

Correlation between Lewis donor/acceptor properties determined by XPS and Brönsted acid/base properties determined by rest-potential measurements, for aluminium and silicon oxides

M. CASAMASSIMA, E. DARQUE - CERETTI

Ecole des Mines de Paris, CEMEF, Sophia Antipolis, F-06560 Valbonne, France

A. ETCHEBERRY, M. AUCOUTURIER*

*Laboratoire d'Electrochimie Interfaciale, and *Laboratoire de Physique des Solides, CNRS, - 1 pl. A. Briand, F - 92195 Meudon Cedex, France*

In order to qualify the reactivity of various aluminium and silicon oxide substrates for elastomer adhesion applications, X-ray photoelectron spectroscopy (XPS) and rest-electrochemical potential measurements have been performed on those surfaces. The interpretation of XPS binding energy shift measurements in terms of Fermi level variation from one surface to another, as proposed by Mullins and Averbach in 1988, is discussed in view of results on an aluminosilicate compound surface. The correlation with electrochemical rest-potential measurements on an anodized aluminium surface and a silane coupling agent is described and discussed. The possibility of surface reactivity assessment through correlated XPS and electrochemical measurements for metal oxides is demonstrated.

1. Introduction

The acid/base properties of a surface, described with a view to the prediction of interfacial bonding for instance in adhesion [1], may be defined either from the point of view of electronic exchange (Lewis definition) or from the point of view of its ability to react with H^+ or OH^- ions (Brönsted definition). Both definitions may be relevant for the prediction of adhesion mechanisms, depending on the type of interactions implied in the adhesive bond [2]: electrostatic charge transfer, polarization, or electron exchange interactions. A comprehensive description of all these interactions would require a complete knowledge of the electronic (and chemical) structure of the first atomic (or molecular) layer of both adhesion partners. Although sometimes modelled through *ab initio* computation [3] and evidently only for perfectly pure compounds, the theoretical and experimental knowledge of the superficial layer electronic and chemical structure is a difficult problem.

X-ray photoelectron spectroscopy (XPS) is a powerful tool to investigate the electronic structure [4] and acid/base reactivity [5], but because it is performed under a high-vacuum environment, the results obtained through this technique may not be representative of the actual surface involved in the adhesion process itself. On the other hand, *in situ*

characterization gives only partial information; for instance, electrochemical or titration measurements give access to information on the Brönsted acidity/basicity; the most common is the point of zero charge (p.z.c.) defined as the pH of the solution in chemical equilibrium with the surface in its neutralized state through adsorption of H^+ and/or OH^- ions.

In the particular case of an oxide, it has been proposed that a correlation should exist between the electronic donor/acceptor behaviour of the surface (i.e. Lewis acidity/basicity) and its Brönsted acid/base behaviour (e.g. p.z.c.). Such a correlation has been demonstrated [6, 7] through Fermi energy determination by XPS, and through p.z.c. measurements for aluminium, silicon and magnesium oxide powders. For flat surfaces of massive oxides, the experimental determination of p.z.c. is generally impossible, and we showed in a previous paper [8] that electrochemical rest-potential measurements in aqueous solution could be, at least for anodic aluminium oxides, a convenient means to estimate the Brönsted acid/base properties of such an oxide surface. In the same paper, we confirmed the interpretation proposed by Mullins and Averbach which assumes that the O_{1s} binding energy shift measured by XPS on aluminium, magnesium or silicon oxide surfaces is due to surface variation of the Fermi level of the oxides and can be thus considered as

an indicator of the Lewis donor/acceptor behaviour of the surfaces. The correlations between the Lewis donor/acceptor behaviour obtained by XPS measurements and the Brønsted acid/base behaviour obtained through electrochemical rest-potential measurement have been established.

The aim of the present work was to point out some interpretation problems raised by the preceding results, to present further experimental results, which clarify some of those problems, and to discuss the obtained acid/base classification in view of recent literature publications [2, 9].

