

## X-ray photoelectron spectroscopy and dark DC conductivity of argon-ion implanted organic films over a wide temperature range

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 S311

(<http://iopscience.iop.org/0953-8984/3/S/049>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 11:25

Please note that [terms and conditions apply](#).

## X-ray photoelectron spectroscopy and dark DC conductivity of argon-ion implanted organic films over a wide temperature range

Richard J Ewen, Colin L Honeybourne and Callum A S Hill  
Bristol Polytechnic, Frenchay, Bristol BS16 1QY, UK

Received 25 April 1991

**Abstract.** Films of metal-free phthalocyanine (MFPC) and 1,8-dihydrodibenzo[b,i]-[1,4,8,11]tetra-aza-[14]-annulene (TAA) were studied. The compounds were deposited by vacuum sublimation on to: (i) quartz substrates for UV-vis spectroscopy; (ii) Teflon disks for reflection measurements; (iii) stainless steel stubs for x-ray photoelectron spectroscopy (XPS); and (iv) interdigitated platinum electrodes on alumina for electrical conductivity measurements. The transmission UV, visible and IR spectra of the compounds were unchanged following bombardment by 10 kV argon ions, indicating that any damage caused was confined to only a thin surface layer. The x-ray photoelectron spectra of both of the compounds were substantially modified following bombardment by 10 kV argon ions. In both cases the hydrocarbon-type carbon levels increased, the intensities of the nitrogen peaks were decreased, and a new peak due to implanted argon was observed, indicating severe damage to the surface of the films. The electrical conductivities of all samples exhibited increases of up to six orders of magnitude following argon-ion exposure. On the basis of the XPS results and the form of the conductivity against temperature curves, it was concluded that the damaged surface was composed substantially of amorphous carbon.

### 1. Introduction

The interactions of ion beams with solids have been studied for many years (Carter and Grant 1976, Eisen and Mayer 1976), although such studies have been largely confined to the ion bombardment of semiconductors and metals. It is only comparatively recently that attention has been given to the effects of ion beam exposure on organic materials.

A number of papers have appeared on the chemical effects of such exposure (Puglisi *et al* 1982, Foti *et al* 1983), and the possibility of using this technique in the production of ions from organic solids for mass spectroscopic analysis has also received attention (Magee 1983). Some effects of ion beam exposure on the structure of an organic solid have been reported (Vareille *et al* 1981). Large conductivity increases in polymeric films following ion bombardment have been noted (Abel *et al* 1982, Venkatesan *et al* 1984a, Wasserman *et al* 1984).

The electrical and other physical properties of thin sublimed films of organic compounds have been found to be altered dramatically by exposure to ion beams of very high energy (Forrest *et al* 1982, Kaplan *et al* 1984, Venkatesan *et al* 1984b).

## 2. Experimental details

For the purposes of this study two conjugated macrocyclic ligands were selected: phthalocyanine (MfPc) (figure 1(a)), and 1,8-dihydrodibenzo[b,i][1,4,8,11]tetra-aza-[14]-annulene (TAA) (figure 1(b)). Both were prepared by standard literature methods (Lever 1965, Badger *et al* 1964, Hiller *et al* 1968) and were purified before use by repeated vacuum sublimation, recrystallization and/or column chromatography, as appropriate.

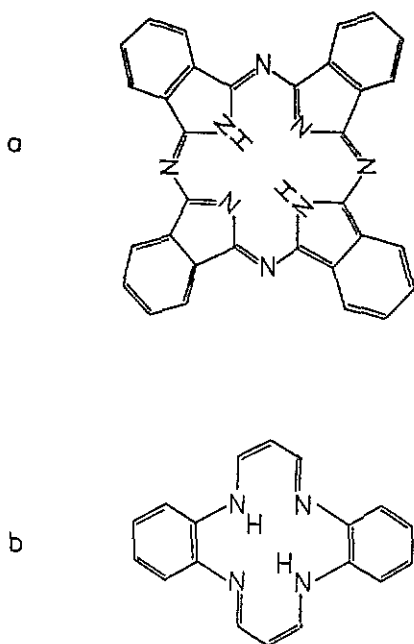


Figure 1. Structures of the molecules used in the investigation: (a) phthalocyanine (MfPc); and (b) dihydrodibenzo[b,i][1,4,8,11]tetra-aza-[14]-annulene (TAA).

