Is amorphous silicon played out?

from J.I.B. Wilson

IN spite of enthusiasm for amorphous silicon as a means of making cheap photovoltaic diodes, the improvement of the performance of these diodes has recently been slow and difficult. So is amorphous silicon destined to be a false trail in the search for a cheap solar cell? Although some Japanese companies (principally Sanyo Electric Co.) have set up production lines for these solar cells, chiefly for use in consumer products such as calculators, large-scale power conversion requires a better efficiency than the present about 7 per cent. The main barrier to further improvement is the poor photocurrent, caused by the high concentration of imperfections in the material. These trap the free charges produced by light and inhibit their collection by the metal contacts.

Scepticism about the potential of amorphous silicon cells is easily justified. It has always been suspected that an amorphous semiconductor will have unavoidably poor electrical characteristics, even when it is passivated with hydrogen produced by the plasma decomposition of silane gas (SiH_4). So is it possible to improve the electrical conductivity of this hydrogenated amorphous silicon (a-Si:H) only by sacrificing the high optical absorption of the amorphous structure? Although the hydrogen will reduce strain in the structure and reduce the number of unsatisfied silicon bonds, it will not necessarily control the concentration of defects, so that hydrogen content is not in itself a measure of the structural disorder.

Indeed, recent papers[1,2] suggest that in a-Si:H the structural disorder rather than the hydrogen content controls the optical absorption, especially below the 'bandgap', even though the removal of hydrogen by heating leads to both a deterioration in semiconducting behaviour and an increase in optical absorption. This suggests that if the optical absorption is to remain high, then the electrical behaviour of devices made with a-Si:H may always be limited by intrinsic structural disorder even if the structure is modified with hydrogen or fluorine. This conflict is already accepted in efforts to develop solar cells, and more complicated structures than a simple metallurgical junction have been suggested as ways of increasing the photocurrent without abandoning the simplicity of the plasma technique of depositing semiconductors.

In spite of theoretical estimates of the position in the energy level scheme of particular defects, such as unsatisfied silicon 'dangling' bonds and those produced by silicon-hydrogen groups, the

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inverse process of identifying bandgap energy levels with the physical entities to which they correspond has been unsuccessful, largely because of disagreement about the actual distribution of these energy levels within the bandgap. (Only in a pure crystalline semiconductor is this bandgap completely disallowed.)

Since the bandgap levels are those responsible for photoluminescence and photoconductivity, as well as for the control of electrical conduction, it is surprising that there should still be so many uncertainties. One difficulty in the interpretation of experimentally determined distributions is that the surface of the semiconductor (or its interface with an electrical contact) may contribute a substantial number of additional energy levels, perhaps with an energy distribution different from that in the semiconductor bulk. Another is that some experimental techniques are insensitive to any structure in the distribution. Thus field effect measurements (using a metal oxide-semiconductor transistor) give a mid-bandgap density of energy levels of $\sim 10^{17}$ cm^{-3} eV^{-1}, whereas a transient capacitance technique (deep-level transient spectroscopy), which is said to distinguish between bulk and surface effects, has given a surprisingly low value of $\sim 10^{15}$ cm^{-3} eV^{-1}. There is, however, disagreement about the interpretation of this data[3].

Moreover, there is one intriguing electrical conductance phenomenon for which the simple one-electron model of the energy levels due to defects appears to be inadequate — the 'Staebler–Wronski effect'. This consists of photostructural changes when a-Si:H is illuminated with a high flux of visible wavelength photons[4]: the electrical conductivity gradually decreases by a small factor, but the subsequent dark conductivity decreases by up to 10,000 times. These changes can be reversed by annealing the sample at $\sim$ 150°C for some minutes, but there is no distinct temperature threshold. Although similar effects can be produced by adsorption on the surface, this is definitely a bulk effect and is ascribed to a movement of the Fermi level towards the middle of the bandgap. The phenomenon does not occur in heavily doped p- or n-type samples.

An explanation invoking self-trapped excitons has been proposed by Elliot[5], while a more elaborate model due to Adler[6] successfully explains variations of the effect in lightly doped samples as well as other experimental observations. Adler proposes that two adjacent neutral dangling bonds (T_3^0) in the predominantly tetrahedral lattice (for not all dangling bonds are removed by hydrogen) are dehybridized from their usual sp^3 character to the (trigonal) sp^2-p_z form. The transfer

of an electron creates a pair of charged centres, an acceptor (T_3^+) and a donor (T_3^-), but their energy levels within the bandgap are thought to be inverted compared with those of the usual substitutional impurity donors and acceptors.

On Adler's model, interconversion is prevented by a potential energy barrier, for the charge centres have different bond angles within the lattice. On this view, the decrease in photoconductivity and the shift in Fermi level observed in the Staebler–Wronski effect are produced by the asymmetric trapping of free charges at these energy levels, with a consequent conversion of neutral donors to acceptors. The increased concentration of acceptors causes the Fermi level to move downwards, giving a lower dark conductivity. Thermal annealing helps the potential barrier to be overcome, assisting a gradual return to the orginal T_3^0 states. (An inverse effect occurs when the initial position of the Fermi level favours the conversion of neutral acceptors to donors.)

Although the Staebler–Wronski effect is of little importance for the operation of solar cells (because the photoconductivity changes are too small to have much effect on the cell resistance), it does demonstrate the complexity of the defects in this disordered solid. These must be better understood before it can be told whether their presence is unavoidable. And even as things are, useful solar cells can be made from plasma-deposited amorphous silicon of existing quality, while other devices are not far behind. Further improvements in the material, either during production or by treatment afterwards, should still be possible. □

1. Cody, G.D., Tiedje, T., Abeles, B., Brooks, B. & Goldstein, Y. *Phys. Rev. Lett.* 47, 1480 (1981).
2. Deneuville, A., Mini, A. & Bruyere, J.C. *J. Phys. Solid State Phys.* 14, 4531 (1981).
3. *Proc. 9th int. Conf. on Amorphous & Liquid Semiconductors, Grenoble, 1981 J. de Physique* 42, Suppl. 10, c-4 (1981).
4. Staebler, D.L. & Wronski, C.R. *Appl. Phys. Lett.* 31, 292 (1977).
5. Elliot, S.R. *Phil. Mag.* B39, 349 (1979).
6. Adler, D. *J. de Physique* 42, Suppl. 10, pc4-3 (1981).

Corrigendum *from B.T. Pickering*

In commenting in these columns on the sequence of the common precursor to vasopressin and its neurophysin I stated that it held no surprises (*Nature* 295, 280; 1982). However I also stated that the signal sequence is separated from that of vasopressin by a pair of basic residues which re-examination of Fig. 4 in the paper by Land *et al.* (*Nature* 295, 299; 1982) shows to be incorrect. Indeed, had it been so, this would have been a surprise, since the membrane-associated cleavage of prepeptides is not thought to involve basic residues.