# Organo-metallic interfaces studied by positron annihilation spectroscopy

2001 J. Phys.: Condens. Matter 13 1857

(http://iopscience.iop.org/0953-8984/13/9/309)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **13** (2001) 1857–1867 www.iop.org/Journals/cm PII: S0953-8984(01)18010-0

# Organo-metallic interfaces studied by positron annihilation spectroscopy

**C E Tucker**[1], **F A Smith**[1] **and P G Coleman**[2]

[1] Physics Department, Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK
[2] Department of Physics, University of Bath, Bath BA2 7AY, UK

Received 13 October 2000

## Abstract

The physical and electronic structures of simple Langmuir–Blodgett films ($\omega$-tricosenoic acid and 12–8 diacetylene) and the film/substrate interfaces have been investigated by Doppler broadening spectroscopy of annihilation radiation and positronium formation spectroscopy, following implantation of monoenergetic positrons in the energy range 0.02–30 keV. The annihilation parameters are sensitive to the insertion of the diacetylene group into an otherwise very similar film, and to polymerization of the film, but not to the presence of cadmium ions in the bulk films. The results suggest the presence of an interface state at which positrons annihilate lower-than-average-momentum electrons; one may cautiously conclude from results for monolayer films that the positron response to this state may be determined by the presence of cadmium ions as well as the nature of the substrate.

## 1. Introduction

There are many examples in which charge transport across an organic/metallic interface is fundamental to the performance of fast electronic devices. Sensitive radiation detectors, high-speed switching circuits and most opto-electronic devices all rely on rapid movement of charge across a potential barrier the height and width of which is determined by the disparate atomic or molecular structures in contact. A good deal of the activity in this field seeks to exploit the unique characteristics of Langmuir–Blodgett (LB) films. The present work forms part of a multi-spectroscopic investigation into some of the important factors that characterize the interface between LB films and commonly used metallic and semiconducting substrates.

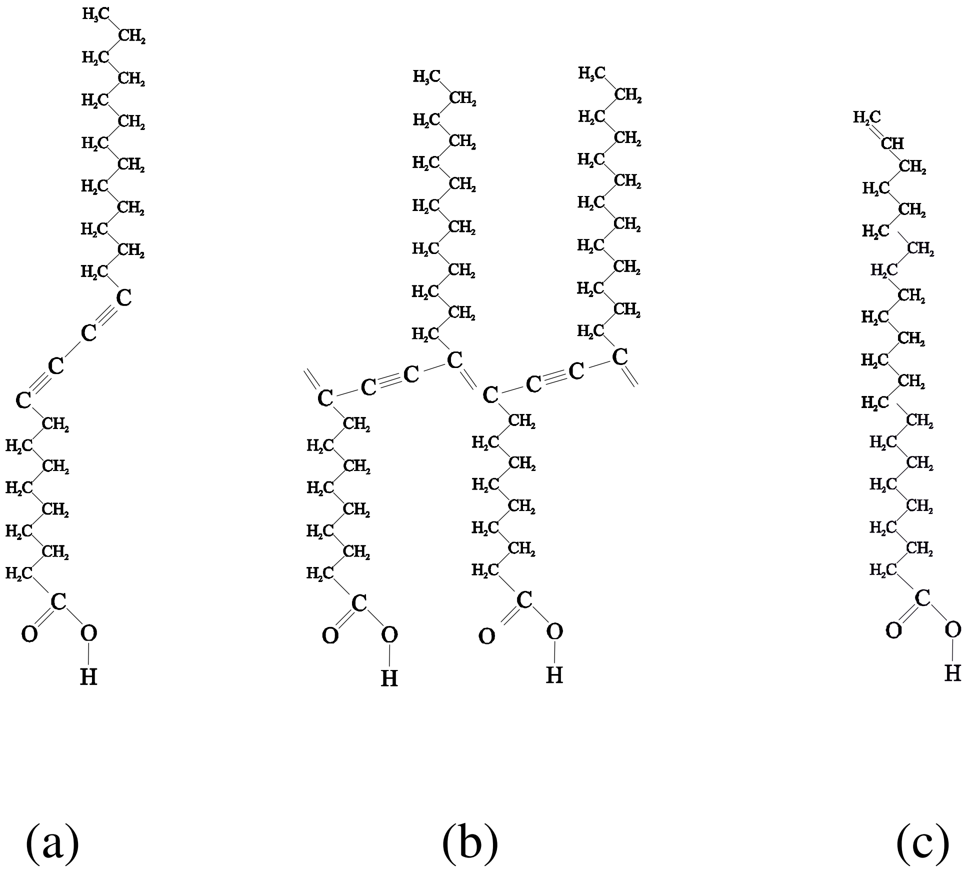
LB films are characterized by a well-ordered layer structure, the thickness of each layer being equal to the extended length of the molecule when its axis is normal to the substrate surface. In many cases, however, the axis can make an angle with the substrate. This depends upon both the molecular groups and the nature of the substrate involved in the attachment, as well as on the deposition surface pressure used in the transfer from the water sub-phase to the substrate. In the case of one of the films used in this study, $\omega$-tricosenoic acid [1], the angle can be as low as 68° for a surface pressure of 25 mN $m^{-1}$. For the purpose of characterizing the film/substrate combination, as in the present case, it is necessary to minimize any dependence

