Solid State Communications, Vol. 20, pp. 969-972. Pergamon Press. Printed in Great Britain.

DOPING, SCHOTTKY BARRIER AND p-n JUNCTION FORMATION IN AMORPHOUS GERMANIUM AND SILICON BY rf SPUTTERING†

W. Paul, A. J. Lewis, G. A. N. Connell and T. D. Moustakas

Division of Engineering and Applied Physics, Harvard University
Cambridge, Massachusetts 02138, U.S.A.

(Received 21 September 1976 by J. Tauc)

A method is described for preparing doped specimens of amorphous germanium and amorphous silicon by rf sputtering. We present conductivity and thermoelectric power measurements which demonstrate that doping has been achieved, and sketch some photoconductive properties of the material. To demonstrate device potential, we have fabricated Schottky barriers and p-n junctions and present i-V characteristics and a photovoltage spectrum.

For controlled doping of amorphous germanium (a-Ge) and amorphous silicon (a-Si) to be possible, it is essential that the density of pseudogap states caused by defects be minimized. Deposition or annealing at high temperature usually decreases the conductivity attributable to hopping at the Fermi level and this is almost certainly related to a decrease in the defect state density.[1,2] Similarly, incorporation of controlled amounts of hydrogen during deposition by sputtering reduces the low temperature conductivity and the spin density, but by orders of magnitude, implying that this is an even more effective way of reducing the defect state density.[2,3] A third, and very effective, method is to produce a-Ge and a-Si by the glow discharge decomposition of germane and silane,[4,5] which yields material with remarkably low values of the conductivity, pseudogap state density (as inferred from field effect measurements) and spin density.

Efforts to dope chemically the pure Ge and Si prepared by evaporation or sputtering have not been successful because the starting material has too many defect states. In contrast, glow-discharge work at Dundee[6] and subsequently elsewhere[7,8] has shown that partial pressures of PH_3 or B_2H_6 added to the GeH_4 or SiH_4 can be used to dope Ge and Si with P or B. For example, the Dundee group finds that the room temperature conductivity may be changed by ten orders of magnitude and that p-n junctions with quite good rectification characteristics may be produced. They argue that the Fermi level in a-Si is varied through 1.2 eV and that relatively narrow bands of donor or acceptor states are introduced into the gap near the conduction or valence band edges.

In this letter, we shall report the doping of rf sputtered a-Ge and a-Si by the simultaneous removal of pseudogap defect states by hydrogen incorporation and the introduction of donor or acceptor states due to P or B. The a-Ge and a-Si produced is controllably n- or p-type and p-n junctions show very good rectification characteristics. It is proposed that this method constitutes a viable alternative to the glow discharge technique. Four kinds of rf sputtered a-Ge and a-Si samples will be discussed. One, labelled "0 at .% H", was prepared in 5 x 10^{-3} Torr of argon. Another was prepared in a mixture consisting of 5 x 10^{-3} Torr of argon and (5-7) x 10^{-4} Torr of hydrogen. (All gauge readings were corrected by gas sensitivity factors.) For both a-Ge and a-Si this gives samples containing about 6 at .% H.[9] Finally, doped samples were prepared in 5 x 10^{-3} Torr of a mixture of either B_2H_6 (1860 ppm) in argon or PH_3 (2180 ppm) in argon together with the (5-7) x 10^{-4} Torr of hydrogen. a-Ge and a-Si were deposited at rates of 3 Å/sec and 1.5 Å/sec, respectively, onto substrates held at either room temperature or 250°C. Details of our sputtering system and measurement technique have been pub-

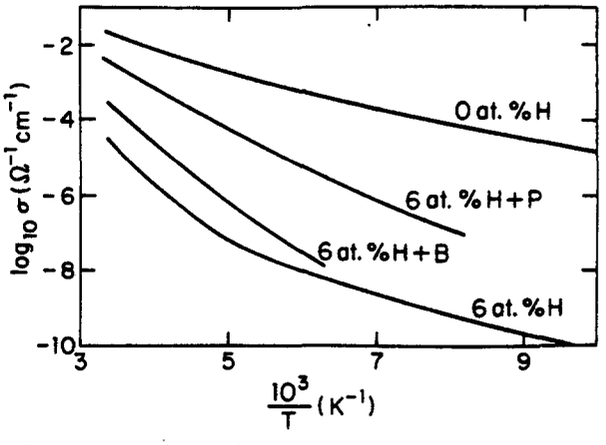

Fig. 1. Conductivity versus reciprocal temperature for a series of sputtered a-Ge films prepared at room temperature.

†Work supported by the National Science Foundation (Contract Nos. DMR75-18477 and DMR76-01111) and the Joint Services Electronics Program (Contract No. N00014-75-C-0648).

lished elsewhere.[2,3] Here we confine ourselves to presenting only the primary evidence that doping has been achieved, and do not attempt to describe in any detail the influence of varying the substrate temperature, hydrogen or dopant gas pressures, etc., on the material properties.