2. XPS determination of Fermi level shifts on aluminium and silicon oxide surfaces

The XPS measurements were conducted on a series of industrial or laboratory specimen surfaces (Table I). The specimens can be divided into two series. The first series contains oxides with Al–O bonds: aluminium specimens anodized under various conditions (A, B, C, D, E), an Al₂O₃ monocrystal (O) and an industrially sintered Al₂O₃ specimen (F). The second series is constituted of oxide surfaces with Si–O bonds: the two different faces of a floating glass (G, H), an optical microscope slide (I), an anodized aluminium specimen coated with a silane coupling agent (J), a silica aerogel (K) and a pure SiO₂ layer obtained by oxidation of electronic silicon (L).

The binding energies of O_{1s}, Al_{2p} and Si_{2p} photoelectrons were measured in a Riber Mac II XPS spectrometer following a procedure of energy calibration and irradiation delay which avoids charging effects as much as possible [8]. For O_{1s} signals, the position of the peak centroids is considered rather than the maximum position to take into account all oxidized species on the surface. Results are presented in Fig. 1, showing the variation of the energy position of the O_{1s} peak as a function of the energy position of the cation peak, for each specimen series. A good alignment of the experimental points on straight lines with a slope of 1 is obtained; this validates the hypothesis that the binding energy shifts measured on oxygen

and on the cation are due to a shift of the Fermi energy of each specimen, as proposed by Mullins and Averbach [7] and explained in our previous paper

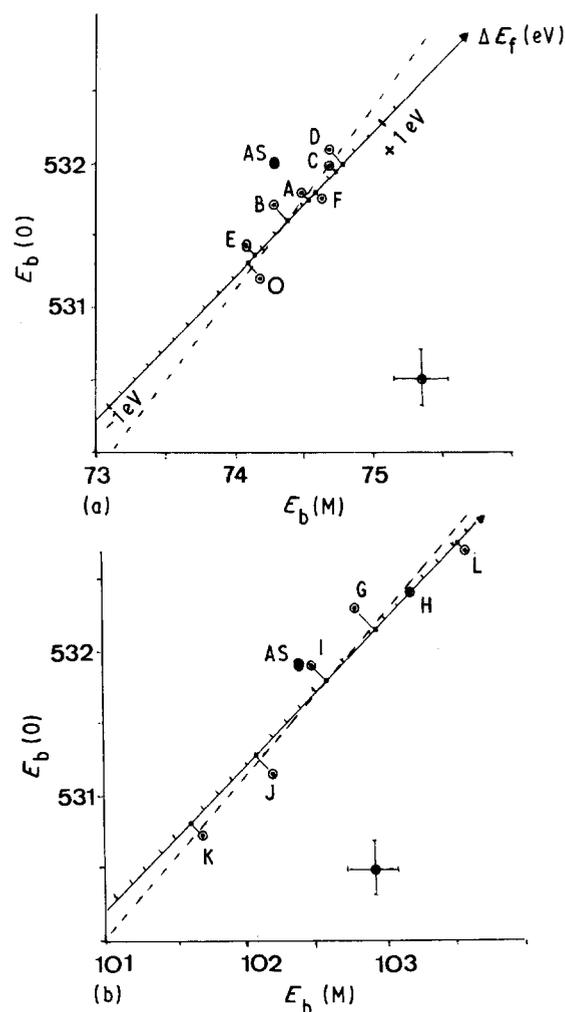


Figure 1 $E_b(O)$ versus $E_b(M)$ diagrams for both oxide families and determination of the Fermi energy. (○) Experimental points, (---) least square linear regression, (—◆—) points projected on the straight line of slope = 1. The uncertainties are indicated by the cross on the bottom right of each diagram. The letters refer to Tables I and III. The aluminosilicate sample (● = A S) appears in both diagrams. (a) Oxides of the Al–O bond family; (b) oxides of the Si–O bond family.