0953-8984/01/091857+11$30.00 Printed in the UK

on film fabrication conditions by using as high a surface pressure as possible in order to maximize the tilt angle with respect to the substrate.

Molecular packing within a layer is determined by the molecular groups forming the chain, as well as by the deposition surface pressure. In the case of a long-chain aliphatic molecule, the $CH_2$ group carbon atoms form a flat zigzag, the close-packed structure resulting from hydrogen atoms in a $CH_2$ group on one molecule fitting into depressions between the hydrogen atoms of adjacent molecules. Even here there are three possible close-packed structures involving the $C_2H_4$ repeat units that have similar packing densities: orthorhombic, monoclinic, and triclinic.

The molecular structures used in this study were as follows: (a) $\omega$-tricosenoic acid $[CH_2CH(CH_2)_{20}CO_2H]$, (b) monomer (12, 8) diacetylene $[(CH_2)_{11}CH_3C_4(CH_2)_7CO_2H]$, and (c) polymer (12, 8) diacetylene. The structures are represented in figure 1 and the various LB film/substrate combinations are summarized in table 1.



(a) (b) (c)

**Figure 1.** (a) Monomer (12–8) diacetylene. (b) Polymer (12–8) diacetylene. (c) $\omega$-tricosenoic acid. Each molecule contains twenty $CH_2$ groups and attaches to the substrate via the carboxyl group at its hydrophilic end. However, the nature of the inserted diacetylene group in (a) and (b) and its slight reorientation with respect to the molecular axis upon polymerization, the angle the molecular axis makes with the substrate, and the spatial extent of the $H_2C{=}CH$ group at the hydrophobic end of (c) combine to make films (b) and (c) thinner than (a) by ~10% when attached to the substrate.

**Table 1.** Combinations of film, sub-phase condition, and substrate used in this work. A feature common to all films is that the same group, COOH, is used to attach the film to the substrate.

| Langmuir–Blodgett film | Sub-phase condition | Substrate |
|---|---|---|
| (i) $\omega$-tricosenoic acid (1- and 19-layers) | (i) Pure water | (i) 2 $\mu$m gold |
| (ii) 2–8 diacetylene monomer (1-, 3-, 19-, and 49-layers) | (ii) Pure water with added $Cd^{2+}$ ions | (ii) $\sim$2 nm $SiO_2$ on 300 $\mu$m Si |
| (iii) 12–8 diacetylene polymer (1-, 3-, 19-, and 49-layers) | | (iii) etched Si (300 $\mu$m) |

The cogent reasons for using low-energy positrons to investigate these soft-condensed-matter systems are that they are sensitive both to the complex phase diagrams of the bulk film and to the specific attachment mechanisms that exist between the film and its substrate. Earlier studies of LB films by positron annihilation have shown the technique to be sensitive to chemical composition and to disorder resulting from heating and ion bombardment [2, 3]. The motivation for measuring the Doppler broadening of positron annihilation radiation from this range of samples has been threefold: firstly, to explore the influence on the chosen annihilation parameters of two different conditions of the sub-phase used in the preparation of the LB films; secondly, to investigate the dependence of the positron annihilation characteristics of three LB films that have different structural and electronic properties; thirdly, to assess the information that positron annihilation can provide about the interface between one of these films and three widely different substrates.

