

catalysts. Films formed on the liquid surface consisting of *cis*-polyacetylene at low polymerisation temperatures and *trans*-polyacetylene at high temperatures. Electron microscopy (*Nature* **282**, 286; 1979) shows these films to be mats of fibres of about 20 nm diameter and low density,  $0.4 \text{ g cm}^{-3}$  compared with a theoretical value of  $1.2 \text{ g cm}^{-3}$ .

Shirakawa in conjunction with A.G. McDiarmid and coworkers at the University of Pennsylvania measured the electrical properties of these films (*Phys. Rev. Lett.* **39**, 1098; 1977; *Chem. Commun.* 578; 1977). The conductivity of the *trans* polymer is in the range  $10^{-4}$ – $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$  which makes it a semiconductor and not particularly interesting. The *cis* polymer has a conductivity of about  $10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$ . However on exposure to iodine vapour to dope the polymer with 68% iodine ( $\text{CHI}_{0.22}$ )<sub>x</sub> the conductivity of the *trans* polymer increased to  $40 \text{ ohm}^{-1} \text{ cm}^{-1}$ . At 1% iodine the polymer took on a silvery metallic appearance and went through an insulator-to-metal transition. The *cis*-polyacetylene reached conductivities of  $10^2$ – $10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$ , 11 orders of magnitude above the pure polymer values.

A range of dopants can be used (*J. Am. Chem. Soc.* **100**, 1013; 1978) and, in the same way as in semiconductors, both p and n-type materials can be produced such that a simple diode is made. Recently experimenters have used arsenic pentafluoride rather than iodine as it is less easily lost by evaporation. If the films are stretched to three times their original length the conductivity as doped becomes anisotropic, 2,000–3,000  $\text{ohm}^{-1} \text{ cm}^{-1}$  parallel to the stretch direction and 100–200  $\text{ohm}^{-1} \text{ cm}^{-1}$  perpendicular. Because the film resembles a knitted structure it is not clear to what extent this reflects changes in inter-fibre contacts and to what extent it is due to internal structural changes. F.E. Karasz, J.C.W. Chien and coworkers at the University of Massachusetts in cooperation with McDiarmid have been looking at the effect of varying polymerisation conditions and have found increases in conductivity if films are prepared at low densities and then pressed (*J. Polym. Sci. Lett.* **17**, 779; 1979).

A wide variety of spectroscopic techniques has been applied to the doped films but there is still much to learn. R.H. Baughman and S.L. Hsu of Allied Chemical report finding  $\text{I}_3^-$  and  $\text{I}_2^-$  in iodine-doped films (*J. Polym. Sci. Lett.* **17**, 185; 1979). T.C. Clark and G.B. Street of IBM say that oxidation always occurs to produce ionised chains with the counter-ions intercalated between the chains. When the charge density is sufficiently high the charges delocalise along the chain and the material becomes conducting (Preprints, A.C.S. Honolulu Meeting, 1979; *Chem. Commun.* 1066; 1978).

A number of related systems have been studied. Poly(*p*-phenylene) ( $\text{C}_6\text{H}_4$ )<sub>x</sub> has a

## Role of hydrogen in amorphous silicon

from P.G. LeComber

SINCE 1975, when it was first demonstrated that it was possible to control the electrical properties of amorphous silicon (a-Si) by substitutional doping (see Spear & LeComber *Phil. Mag.* **33**, 935; 1976), there has been a tremendous increase in the number of laboratories throughout the world working on both the fundamental properties of this material and its possible applications in solar cells, low-cost p-n junction diodes, thin film transistors, vidicon camera tubes and in electro-photography. With the recent announcement by the Sanyo Company of Japan that it is manufacturing calculators, watches and clocks powered by a-Si solar cells, we can expect this effort to be intensified still further.

The particular form of a-Si which has aroused all this interest is prepared as a thin film about  $1 \mu\text{m}$  thick by the decomposition of silane ( $\text{SiH}_4$ ) gas in an r.f. glow discharge. It is now known that this material contains upwards of a few percent of hydrogen and in fact many workers (but not all) believe that these relatively large concentrations are essential for the good electronic properties of these films. In view of the potential of a-Si in a wide variety of applications it is clearly important to understand the role of hydrogen in producing and possibly limiting its desirable properties.

In a recent issue of *Physical Review Letters* (**44**, 43; 1980), D.C. Allan and J.D. Joannopoulos, at the Massachusetts Institute of Technology, have calculated the electronic states and total energies of the various configurations in which H atoms could be bonded into the amorphous silicon network. Allan and

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conductivity of  $10^{-14} \text{ ohm}^{-1} \text{ cm}^{-1}$  which rises to  $100 \text{ ohm}^{-1} \text{ cm}^{-1}$  with arsenic pentafluoride. This polymer is a very stable powder (*J. chem. Phys.* **71**, 1506; 1979). Poly(vinylphenylene) ( $\text{-(CH=CH-C}_6\text{H}_4\text{)-}_x$ ) has a conductivity of  $10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$  rising to  $3 \text{ ohm}^{-1} \text{ cm}^{-1}$  at 57% arsenic pentafluoride. This material has a degree of polymerisation of only eight, barely a polymer at all (*Polymer* **20**, 1441; 1979). Polydiacetylenes ( $\text{-(CR=C=C-CR)-}_x$ ) are of interest in that the polymers can be prepared as large single crystals by solid state polymerisation of monomer crystals where the monomers are already aligned in the right way for chain formation. Despite the chains being continuous through the crystals and their metallic appearance they

are not conductive as apparently they have no charge carriers (*J. Polym. Sci. Phys.* **14**, 2037; 1976). Simple models suggest that in long conjugated chains with all the bond lengths equal, electrons should be thermally excited into the conduction band at room temperature. This does not happen, apparently because all the bond lengths are not equal (due to the Jahn-Teller effect, for the cognoscenti) and because internal rotation about the bonds interrupts the conjugation. In addition to understanding charge mobility within the chains one needs to know how the charges transfer from one chain to another, which must partly be a function of chain length. Unfortunately this is all but unmeasurable since the

Joannopoulos claim that there are limitations in previous publications on this subject and conclude that strongly interacting nearest-neighbour silicon monohydrides have an important role, particularly in the interpretation of the photoemission spectra. They also find that the energy gap increases with increasing H content, in agreement with published optical data. Their results show that the valence band recedes rapidly with increasing H content but that the conduction band remains essentially unchanged. Possibly their most interesting conclusion, however, concerns the large  $\epsilon_y$  peak in the density of localised gap states that is observed in field effect and other experiments. Since it is believed that it is these  $\epsilon_y$  states that at present limit the performance of a-Si solar cells, by understanding the nature of these states one might be able to reduce their numbers. Allan and Joannopoulos suggest that local fluctuations in the hydrogen content can create localised states near the valence band edge and that these could be the origin of the  $\epsilon_y$  states. It would be ironic if hydrogen, thought by many to be essentially only a positive factor in producing the good electronic properties of a-Si, turns out to be responsible through these fluctuations for limiting the performance of a-Si solar cells! This suggestion cannot be the whole story, however, since a-Si produced by thermal evaporation contains essentially no hydrogen and has an even larger number of states around  $\epsilon_y$  than the films produced from silane. Nevertheless many laboratories will be interested in seeing if this suggestion by Allan and Joannopoulos provides, at the least, some clue to how to decrease the number of these states and thereby improve the efficiency of a-Si solar cells.