Films of the materials were prepared by sublimation on to suitable substrates, under a vacuum of approximately  $10^{-6}$  mbar, using an Edwards E306A coating unit. The materials were evaporated from a tantalum boat. The thicknesses of the films for the electrical measurements were measured using an Edwards FTM4 film thickness monitor during deposition. Film thicknesses for the other experiments were estimated spectroscopically. Film thicknesses were in the region of 200 nm.

Samples for x-ray photoelectron spectroscopy (XPS) were prepared by evaporation onto stainless steel substrates. Photoelectron spectra were recorded using a VG Scientific ESCALAB Mk II. All spectra were recorded using an unmonochromatized x-ray source with an aluminium anode giving a primary line at 1486.6 eV.

Samples for UV-vis spectroscopy were prepared by evaporation on to the optical face of a quartz cuvette for transmission studies, or on to Teflon disks for reflection

measurements. Spectra were taken using a Perkin-Elmer 559 spectrometer (transmission), and a PYE-Unicam SP500 Series 2 spectrometer (reflection).

Infrared spectra were recorded for samples prepared by sublimation on to NaCl plates, using a Perkin-Elmer 681 infrared spectrometer. The spectra of samples before and after deposition were identical, indicating that the materials did not decompose during sublimation.

Two-electrode electrical measurements were performed on samples evaporated on to Rosemount Platfilms (Type 80E 11268). A Platfilm consists of a 3 mm × 3 mm square of alumina with a platinum interdigitated electrode pattern on one side, and a platinum heater/thermometer on the reverse, to which platinum wires are attached. The thermometer was calibrated prior to use. Each Platfilm was mounted on a cell designed to ensure good thermal contact with the heating/cooling probe. All the electrical measurements were carried out in the ESCALAB under a vacuum of better than 10<sup>-8</sup> mbar. The current flowing through each film, with a potential of 1.0 V applied, was measured as a function of temperature (*T*) over the range 130 < *T* < 435 K.

Samples were bombarded with argon (Ar<sup>+</sup>) ions in the analytical chamber of the ESCALAB using the VG AG2 argon ion gun. In all cases the accelerating potential used was 10 kV. Samples for the electrical studies were exposed for 60 s to give a total ion dose of approximately 10<sup>15</sup> ion cm<sup>-2</sup>, estimated by measuring the beam current on a conducting target of known area.

### 3. Results and discussion

The depth to which an ion or atom penetrates a solid is determined by the rate at which it loses kinetic energy. Energy loss may occur via atom-atom collisions, or by the excitation of atomic electrons, depending on the kinetic energy of the incident particle. In the case of particles of relatively low kinetic energy, such as those employed in these experiments, energy loss would occur predominantly via nuclear processes, with electronic excitations making only a very small contribution. Such a low-energy particle would be subject to a large number of atomic collisions before coming to rest, and thus would be expected to cause scatter in the collision track of the particle and confine the damage to the surface regions of the target material. For a bombarding particle with a kinetic energy of 10 keV the damage would be expected to be confined to within a few tens of nanometres of the surface.

The transmission infrared (IR), ultraviolet (UV) and visible spectra of the films were unchanged following Ar<sup>+</sup> bombardment of the films for two minutes. Even prolonged etching did not change the spectral profiles. However, the intensities of the absorption bands were systematically diminished due to the reduction in thickness of the films by the etching process. These results are consistent with a model in which damage due to low-energy ion bombardment is confined to a thin surface region, such that the transmission spectra are dominated by the bulk, unaltered material. To the naked eye the samples became darker following ion bombardment.

The reflectance UV and visible spectra (figure 2) were altered by Ar<sup>+</sup> bombardment. The most noteworthy change was the extension of the absorption region into the near IR (700–800 nm).

The phthalocyanine molecule contains 32 carbon atoms and 8 nitrogen atoms. For the purposes of XPS the atom types may be divided as follows: 24 aromatic

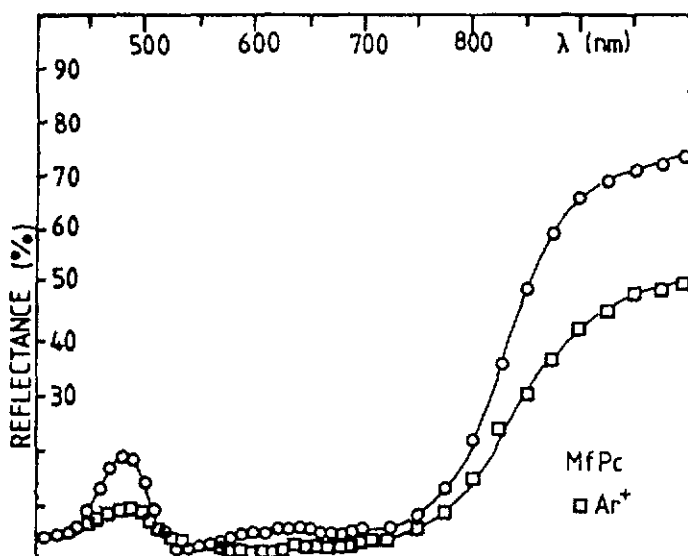


Figure 2. Reflectance UV-VIS spectra of MfPc before and after exposure to 10 keV argon ions.