Films were formed on the chosen substrate using the Langmuir–Blodgett dipping technique, and data were taken from monolayers and from 3-, 19-, and 49-multilayers. Each layer of the 12–8 diacetylene monomer is $\sim$3 nm thick, and each layer of its polymer form is thinner by $\sim$10%. The $\omega$-tricosenoic acid monolayers are also $\sim$10% thinner than the 12–8 monomer. Organic films used in this study therefore range in thickness between $\sim$3 and $\sim$147 nm. Although theoretical descriptions of positron implantation profiles in such systems are expected to be unreliable, especially at the lowest energies used, they were nevertheless determined for a number of incident energies in order to make a comparison with the changes in the observed annihilation parameters.

## 2. Positron moderation, diffusion, and backscatter

The experimental systems under study have large differences in density across the interface (e.g. $\leqslant$1 g cm$^{-3}$ and 19.3 g cm$^{-3}$ for the LB film and the gold substrate, respectively). An incident positron will therefore experience moderation and diffusion in each of the two materials, together with significant backscatter from the substrate back into and through the organic film.

The application of fitting programs such as VEPFIT [4] or POSTRAP6 [5] to the measured annihilation parameters (see section 3.2) can lead to the association between the depth, via the energy of the incident positron, and the nature of the annihilation events. Knowledge of positron stopping profiles required as input to these programs is most reliably obtained from Monte Carlo computations for positron energies greater than $\sim$1 keV. The large investment in both labour and time in the execution of Monte Carlo computations has been circumvented, however, by the construction of scaling models that can account for the penetration into multilayer systems composed of different, but single, elements [6–8]. Adaptations to include the effects of backscatter at the interfaces between multilayers have yielded very acceptable agreement between experiment and the modelled positron annihilation parameters [6, 7]. The scaling procedure is less satisfactory when the layers contain a number of different elements, when there is a large positron backscatter fraction due to large differences in both atomic number and density at the interface, and also when there are effects of next-nearest interfaces [8]. These are all expected to be important considerations in the present work.

We have computed the fractions of implanted positrons stopping in LB film–substrate systems for films of 1 and 19 layers thickness, using the scaling formalism proposed by Ghosh [6] and by Aers *et al* [7], incorporating backscattering. We assume that the LB films have a mean atomic number $Z_{av}$ (=2.91) so that fitting parameters can be determined from the expressions given for monatomic materials. The resulting stopping fractions are presented in figure 2. While these fractions are useful in interpreting the experimental data presented in section 4, one must remember that (i) the theoretical formalism is not expected to be as appropriate at very low incident positron energies (and hence for the monolayer LB films), and (ii) positron diffusion between implantation and annihilation must be taken into account because the experimental data reflect the annihilation profile, rather than the stopping profile. We shall return to this last point later.

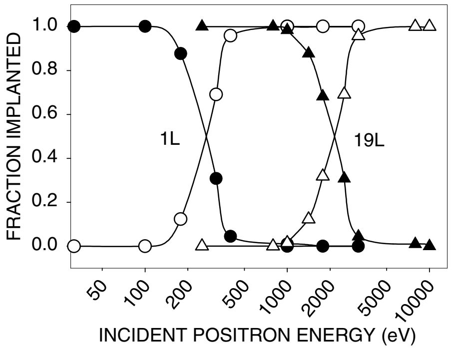


**Figure 2.** Fractions of positrons stopping in LB film (solid symbols) and gold substrate (open symbols) as a function of incident positron energy, calculated using the scaling formalism of references [5] and [7], including backscattering. Circles: monolayer. Triangles: 19 layers.

## 3. Experimental procedure

### *3.1. LB film preparation*

The film/substrate combinations of figure 1 and table 1 were prepared under standard clean-room conditions. In order to improve the adhesion and general quality of LB films having a carboxyl group at the hydrophilic end of the molecule, it is normal practice to add a cadmium salt ($10^{-3}$ M $CdCl_2$ with the pH adjusted to 6.3) to the pure-water sub-phase. These ions were always used in the preparation of the diacetylene films. Sufficiently stable films of $\omega$-tricosenoic acid could be prepared without the addition of $Cd^{2+}$ ions, however. All substrates could be considered to be infinitely thick apart from the untreated silicon that had a thin layer ($\leqslant$2 nm) of oxide. Treatment with concentrated HF acid was used to ensure the removal of all labile groups in forming the etched silicon surface.

