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SUBSTITUTIONAL DOPING OF AMORPHOUS SILICON

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It is shown that the electrical conductivity of a tetrahedral amorphous semiconductor can be controlled over many orders of magnitude by doping with substitutional impurities. Experiments were carried out on *a*-Si specimens prepared by the glow discharge technique, with phosphorus and boron impurity levels between 5×10^{-6} and 10^{-2} ppv.

THE CONTROL of the electronic properties of crystalline semiconductors achieved by doping with substitutional impurities was a most significant factor in the development of semiconductor physics and solid state electronics. So far, attempts to control the properties of amorphous tetrahedrally coordinated semiconductors in the same systematic way have not been successful.[1] Several workers in the field have expressed the opinion that amorphous semiconductors may well be insensitive to doping.[2,3] It is argued that if, for instance, a pentavalent atom is introduced during the deposition of the *a*-Ge or Si specimen it will be accommodated into the random network structure in such a way that the additional bond is satisfied.

Up to now it has not been possible to carry out an experimental check of this basic hypothesis. The main reason lies in the high level of the localised state density normally found in the mobility gap of evaporated or sputtered *a*-Si[4] and *a*-Ge and presumably of other suitable materials. These states, thought to arise from point defects and microvoids, can be reduced in density by annealing, but the available evidence suggests that at room temperature the predominant transport still occurs by hopping of holes through the localised states.[4,6] Thus, even if it were possible to incorporate something like 10^{19} cm^{-3} atoms of a shallow donor or acceptor impurity, the excess carriers would condense into defect states without moving the Fermi level by more than a few kT.

Clearly, if one wishes to explore the possibility of substitutional doping in an amorphous semiconductor, the test material will have to satisfy the following requirements: (i) a very low overall density of gap states, and (ii) a narrow range of band-tail states below ϵ_c and above ϵ_v. Both these criteria are met by *a*-Si specimens prepared from the gas phase by the decomposition of silane (SH_4) in a r.f. glow discharge. The extensive work in this laboratory on the electrical[5,6] and optical properties[7,8] and on the distribution of localised states[4,9] has shown that in specimens deposited at a relatively high substrate temperature (500–600 K), gap state densities are remarkably low and that the density of states at the Fermi level, $\mathfrak{N}(\epsilon_f)$, is 10^{17} cm^{-3} eV^{-1} or less. In addition, the electron tail states lie within 0.2 eV of ϵ_c. No information is as yet available about states above ϵ_v, but it is likely that approximately the same applies as for the electron tail states.

The results of transport experiments on these specimens also show that at room temperature conduction takes place predominantly in the extended electron states above ϵ_c. The activation energy of the conductivity thus represents $\epsilon_c - \epsilon_f$. (In the following we shall neglect the small difference between $\epsilon_c - \epsilon_f$ and $(\epsilon_c - \epsilon_f)_0$, the value extrapolated to $T = 0$).

It seemed, therefore, of considerable interest to test the feasibility of substitutional doping on glow discharge specimens prepared at a substrate temperature between 500 and 600 K. In our experiments on n-type a-Si, we pre-mixed the silane in a 2 l. flask with carefully determined small amounts of phosphine (PH_3). By measuring the partial pressure with a sensitive transducer it was possible to add a few vppm of phosphine to the silane with a reasonable degree of accuracy. In the following, the amount of doping will be expressed by the ratio N_{PH_3}/N_{SiH_4}, where N represents the number of molecules per unit volume in the gaseous mixture. A small part of the mixture was then passed at a constant rate through the reaction tube where it was decomposed in the glow discharge.

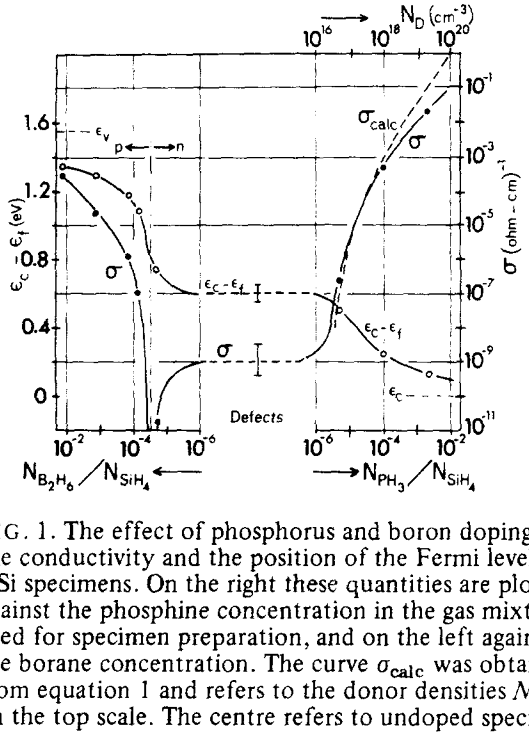

FIG. 1. The effect of phosphorus and boron doping on the conductivity and the position of the Fermi level in a-Si specimens. On the right these quantities are plotted against the phosphine concentration in the gas mixture used for specimen preparation, and on the left against the borane concentration. The curve σ_{calc} was obtained from equation 1 and refers to the donor densities N_D on the top scale. The centre refers to undoped specimens.

A similar series of experiments was carried out to investigate the possibility of producing p-type a-Si by adding small amounts of diborane (B_2H_6) to the silane. The specimens used, between 0.5 and 1 μm thick, were fitted with evaporated surface electrodes for measuring the conductivity σ and its temperature dependence. X-ray photographs showed that by incorporating the above impurities we did not cause the formation of microcrystalline regions.