hydrocarbon-type atoms, 8 carbon atoms which are bonded to 2 nitrogen atoms, 6 aza nitrogen atoms and 2 pyrrole nitrogen atoms.

The XPS spectrum of the carbon 1s region of MfPc (figure 3(a)) is composed of two unresolved peaks, each giving rise to a shake-up satellite (Niwa *et al* 1974, Ewen and Honeybourne 1991). The largest peak at the lowest binding energy is due to the 24 hydrocarbons (C1), the next largest peak to higher binding energy is due to the 8 carbons bonded to nitrogens (C2), and the two remaining peaks (C3 and C4) are shake-up satellites of C1 and C2 respectively.

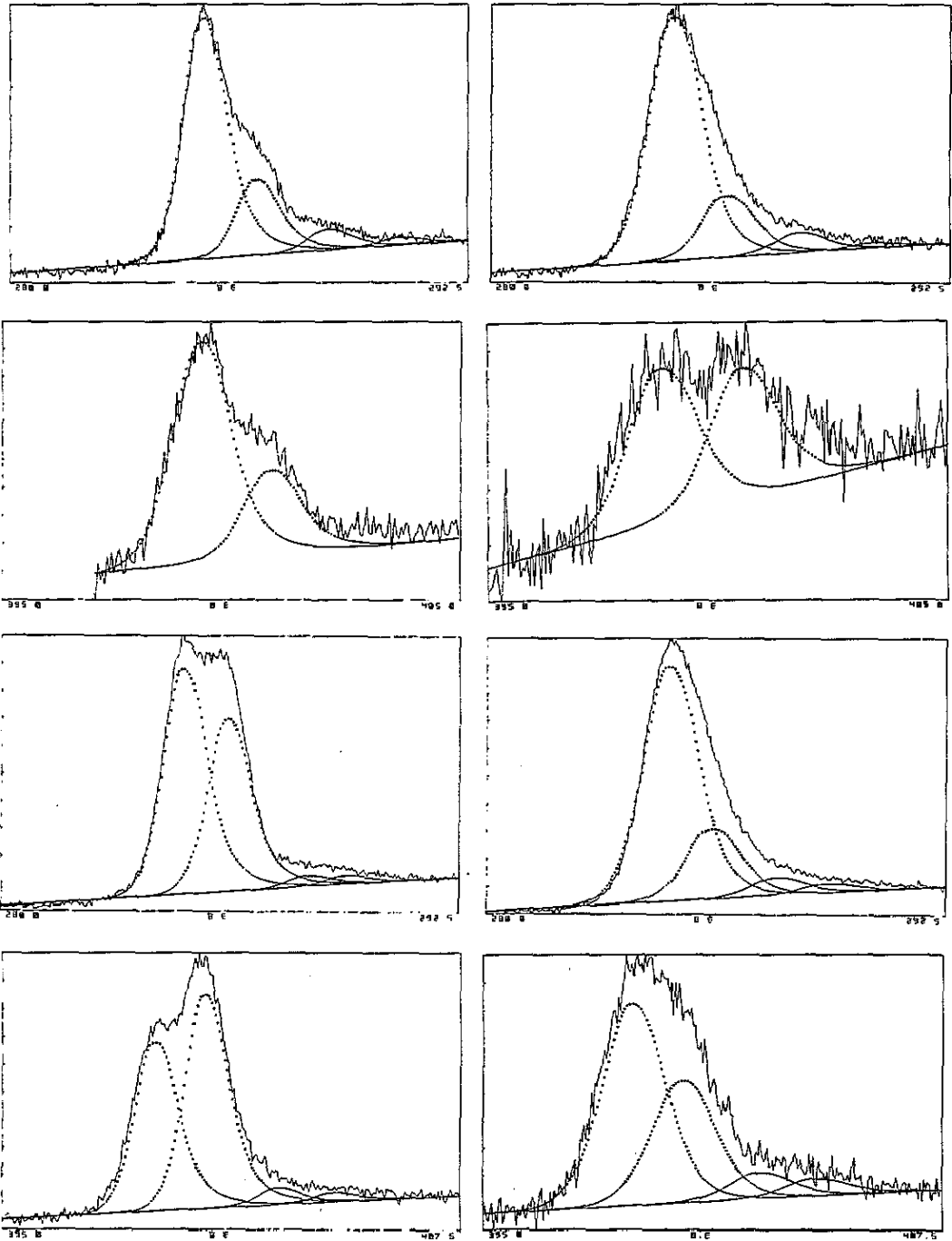
Similarly, the nitrogen 1s region is composed of two unresolved peaks (figure 3(b)) due to the nitrogen atoms in different environments, where the larger peak at lower binding energy is due to the aza nitrogen atoms (N1) and the smaller peak at higher binding energy is due to the pyrrole nitrogens (N2). Shake-up satellites from these peaks should also exist, but the signal here is too weak for them to be observed.