TABLE I Classification of the oxide surfaces, XPS binding energy for O_{1s} and relative variations of the Fermi energy extracted from Fig. 1

	$E_b(O_{1s})$ (eV)		ΔE_f (eV)	Uncertainty (eV)	
Surfaces with Al–O bonds	O	Alumina monocrystal	531.2	0 (reference)	–
	E	Chromic anodization	531.4	+ 0.05	± 0.25
	B	Sulphuric anodization sealed	531.7	+ 0.30	± 0.30
	A	Sulphuric anodization	531.8	+ 0.45	± 0.25
	F	Massive alumina	531.7	+ 0.50	± 0.25
	C	Phosphoric anodization	532.0	+ 0.65	± 0.25
	D	Sulphuric anodization (excess sulphur)	532.0	+ 0.70	± 0.30
Surfaces with Si–O bonds	K	Silica aerogel	530.7	– 1.95	± 0.30
	J	Silane coupling agent	531.1	– 1.45	± 0.30
	I	Microscope slide	531.9	– 0.95	± 0.30
	G	Floating glass - tin face	532.2	– 0.60	± 0.35
	H	Floating glass - atmospheric face	532.4	– 0.30	± 0.20
	L	Pure silica	532.7	0 (reference)	–

(the Fermi energy, E_f , is defined as the difference between the energy of the Fermi level and the top edge of the valence band).

This energy shift of the Fermi level, among the specimens of each family may be estimated if one considers that the straight lines of slope = 1 are Fermi energy scales. This has been done in Table I: the Fermi level shift is reported in comparison with a reference in each case; this reference is the Al_2O_3 monocrystal (O) for the Al–O family, and the pure SiO_2 layer (L) for the Si–O family.

3. Electrochemical determination of the acid/base behaviour of Al_2O_3 surfaces

The charge state of aluminium oxide surfaces immersed in an aqueous solution has been characterized by systematic measurements of the electrochemical rest-potential, or open-circuit potential, (E_0), in solutions with various pH. This potential is, in the absence of any specific interactions with the solution, a direct consequence of the structure of the electrical double layer built on the surface in contact with the solution [8, 10].

Fig. 2 shows the results of the variations of E_0 with pH for specimens of the Al–O family (A, B, C, D). (The results on the silane coupling agent, J, are also presented, Fig. 2e, and will be discussed in Section 4.2.)

It appears that inside the pH range of chemical stability of each oxides, the rest-potential values fol-

low laws of the type: $E_0 = -0.06 \text{ pH}$, indicating a "Nernstian" behaviour of the surface, i.e. a behaviour controlled by H^+/OH^- exchanges with the aqueous medium. Thus, the E_0 value for a given pH appears to be a valuable parameter to define the H^+/OH^- equilibrium state for each surface, i.e., its Brönsted acidity/basicity. Table II shows how the E_0 versus pH straight lines are shifted with respect to each other, either from the E_0 axis or from the pH axis point of view.

It is interesting to compare this shift, expressed in pH values, with the p.z.c. values estimated for the same oxide surfaces. In order to obtain these estimated p.z.c. values, the following procedure was applied. The Fermi level shifts for the Al–O family from Table I have been quantified (Table II), considering that the reference specimen (i.e. O, monocrystalline Al_2O_3) has a Fermi energy equal to 3.6 eV in agreement with Mullins and Averbach [6, 7] and with the value of the band gap (7–7.2 eV) given in the literature [11]. The experimental relation proposed by Mullins between the Fermi energy and the p.z.c. [6] was then applied, and estimated values of the p.z.c. can be proposed. The data obtained are listed in Table III. The pH shifts of the E_0 versus pH lines follow the same classification as the estimated Fermi energies and p.z.c. values.

4. Discussion and complementary results

4.1. Lewis acidity/basicity scale

From the preceding results, it has been possible, for each family of oxide surfaces, Al–O family or Si–O family, to propose a classification of their acid/base behaviour from the Lewis point of view. The XPS data could be interpreted, inside a given family, in terms of the position of the Fermi level inside the band gap: the