Figure 1 shows the conductivity of the a-Ge samples prepared at room temperature. In the 0 at .% H film the defect density due to structural imperfections is large enough that conduction occurs near the Fermi energy for all temperatures, as argued from the small, temperature

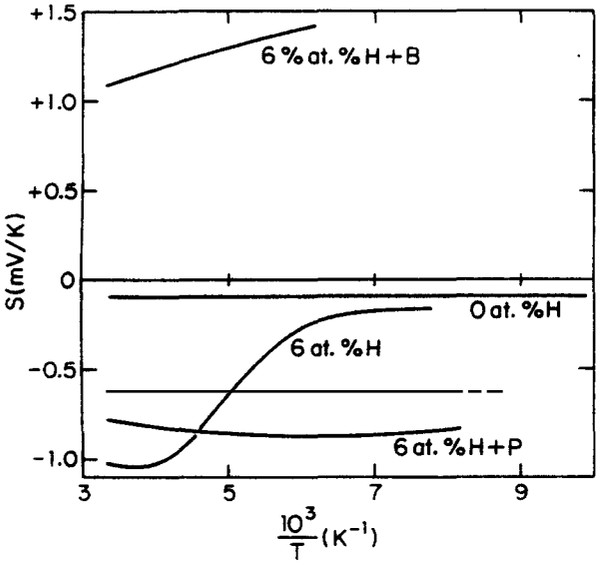

Fig. 2. Thermaelectric power versus reciprocal temperature for the same a-Ge films and conditions as in Fig. 1.

independent thermoelectric power (Fig. 2), and the non-activated conductivity.[10] The film with 6 at .% H has orders of magnitude smaller conductivity because atomic hydrogen attaches to the defects and acts as a compensator for defect-derived states.[2] This defect compensation is efficient enough that carriers in the conduction band dominate the room temperature dc transport, leading to a large, negative thermoelectric power near room temperature. Now notice the effect of adding the doping gas to the argon-hydrogen mixture. The addition of the phosphine produces material with two orders of magnitude more conductivity. From the thermopower, this sample is n-type and displays a well-defined but small activation energy for thermal carrier generation from 200-300 K. On the other hand, the addition of diborane results in a smaller increase in the conductivity, but the thermopower is now p-type. Again, there is a well-defined activation energy for thermal carrier generation from 200-300 K. These results demonstrate conclusively that doping has been achieved.

Entirely similar effects are observed in a-Si. The conductivity of a 6 at .% H film is lower by seven orders of magnitude than that of an unhydrogenated film. The room temperature values of the conductivity together with the activation energies for conduction (E_σ) and thermopower (E_s) are given in Table I.

An estimate for the movement of the Fermi level by doping is given by

$$\Delta E_f = E_{opt} - E_{FC} - E_s(\text{n-type}) - E_s(\text{p-type})$$

where E_{opt} is the band gap determined by optical absorption and E_{FC} allows for the possibility of a Franck-Condon effect. The question of Franck-Condon effects is pertinent because we find a non-zero value for $E_\sigma - E_s$. In the 6 at .% H a-Ge sample, we estimate that $E_{opt} \sim 1.1$ eV, giving $\Delta E_f \sim 0.9$ eV-E_{FC}. From both the optical and photoconductivity edges in the 6 at .% H a-Si film, we estimate that $E_{opt} \sim 1.6$ eV, giving in this case $\Delta E_f \sim 1.2$ eV-E_{FC}. The extent of these Fermi level shifts, regarded as indices of sensitivity to doping, compare favorably to those of the Dundee group, who assume $E_{FC} = 0$. Moreover, it seems likely that even more Fermi level movement can be achieved by optimizing the substrate temperature and the partial pressures of the hydrogen and the doping gas. If so, then the rf sputtering method might permit the production of material with a wider range of properties than the glow discharge method.

Changes in the photoconductive response with n- and p-doping have also been measured. For example, the room temperature steady state photoconductivity at 2 eV of hydrogenated a-Si, prepared at 250°C, is reduced by the B-doping by

Table I. The dc transport properties of doped amorphous germanium and amorphous silicon films prepared at room temperature

Sample	a-Ge				a-Si			
	σ(300 K) (Ω^{-1} cm^{-1})	E_σ (eV)	E_s (eV)	$E_\sigma - E_s$ (eV)	σ(300 K) (Ω^{-1} cm^{-1})	E_σ (eV)	E_s (eV)	$E_\sigma - E_s$ (eV)
0 at .% H	2×10^{-2}	(a)	(a)	----	3×10^{-3}	(a)	(a)	----
6 at .% H	2×10^{-5}	0.44	(b)	----	2×10^{-10}	0.36	(c)	----
6 at .% H+P	4×10^{-3}	0.24	0.05	0.19	4×10^{-6}	0.42	0.20	0.22
6 at .% H+B	3×10^{-4}	0.32	0.14	0.18	7×10^{-7}	0.43	0.24	0.19

[a] Non-activated conduction occurs near the Fermi energy.