A histogram of the atomic percentages of each peak obtained by curve-fitting these spectra is given in figure 4(a). The pre-exposure C1:C2 and N1:N2 ratios are in agreement with the expected values.

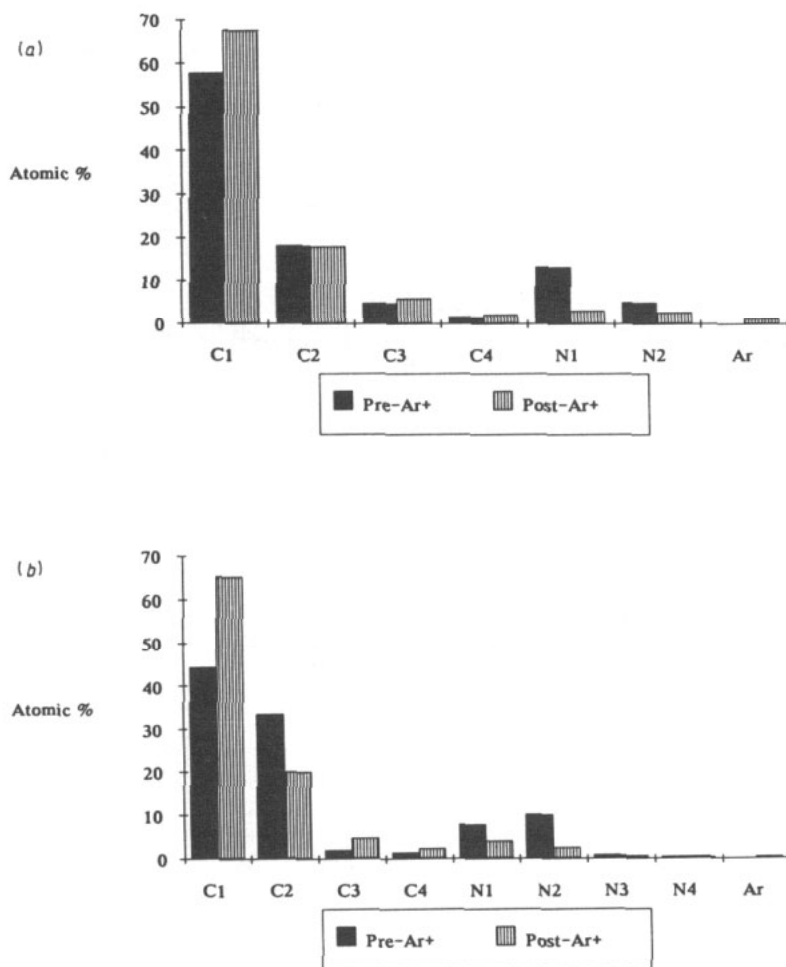
The XPS spectra of TAA before and after argon ion exposure are shown in figures 3(c) (C 1s) and 3(d) (N 1s). The TAA molecule contains 18 carbon atoms (10 hydrocarbon and 8 C-N type) and 4 nitrogen atoms (2 N-H and 2 aza). The C 1s region of TAA before bombardment exhibited two unresolved peaks (C1 and C2), where the lower binding-energy peak is due to the hydrocarbon-type carbon, and the higher binding-energy peak is due to the carbon atoms which are bonded to nitrogen atoms. Peaks C3 and C4 are shake-up satellites of C1 and C2 respectively.