### 3.2. *Positron beam line*

The beam line [9] was able to produce positrons having energies between 20 eV and 30 keV. A total flux of $\sim 5 \times 10^4$ positrons per second was incident on the sample surface within a spot size of 10 mm. This was much smaller than the size of the film samples, which were prepared on a $3'' \times 1''$ glass microscope slide. Annihilation photons were detected by a HPGe detector positioned at 90° to the incident beam and in line with the sample slide. The count rate in the detector at 511 keV was $\sim 650\ \mathrm{s}^{-1}$, so adequate statistics was achieved with counting times of 2000 s per energy point.

### 3.3. *Data analysis*

Recorded photon energies at the HPGe detector covered the range ∼380 keV to ∼520 keV. This permitted a lineshape analysis of the annihilation photopeak, centred at 511 keV, as well as a measurement of $3\gamma$ annihilations arising from the decay of ortho-positronium (o-Ps). The annihilation peak lineshape was characterized by the area ratios of the conventional shape parameters $S$ and $W$ [10]. The values of $S$ and $W$ are determined by the extent of Doppler broadening suffered by the peak, and therefore the electron momentum density at the annihilation sites and the amount of positronium formed. An indication of the ratio of $3\gamma/2\gamma$ annihilations, and hence the o-Ps formation fraction, was obtained by dividing the total valley counts by those in the photopeak, the former being determined from the integrated counts in the spectrum between the end of the Compton edge and the beginning of the photopeak (∼380 keV to ∼490 keV). We shall call this ratio the $F$-parameter. To check that electrostatic charging of the film did not lead to artifacts in the data collected, measurements were performed with and without the flooding of the samples by electrons from a nearby hot filament; no differences in the data collected under the two conditions were observed.

Positrons of energies $E$ in the range 20 eV to 30 keV were incident normally on the film/substrate structures. The parameters $W(E)$, $S(E)$, and $F(E)$ were measured; all tended to a constant value at the highest positron energies. It was therefore assumed that the parameters at $E \approx 30$ keV applied to the bulk of the substrate. Values at smaller energies were then normalized for each film/substrate combination to give, for example, $W(E)/W(30)$. It is these ratios that are plotted in the following figures. Figure 3 illustrates the greater sensitivity of the $W$-parameter over the $S$-parameter (by a factor of about 2), here for 1- and 49-layer monomer 12–8 diacetylene on gold. All subsequent data interpretation is therefore based only on the parameters $W$ and $F$.

## 4. Results and discussion

Different film thicknesses are used to investigate the sensitivity of positron annihilation spectroscopy to (i) sub-phase conditions, (ii) polymerization of monomer films, and (iii) changing the substrate.

### 4.1. *Comparison between films*

Figures 4(a) and 4(b) show the $W$-parameter for 3, 19, and 49 layers of monomer and polymer diacetylene, respectively. The measured parameters for the thicker films are considered truly to represent the ‘bulk’ values for the films, and demonstrate the positron’s sensitivity to polymerization. The three-layer value is lower for reasons which will be discussed below.

The normalized $W(E)$ for 19 layers of both forms remain largely constant up to 1 keV. The fact that this result is in agreement with the simulation of figure 2, which predicts that at

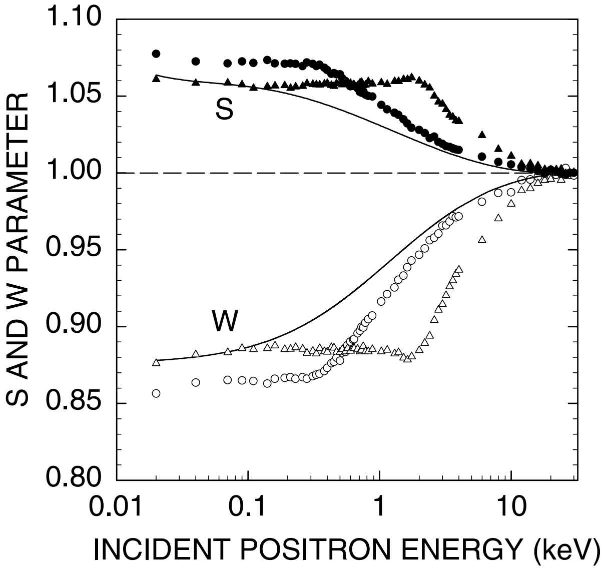


**Figure 3.** The parameters $W$ and $S$ for 3 and 49 layers of diacetylene film on gold, normalized to the bulk gold values at 30 keV. Solid curves are fits to the data for the bare gold substrate. Circles: 3 layers; triangles: 49 layers.