[b] The temperature range of the data is too limited to determine an activation energy.

[c] The resistance of the sample is too large to obtain thermopower measurements.

a factor of 10^3 and increased by the P-doping by a factor of 10 while the photoconductivity edges shift to smaller photon energies in both cases. Thus, in the hydrogenated a-Si, the photoconductivity shows an onset at approximately 1.5 eV with no measureable photoconductivity at lower energies. The introduction of P and B shifts the onset to lower energy by about 0.5 eV. This result provides an indirect indication that the undoped hydrogenated material has a small state density in the gap since excitations from gap states are not detectable.

The photoconductive response of a-Si is also observed to depend sensitively on the conditions of preparation, such as hydrogen pressure and substrate temperature. For example, raising the substrate temperature from room temperature to 250°C increases the photoconductivity and lengthens the response time from microseconds to milliseconds. Careful optimization of preparation parameters will therefore be required to produce the best photoconductive, and by inference, photovoltaic material.

Schottky barrier and p-n junction devices have been fabricated. The devices are produced in a sandwich configuration by sputtering amorphous materials onto predeposited electrodes and later evaporating top electrodes. The devices normally have areas of about 0.005 cm^2. To date the transition from p to n material in the p-n junctions has been made by the replacement of B_2H_6 by PH_3, during a period when no rf power is applied to the target, and abrupt junctions are expected to result.

Determining the precise characteristics of these junctions alone is complicated by the problem of making low resistance, non-rectifying contacts to the p and n material. This problem is exacerbated when making material at high temperatures, since many possible bottom electrode materials cannot be used because they promote the early crystallization of the amorphous film or react to form germanicides or silicides.[11]

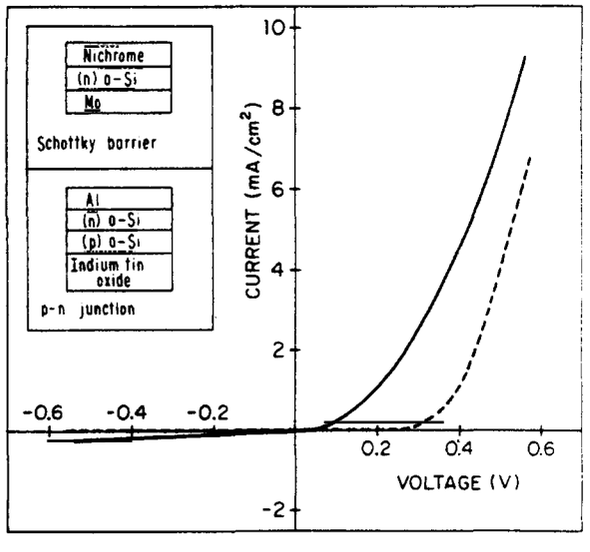

Fig. 3. Current-voltage characteristics, measured at 303 K, of an a-Si p-n junction (solid line) and a Mo/(n) a-Si Schottky barrier (broken line).

However, in investigating this electrode problem, it was found that some metals formed Schottky barriers with the doped material that were interesting in themselves. An example is shown in Fig. 3. The i-V characteristic of an n-doped a-Si film, deposited at 250°C as described earlier, when sandwiched between a bottom Mo electrode and a top nichrome electrode, is shown. Excellent rectification results, with more current flowing when the Mo electrode is positive with respect to the nichrome electrode, here held at ground potential. Thus the dominant barrier occurs at the Mo/(n)a-Si interface. In agreement with this result, the i-V characteristic of a companion nichrome/(n)a-Si/nichrome structure, while not ohmic to voltages of order 0.5 V, demonstrates that the nichrome/(n) a-Si contact has low resistance and would not limit the forward current in the Mo/(n)a-Si/nichrome structure.

Similar experiments with other conducting materials suggest that nichrome and Al may be used to contact adequately the n-type material, and Mo, nichrome and indium tin oxide to contact adequately the p-type material, in studies of p-n junctions. (It should be emphasized that not all of these materials can be used as bottom electrodes for high temperature depositions.) We note that the work function of the metal appears to play a role in the determination of the barrier height, in contrast to the observations on barriers on crystalline Si,[12] and we plan to investigate Schottky barrier formation at high work function/(n)a-Si and low work function/(p) a-Si interfaces. In this connection, we observe that the work function of nichrome is close to that of intrinsic Si, which may explain its usefulness in contacting both n- and p-type material.