Figure 1 summarises the results that have been obtained. On the right hand side of the graph, the room temperature conductivity is plotted against N_{PH_3}/N_{SiH_4}. The effect of boron doping is shown on the left on a plot of σ vs $N_{B_2H_6}/N_{SiH_4}$. Figure 1 also includes the position of the Fermi level, $\epsilon_c - \epsilon_f$, measured from the onset of the extended electron states. The values of σ and $\epsilon_c - \epsilon_f$ indicated in the centre of the graph are representative of the undoped specimen, where the position of ϵ_f is determined by structural defects in the gap states.

First consider the effect of including phosphorus in the structure. Even a minute quantity, corresponding to $N_{PH_3}/N_{SiH_4} \simeq 6 \times 10^{-6}$ causes a sharp rise in σ by over two orders of magnitude. With increasing phosphorus doping the Fermi level approaches the onset of the electron tail states at about 0.2 eV below ϵ_c. The rapidly rising density of localised states at this energy slows down the rate of increase of σ. However, it can be seen that with a mixture ratio of 2×10^{-3} an appreciable fraction of these states has been filled; $\epsilon_c - \epsilon_f$ now lies at 0.15 eV and $\sigma \simeq 10^{-2}$ $(\Omega\,\text{cm})^{-1}$. Thus the effect of the pentavalent impurity has been to increase the conductivity of a-Si by seven orders of magnitude and to move ϵ_f continuously to within 0.15 eV of ϵ_c. It would be difficult to explain these results by any model substantially different from that accepted for the crystalline case. We conclude therefore that pentavalent impurity atoms, up to an appreciable density, can be incorporated substitutionally into the random network, where they produce donor states within 0.1 eV of the extended electron states.

The density of state distribution $\mathfrak{N}(\epsilon)$ in the specimens investigated here is known from field effect measurements between $\epsilon_c - 0.6$ eV and $\epsilon_c - 0.18$ eV. It is thus possible to calculate σ as a function of the donor density, N_D. To a reasonable approximation we can write in the present case

$$N_D \simeq \int_{\epsilon_c - 0.6\,\text{eV}}^{\epsilon_c} \frac{\mathfrak{N}(\epsilon)\,d\epsilon}{\exp\left[(\epsilon - \epsilon_f)/kT\right] + 1} \qquad (1)$$

so that by numerical integration ϵ_f can be found as a function of N_D. The conductivity is then given by

$$\sigma = e\mu_c N_c \exp\left[-(\epsilon_c - \epsilon_f)/kT\right]. \qquad (2)$$

With the values of $\mu_c \simeq 2$ cm^2 V^{-1} sec^{-1} and $N_c \simeq 10^{19}$ cm^{-3} determined in the previous work, the broken line in Fig. 1 is obtained. The horizontal position of σ_{calc} has been adjusted to give best agreement with the experimental curve. This determines the N_D scale shown at the top of Fig. 1. The agreement between the two curves is quite satisfactory at the lower doping levels. In this range we can write

$$\frac{N_D}{N_{Si}} = K_D \frac{N_{PH_3}}{N_{SiH_4}} \tag{3}$$

where $N_{Si} \simeq 5 \times 10^{22}$ cm^{-3} denotes the density of Si atoms in the solid. Comparison of the two horizontal scales suggests that $K_D \sim 0.2$, which means that only about 20% of the phosphine molecules in the gaseous mixture will provide a donor in the amorphous film. There seem to be two possible explanations: either the phosphine decomposes less readily in the glow discharge than the silane, or 80% of the donors incorporated into the specimen have their additional valency satisfied in the random network. Further work is necessary to decide which mechanism is applicable or whether both contribute.

Preliminary measurements of the thermoelectric power of these specimens give a negative S; the photoconductive response of lightly doped specimens (10^{-7}–$10^{-6}\,\Omega^{-1}$ cm^{-1}) is remarkably high, with unit quantum efficiency in the red and green spectral regions.

Turning now to the boron doped samples, it is interesting to note that up to $N_{B_2H_6}/N_{SiH_4}$ of about 2×10^{-5} the predominant conduction path remains in the extended electron states. As the Fermi level is moved past the density of states minimum at $\epsilon_c - \epsilon_f \simeq 0.85$ eV[4,9] in the centre of the mobility gap, the specimen becomes suddenly p-type and σ rises by several orders of magnitude. It is most likely that in the glow discharge specimens used here, deposited at a fairly high temperature, the transport now takes place predominantly in the extended hole states at ϵ_v. The conductivity activation energy changes to $\epsilon_f - \epsilon_v$ and the value of $\epsilon_c - \epsilon_f$ plotted in Fig. 1 has been obtained by subtracting the observed activation energy from the value of $\epsilon_c - \epsilon_v \simeq 1.55$ eV.[6,7] Again it can be seen that with increasing boron content the rapid movement of ϵ_f towards ϵ_v slows down when the known density of states maximum at $\epsilon_c - \epsilon_y \simeq 1.2$ eV[4,6,7] is approached. It should be noted that evaporated or low temperature glow discharge films (deposition temperature $\lesssim 350$ K) possess very much higher densities of defect states at ϵ_y, so that in these materials hole hopping transport, rather than extended state conduction, occurs at room temperature.

On the basis of the results summarised in Fig. 1 we should like to conclude that, contrary to earlier suggestions, it is possible to incorporate substitutionally both pentavalent and trivalent impurities into a tetrahedral amorphous semiconductor such as Si. The fact that the electrical properties of the amorphous n-type or p-type films can be varied over a wide range in a systematic and reproducible manner could lead to more extensive applications of these materials. The present work in our laboratory is concerned with a more detailed investigation of the transport and optical properties of doped a-Si and Ge films and with their density of state distribution. These results will be published shortly.

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