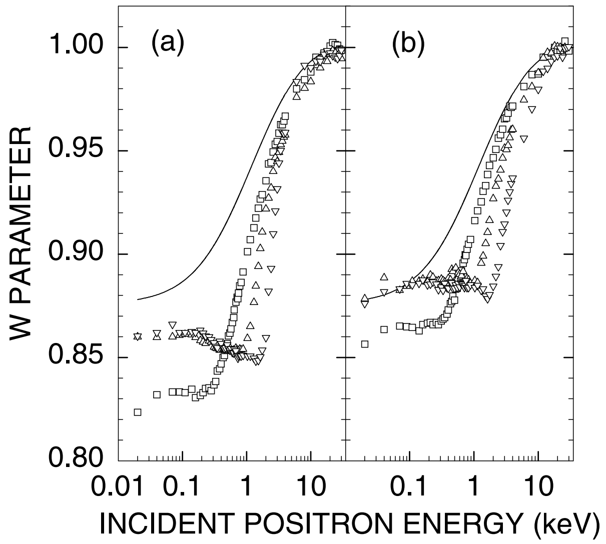


**Figure 4.** $W(E)$ for 3, 19, and 49 layers of (12–8)-diacetylene on a gold substrate. (a) monomer, (b) polymer. □: 3 layers; △: 19 layers; ▽: 49 layers. Solid curves: fits to data for the bare gold substrate.

these energies all of the incident positrons are stopped in the film, implies that the effects of post-implantation diffusion are not significant.

The sharpness of the onset of the increase in $W$ above 1 keV, and the visible presence of a dip in some of the data indicate the presence of an interface state with a lower characteristic

$W$-parameter. Diffusion to this interface through the film is considered to be a contributory factor in producing the lower $W$-values for the three-layer monomer and polymer films. Figure 5 shows the data for 49-layer polymer diacetylene together with a fit by the program VEPFIT. The fit assumes an interface region between 147 and 150 nm and an interface $W$-parameter of 0.825; a variety of other combinations of interface width and $W$-value would give equally good fits, but would not change the interpretation. This low value of $W$ indicates that at the interface the positrons are annihilating lower-momentum electrons. Fitted diffusion lengths in the film and substrate, $\sim 10^1$ nm in both, are consistent with the observation of lower characteristic $W$-parameters for the 9 nm thick three-layer films (0.83 for the monomer and 0.865 for the polymer), and higher values for the thicker films (0.86 for the monomer and 0.885 for the polymer). It is noticeable that the decrease in $W$ begins in the thicker monomer films at $\sim$0.2 keV (figure 4(a)) but not until $\sim$0.7 keV in the polymer (figure 4(b)) where the effect of the polymerization across the molecular axis might be expected to reduce the diffusion length even further.

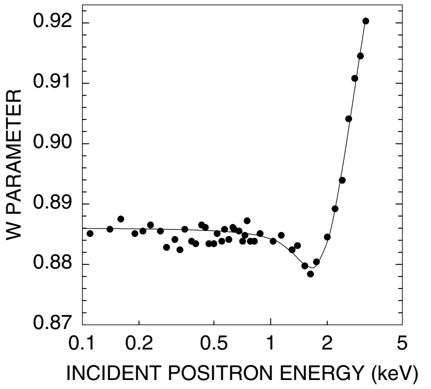


**Figure 5.** $W(E)$ for 49 layers of polymer (12–8) diacetylene on gold. Solid line: the fit using VEPFIT. The dip at 1.75 keV indicates the presence of an interface state (see the text).