The i-V characteristic of a typical p-n junction structure is shown in Fig. 3. The amorphous p and n materials, sandwiched between

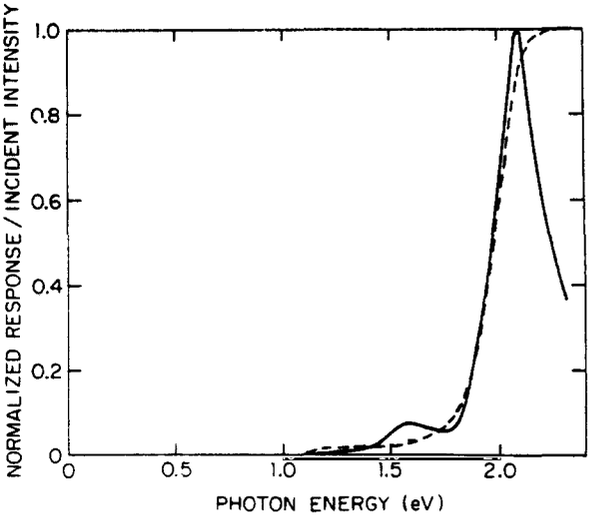

Fig. 4. Spectral dependence of the photovoltage of an a-Si p-n junction (solid line). The dashed line is the spectral dependence of photoconductivity of the phosphorous doped sample. Above 1.8 eV photoconductivity data are the same for the hydrogenated, p and n samples.

an indium tin oxide bottom electrode and an aluminum top electrode, were sputtered at 250°C. Thermopower measurements on codeposited specimens of the p and n materials gave $E_s \sim 0.2$ eV in both cases. Again, rectification is observed, with more current flowing when the indium tin oxide electrode is positive with respect to the Al electrode, as expected. Although the device configuration is not by any means optimum for large photovoltaic response, it is of interest to measure the spectral dependence of its photovoltage normalized to incident light intensity. This is shown in Fig. 4 for light transmitted through the indium tin oxide electrode. Measurable response begins at about 1.1 eV, but a rapid increase in response does not occur until about 1.7 eV. The position of the latter matches both the optical absorption edge and, as also shown in Fig. 4, the rapid rise in photoconductivity of the a-Si. The weak maximum at 1.6 eV is most likely an effect of constructive interference within the amorphous layers. These data are very similar to those of Spear et al. on p-n junctions[13] and to those of Carlson and Wronski on amorphous Si p-i-n junctions made by glow discharge.[8]

In summary, we have demonstrated that, through the simultaneous incorporation of H to remove the pseudogap states produced by defects, and of B or P to introduce relatively shallow acceptor or donor states, we have been able to dope amorphous germanium and silicon either n- or p-type and vary the resistivity by orders of magnitude. This material shows interesting photoconductive, photovoltaic, Schottky barrier and p-n junction characteristics, suggesting the advisability of further evaluation for semiconductor devices such as solar cells, where cost as well as performance is important.

Acknowledgments - We would like to thank J. R. Pawlik for many valuable discussions and Bob Centamore for his great efforts in preparing the materials. We also thank J. C. C. Fan for preparing the indium tin oxide, Dave MacLeod and Louis DeFeo for their technical help, and David Anderson for a critical reading of the manuscript.

REFERENCES

1. PAUL, W., CONNELL, G.A.N. and TEMKIN, R., Adv. in Phys. 22, 529 (1973).
2. LEWIS, A.J., Phys. Rev. B14, 658 (1976).
3. CONNELL, G.A.N. and PAWLIK, J.R., Phys. Rev. B13, 787 (1976).
4. LeCOMBER, P.G., MADAN, A. and SPEAR, W.E., J. Non-Cryst. Sol. 11, 219 (1972).
5. JONES, D.I., SPEAR, W.E. and LeCOMBER P.G., J. Non-Cryst. Sol. 20, 259 (1976).
6. SPEAR, W.E. and LeCOMBER, P.G., Phil. Mag. 33, 935 (1976).
7. KNIGHTS, J.C., AIP Conf. Proc. 31, 296 (1976).
8. CARLSON, D.E. and WRONSKI, C.R., Appl. Phys. Lett. 28, 671 (1976).
9. The method used to determine the hydrogen concentration is that of Ref. 3, which is based on the oscillator strengths of the Ge-H and Si-H vibrations. As a result, it measures only the hydrogen which is bonded to the network.
10. LEWIS, A.J., Phys. Rev. B13, 2565 (1976).
11. HERD, S.R., CHAUDHARI, P. and BRODSKY, M.H., J. Non-Cryst. Sol. 7, 309 (1972).
12. KURTIN, S., McGILL, T.C. and MEAD, C.A., Phys. Rev. Lett. 22, 1433 (1969).
13. SPEAR, W.E., LeCOMBER, P.G. and BRODSKY, M.H., Appl. Phys. Lett. 28, 105 (1976).