The nitrogen 1s region of TAA is composed of two unresolved peaks (figure 3(d)), where the peak at lower binding energy is due to the aza nitrogen atoms (N1) and the peak at higher binding energy is due to the nitrogens bonded to hydrogens (N2). Here the shake-up satellites of N1 and N2 are observable (N3 and N4 respectively).

A histogram of the atomic percentages of each peak obtained by curve-fitting these



**Figure 3.** XPS spectra before (left) and after (right) exposure to argon ions. Top to bottom: (a) C 1s region of MfPc; (b) N 1s region of MfPc; (c) C 1s region of TAA; (d) N 1s region of TAA. (Curve-fitted peaks (left-right) C/N 1,2,3,4.)



**Figure 4.** Atomic percentages for (a) MIPc (top) and (b) TAA (bottom) before and after exposure to argon ions.

spectra is given in figure 4(b). Here the C1:C2 ratio is as expected, but N2 is slightly larger than anticipated.

It is clear from figures 3 and 4 that following  $\text{Ar}^+$  bombardment there was a considerable rise in the percentage of hydrocarbon-type carbon, a fall in the percentage of nitrogen and the appearance of a small but measurable quantity of argon. All peaks became broader (from about 1.2–1.6 eV FWHM), but the basic structures were still apparent. It is proposed, therefore, that the surface molecules were substantially damaged, leading to a thin layer composed mostly of amorphous carbon implanted with argon. If the amorphous carbon layer were only a few nanometres thick, then a signal from the underlying, undamaged material would be expected, but the peaks would be weaker and broader, as was observed here.

The electrical conductivities of all the films showed a dramatic increase upon  $\text{Ar}^+$  exposure, then fell exponentially immediately following bombardment. This exponential decay may have been due to the decay of free radicals. The bombardment

process has been reported to give rise to a large number of free radicals in the target material (Vareille *et al* 1981). The presence of these free radicals may have given an extra initial contribution to the enhanced conductivity, which decreased as they decayed. The electrical measurements reported here were performed on samples whose conductivities had reached a plateau (several days following the exposure).

The increase in the dark DC conductivity of a stabilized film compared with its pre-exposure value was approximately six orders of magnitude in each case. Some variation in the absolute values measured was noted between samples; this was probably due to discrepancies in the total ion dose received by each sample.

The dependence of the current on the temperature ( $T$ ) was found to follow the expression

$$I = I_0 \exp[-(T_0/T)^{1/4}] \quad (1)$$

where  $T_0$  is a constant obtained from the slope of the  $\ln I$  against  $T^{-1/4}$  plot.

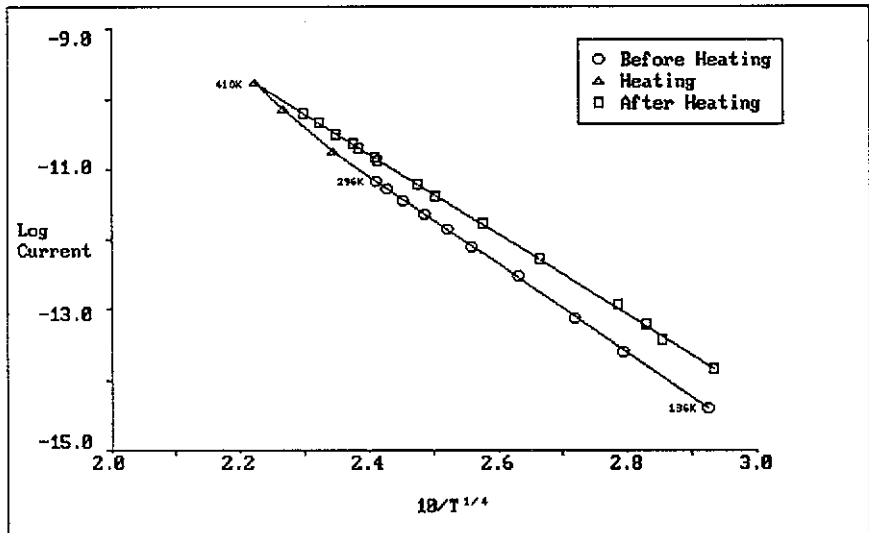


Figure 5.  $\ln I$  against  $T^{-1/4}$  plot for TAA.