Figure 6 shows $W(E)$ for 19 layers of all films described in table 1, on a gold substrate. Since all of the films attach to the substrate via the COOH group at the hydrophilic end of the molecule, the observed differences in $W$ can be interpreted in terms of three important variables: (a) the role of the $Cd^{2+}$ ion as a mediator of binding to the substrate; (b) the presence of the diacetylene group in a molecule otherwise similar to $\omega$-tricosenoic acid; and (c) the influence of the conjugation of this group when the polymerized film forms a double-bond link that creates an easy conduction path normal to the molecular axis.

Positron annihilation spectroscopy appears to be sensitive to the insertion of the diacetylene group into an otherwise very similar LB film, and to the polymerization of the film. This indicates the positron's ability to probe a very delocalized electron system.

The mechanism of bonding at the interface is assumed to result from the incorporation of a single $Cd^{2+}$ ion for every two carboxyl (head) groups at the interface between film and substrate, and is understood to entail the involvement of oxygen $\pi$-bonding orbitals with those of the $Cd^{2+}$ ions [1]. Although these ions are also present at the carboxyl group interfaces within the bulk of multilayer films, the $\omega$-tricosenoic acid data in figure 6 do not exhibit any sensitivity to the existence of the $Cd^{2+}$ ions, either at the interface or in the bulk of the 19-layer (and probably also the 49-layer) films. We believe that the wide variations in measured $W$-parameters for the one- and three-layer films (see below) can be attributed to factors other

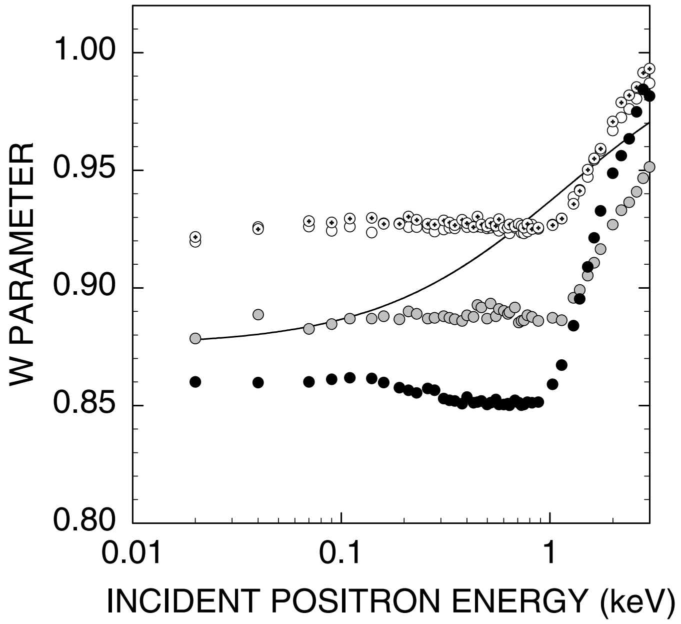


**Figure 6.** $W(E)$ for 19 layers of all three films studied on gold substrates. ○: $\omega$-tricosenoic acid—pure-water sub-phase; ⊕: $\omega$-tricosenoic acid—added $Cd^{2+}$ ions; shaded circles: polymer (12, 8) diacetylene—added $Cd^{2+}$ ions; ●: monomer (12, 8) polydiacetylene—added $Cd^{2+}$ ions. Solid curve: the fit to the data for a bare gold substrate.

than the presence or absence of $Cd^{2+}$ ions at the interface. Therefore, although we can state categorically that there is no measurable response to the presence of $Cd^{2+}$ ions between the adjacent head groups within the bulk of the films, no firm conclusions can be drawn about the ions at the interface.

### *4.2. Monolayer films*

$W$-parameter values for all monolayer films studied, on gold, silicon with native oxide, and passivated (HF-etched) silicon substrates, are shown in figure 7. All parameters are divided by the bulk $W$-value for gold, for direct comparison, as is the bulk value for silicon. Although the energy dependence of $W$ appears to be broadly consistent with the predictions of figure 2, rising from an almost constant value at $E \sim 100$ eV, the proximity of the vacuum and substrate interfaces means that positron migration to either is very likely, and the $W$-values cannot be assigned unambiguously to the 'bulk' monolayer films. This situation is exacerbated by the probable non-thermalization of a high percentage of the positrons with $E$ at or below 100 eV, further increasing their effective diffusion length. Marek *et al* [2] reported that films grown using a pure-water sub-phase were unstable in vacuum; this may have affected the present results to some extent, but measurements at low positron energies were taken within a few hours of mounting the samples in vacuum, so little desorption is expected. Even bearing in mind all of these factors, the results of figure 7 do suggest that the $W$-parameter is sensitive to the structure of the film, to polymerization, to the sub-phase used (indicating that, although the presence of $Cd^{+}$ ions in the bulk films does not affect the positron response, this may not be the case with regard to the interface state), and to the nature of the substrate; the uncertainties referred to above, however, preclude further interpretative discussion.

