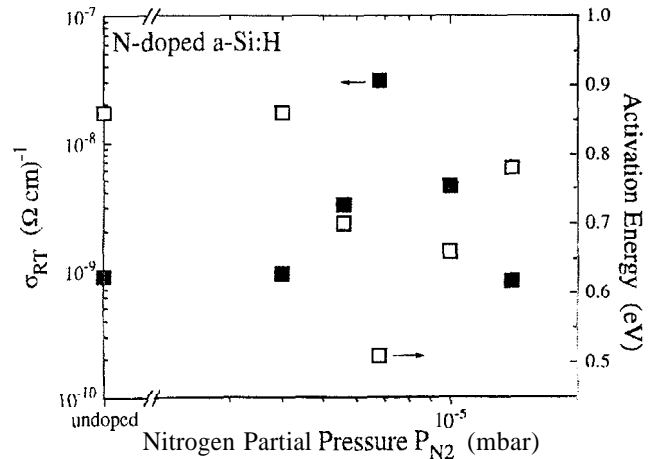

Figure 3: Dark conductivity at room temperature (σ_{RT}) and activation energy (E,) of N-doped a-Si:H films as a function of nitrogen partial pressure (P_{N2}) during deposition.

tivation energy of tlie dark conductivity, decreases to a minimum of ca. 0.5 eV (corresponding to a nitrogen partial pressure $P_{N_2} = 7 \times 10^{-6}$ mbar). A concoritant increase of tlie dark conductivity at room-temperature is measured. P_{N2} higher than $\approx 7.0 \times 10^{-6}$ mbar reverses the trend, a fact being explained by an increased density of deep states. In other words, the structural changes produced by an increased density of threefold coordinated nitrogen more than compensates for the doping effects of tetrahedrally coordinated N. This effect also appears in N-doped a-Ge:H films.

The overall N-doping process appears to he more efficient in a-Ge:H than in a-Si:H films. An explanation should necessarily consider tlie DOS of the starting intrinsic materials and the defect levels produced by nitrogen in the a-Ge and the a-Si networks. N-doping in a-Ge:H filins was performed in electronic quality intrinsic material[13,14] having a very low density of states $[g(E)$ N 5×10^{16} cm$^{-3}]$ and a corresponding small Urbach tail energy, E_0 N 50 meV (associated witli topological disorder), both parameters being essential for a highly efficieiit doping process.

According to photothermal deflection spectroscopy data, tlie present rf-sputtered a-Si:H films, on the contrary, possess an extremely high defect density of $g(E)$ N 2×10^{18} cm^{-3} and an Urbach tail energy $E_0 \approx 90$ meV. The low quality of the present a-Si:H samples is, certainly, a lirniting factor to active doping. A very higli defect density in tlie pseudo-gap seems also to bc the problem of other authors[4,15] who addressed

the problem of N-doping in a-Si:H and could not approach the Fermi energy closer than 0.5 eV from the conduction band edge.

The present results do not allow lls to draw definite conclusions about the electronic level produced by N incorporation in a-Si:H. At this point it is even impossible to determine tlie nature of this level which can be a deep donor produced by substitutional nitrogen, or a defect associated with a different configuration of N in tlze a-Si:H network[16]. The only important conclusion up-to the moment is that N-doping affects the transport properties of a-Si:H films. Fig. 3 shows these important changes in activation energy and conductivity. It is worth remeinbering that the doping range corresponds to $P_{N2} < 2 \times 10^{-5}$ mbar values, where the nitrogen content stays below ≈ 1 at. %. Higher P_{N2} in the reaction chamber lead to conductivity variations[4,17] not yet completely understood. More investigations are under way to clarify the point.

IV. Conclusions

This work reports on the doping effects of nitrogen in a-Ge:H and a-Si:H networks. The study discusses the changes produced by minute amounts of N on the electronic properties of the hydrogenated alloys. The experimental data may be interpreted on the basis of conventicnal P- and As-doping in a-semiconductors, following Street's doping model. The main conclusions of the present work follow:

- Nitrogen atoms can enter into the amorphous host with two different bonding configurations: tetrahedral (active dopant) and trigonal (self-compensated site, Ge-N and Si-N alloy phase). Tlie relative concentration of each configuration depends on the total nitrogen concentration in the film;

- The transport properties of the films are substantially affected by the incorporation of nitrogen;

- A shallow donor level located at approximately 50 meV below tlze conduction band edge is produced by N-doping in a-Ge:H. No conclusions referring to donor levels in a-Si:H exist at this stage;

- Nitrogen incorporates very easily in the a.-Si network.

- The defect density of the doped material plays a fundamental role in determining the impurity activity and performance.

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