A typical  $\ln I$  against  $T^{-1/4}$  plot is shown in figure 5, which shows the data obtained from a TAA film after  $Ar^+$  bombardment. Starting from room temperature, the sample was cooled, returned to room temperature, heated, returned to room temperature, cooled and then returned to room temperature. The initial cooling yielded a straight-line plot ( $T_0 = 2.5 \times 10^5$  K), but when the sample was heated to approximately 330 K the slope began to change, and on cooling was found to give a new value ( $T_0 = 1.8 \times 10^5$  K). Similar behaviour was found in all the films studied. The change in slope (giving a higher current at a given temperature) may have been due to an annealing effect, where a more ordered state was attained.

The  $T^{-1/4}$  dependence of  $\ln I$  found from the electrical measurements is consistent with conduction via a variable-range hopping mechanism (Mott 1969). This has been found previously in amorphous carbon (Hauser 1977), and thus supports the view that



Ar<sup>+</sup> bombardment of the samples resulted in the formation of a disordered carbon layer. The  $T^{-1/2}$  relationship found by Forrest *et al* (1982) and Kaplan *et al* (1984) was interpreted on the basis of a conducting grain model, in which charge carriers jump between grains embedded in a non-conducting matrix. However, some doubt has been cast on this interpretation (Elman *et al* 1985).

The calculations of Forrest *et al* (1982) showed that the 2 MeV Ar<sup>+</sup> ions used in their investigation penetrated the bulk of the target material and implanted in the substrate, so that damage was not confined to the surface region but was distributed throughout the bulk of the sample. In the work described herein, we used particles with a kinetic energy which was 0.005 of the magnitude of those used by Forrest *et al* (1982). This difference is reflected in the results that we have obtained.

The results of experiments involving the surface properties of the films (XPS, conductivity, reflectance UV and visible spectra) all exhibited change following Ar<sup>+</sup> bombardment, whereas the results of experiments involving the properties of the bulk of the films (transmission IR, UV and visible spectroscopy) remained unchanged.

### Acknowledgment

We would like to thank the SERC for the provision of the ESCALAB.

### References

- Abel J S, Mazurek H, Day D R, Maby E W, Senturia S D, Dresselhaus G and Dresselhaus M S 1982 *Mater. Res. Soc.; Symp. Proc.* **7** 173-9
- Badger C, Jones R and Laslett R 1964 *Aust. J. Chem.* **17** 1028
- Carter G and Grant W A 1976 *Ion Implantation of Semiconductors* (London: Edward Arnold)
- Eisen F H and Mayer J W 1976 *Treatise on Solid State Chemistry* ed N B Hannay (New York: Plenum)
- Elman B S, Sandman D J and Newkirk M A 1985 *Appl. Phys. Lett.* **46** 100
- Ewen R J and Honeybourne C L 1991 *J. Phys.: Condens. Matter* **3** S303-10
- Forrest S R, Kaplan M L, Schmidt P H, Venkatesan T and Lovinger A J 1982 *Appl. Phys. Lett.* **41** 708-10
- Foti G, Calcagno L and Puglisi O 1983 *Nucl. Instrum. Methods* **209** 87-96
- Hauser J 1977 *J. Non-Cryst. Solids* **23** 21
- Hiller H, Dimroth P and Pfitzner H 1968 *Justus Liebigs Ann. Chem.* **717** 137
- Kaplan M L, Forrest S R, Schmidt P H and Venkatesan T 1984 *J. Appl. Phys.* **53** 732-42
- Lever A B P 1965 *Adv. Inorg. Chem. Radiochem.* **7** 7
- Magee C W 1983 *Int. J. Mass Spect. Ion Phys.* **49** 211-21
- Mott M 1969 *Phil. Mag.* **19** 835
- Niwa Y, Kobayashi H and Tsuchiya T 1974 *J. Chem. Phys.* **60** 799
- Puglisi O, Marletta G, Torrisi A, Foti G and Torrisi L 1982 *Radiat. Eff.* **65** 11-16
- Vareille J C, Decossas J L, Moliton J P, Teyssier J L and Delaunay B 1981 *Solid State Nuclear Track Detect.; Proc. 11th Int. Conf.* ed P H Fowler and V M Clapham (Oxford: Pergamon) pp 59-63
- Venkatesan T, Feldman M, Wilkens B J and Willenbrock W E 1984a *J. Appl. Phys.* **55** 1212-4
- Venkatesan T, Forrest S R, Kaplan M L, Schmidt P H, Murray C A, Brown W L, Wilens B J, Roberts R F, Rupp L and Schonhorn H 1984b *J. Appl. Phys.* **56** 2778
- Wasserman B, Braunstein G, Dresselhaus M and Wnek G 1982 *Mater. Res. Soc.* **27** 423-8