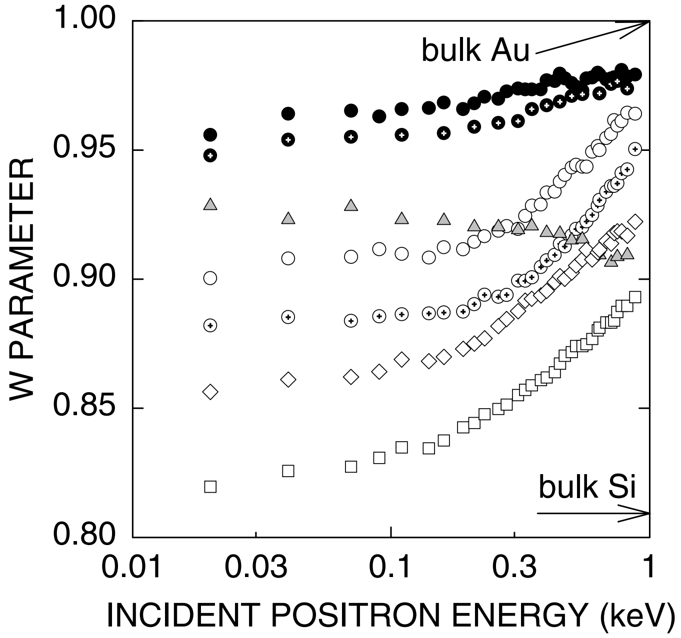


**Figure 7.** $W(E)$ for monolayer LB films on gold and silicon substrates. ●: $\omega$-tricosenoic acid on Si/SiO$_2$—pure-water sub-phase; full crossed circles: $\omega$-tricosenoic acid on Si/SiO$_2$—added Cd$^{2+}$ ions; shaded triangles: $\omega$-tricosenoic acid on passivated Si; ○: $\omega$-tricosenoic acid on Au—pure-water sub-phase; ⊕: $\omega$-tricosenoic acid on Au—added Cd$^{2+}$ ions; ◇: monomer (12, 8) diacetylene—added Cd$^{2+}$ ions; □: polymer (12, 8) polydiacetylene—added Cd$^{2+}$ ions.

### *4.3. Positronium formation*

Figure 8 shows $F(E)$ for 19-layer 12–8 diacetylene and $\omega$-tricosenoic acid films on gold, and that for the bare gold substrate. Recalling that $F$ is associated with the fraction of incident positrons which form o-Ps, and that this only occurs at the surface of gold, one expects to see an increase in $F$ for the substrate as $E$ decreases and an increasing fraction of implanted positrons return to the surface. The increased values of $F$ for the film-covered surfaces point to additional o-Ps formation, possibly at the vacuum interface but probably mostly in the bulk of the films. Figure 8 demonstrates that $F$, like $W$, is sensitive to the structure of the films, but not to the presence of Cd$^{2+}$ ions. (The detection of annihilation radiation from ortho- and para-Ps decays directly affects the values of $W$.) The enhancement in Ps formation in LB films above that for the substrates alone was observed for all of the films studied.

## 5. Conclusions

Positron annihilation measurements have been made on film/substrate systems produced with different combinations of LB molecules and solid substrate surfaces having widely different electronic and structural characteristics. Positron annihilation lineshape and $3\gamma/2\gamma$ ratio parameters ($W$ and $F$, respectively) have been determined for each combination, and stopping profiles calculated using the scaling techniques of Ghosh [6] and Aers *et al* [5, 7, 8] were

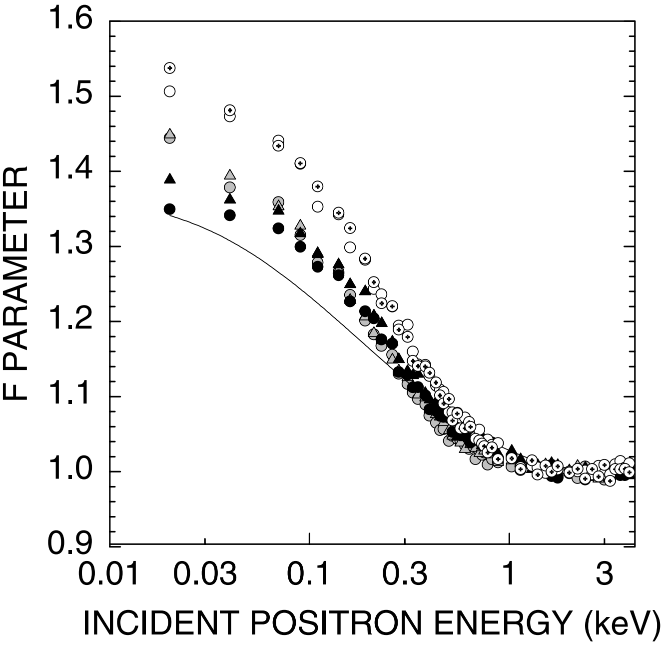


**Figure 8.** $F(E)$ for LB films on Au. ○: 19 layers of $\omega$-tricosenoic acid on Au—pure-water sub-phase; ⊕: 19 layers of $\omega$-tricosenoic acid on Au—added $Cd^{2+}$ ions; shaded circles: 19 layers of polymer (12, 8) polydiacetylene; shaded triangles: 49 layers of polymer (12, 8) polydiacetylene; ●: 19 layers of monomer (12, 8) diacetylene; ▲: 49 layers of monomer (12, 8) diacetylene.

found to be consistent with the data. Measurements of both $W$- and $F$-parameters on the same system have allowed the observation of Doppler broadening and the formation of o-Ps in the films. There are significant differences between the parameters associated with the bulk properties of the three different films used on the same substrate. The data provide evidence of a film–substrate interface state at which lower-momentum electrons are annihilated, but there is no firm indication that this state exists only for those films with $Cd^{2+}$ ions present at the interface. Further research is clearly warranted, but these first measurements already indicate that positron and positronium annihilation spectroscopies have the potential to provide useful information on the structural and electronic properties of LB films and the interfaces between them and solid substrates.

## Acknowledgments

The authors are grateful to Professor E G Wilson for the provision of clean-room facilities, and to Dr R Sudiwala and Dr K Scott for technical assistance and advice. Also, we acknowledge the financial support for CET during the early stages of the work from contract F13P-CT920027 of the European Community.

## References

[1] Petty M C 1996 *Langmuir–Blodgett Films: an Introduction* (Cambridge: Cambridge University Press)
[2] Marek T, Szeles C, Suvegh K, Kiss E, Vertes A and Lynn K G 1999 *Langmuir* **15** 8189

[3] Asai K, Koshimizu M, Ishigure K, Iwai T, Shibata H and Ito Y 1998 *Proc. Int. Riken Workshop on Advanced Techniques of Positron Beam Generation and Control*

[4] van Veen A, Schut H, de Vries J, Hakvoort R A and Ijpma M R 1990 *Positron Beams for Solids and Surfaces (AIP Conf. Proc. No 218)* ed P J Schultz *et al* (New York: AIP) p 83

[5] Aers G C, Jensen K O and Walker A B 1994 *Slow Positron Beam Techniques for Solids and Surfaces* ed E H Ottewitte and A H Weiss (New York: AIP) p 13

[6] Ghosh V J 1995 *Appl. Surf. Sci.* **85** 187

[7] Aers G C, Marshall P A, Leung T C and Goldberg R D 1995 *Appl. Surf. Sci.* **85** 196

[8] Aers G C 1994 *J. Appl. Phys.* **76** 1622

[9] Chilton N B and Coleman P G 1995 *Meas. Sci. Technol.* **6** 53

[10] MacKenzie I K 1983 *Positron Solid State Physics* ed W Brandt and A Dupasquier (Amsterdam: North-Holland) p 196