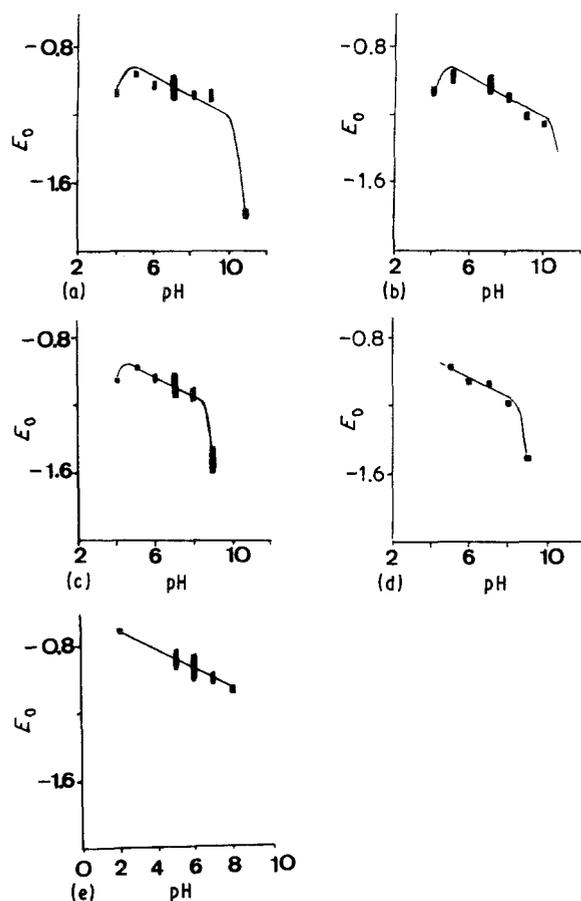


Figure 2 Rest potential, E_0 (V/MSE), versus solution pH relationships for specimens, (a) A, (b) B, (c) C, (d) D, (e) J.

TABLE II Relative position of the $\Delta E_0 = -0.06 \Delta \text{pH}$ straight lines

	E_0 values for pH = 7 (average) (V/MSE)	pH values for $E_0 = -1.00 \text{ V}$ (average)
A	-1.050 V	6.2
B	-1.050 V	6.2
C	-1.100 V	5.4
D	-1.100 V	5.4

TABLE III Comparison of the pH shift at given rest potential, E_0 , with the E_f values (with reference to alumina O: $E_f = 3.6 \text{ eV}$) and the p.z.c. values obtained by the experimental E_f versus p.z.c. relation of [6]

	pH values for $E_0 = -1.00 \text{ V}$	E_f (eV) referred to alumina O	p.z.c.
B	6.2	3.9	6.6
A	6.2	4.05	6.2
C	5.4	4.25	5.6
D	5.4	4.3	5.5

larger the Fermi energy of a surface, the more pronounced is the electron acceptor behaviour with respect to the environment. For instance, the anodic oxides are more electron acceptor (more acidic from the Lewis point of view) than the alumina monocrystal, or the pure silica is more acceptor (more acidic) than the silica aerogel or all the silicate floating glasses. The problem is now to appreciate if the acidity scales obtained for the two oxide family can be compared with each other.

Mullins and Averbach [6, 7] considered that this was possible. Their approach was based on the assumption that the oxides of the different families have an equivalent band structure [12, 13] ("rigid band model") (Fig. 3a), thus the experimental $E_b(O)$ shift between the different oxides must again be interpreted only in variations of Fermi energy variations. On the other hand, other authors [14] consider that simultaneous shift of $E_b(O)$ and $E_b(M)$, between the different oxides, should be interpreted through variation of the electronic density in the valence band of the oxides (Fig. 3b). Incidentally, it may be interesting to compare, in the $E_b(O)$ versus $E_b(M)$ diagram, the binding energies reported in Table II for Noller *et al.*'s paper [14] for a family of Mg–O type oxides: these also strictly follow a proportional law with a slope of 1.

Although the consequences of both interpretations (Fermi energy shift or electronic structure variation) are in the same trend (a larger acidic behaviour for a larger $E_b(O)$), it is important to try to appreciate their respective validity. For this purpose, an aluminosilicate (i.e. an oxidized mineral compound containing both Al–O and Si–O bonds) has been investigated by XPS through the same procedure as the other specimens. The results obtained for this specimen are added to Fig. 1 (point AS). They agree reasonably with the other results. The agreement is better with the oxides of the Si–O family than with the oxides of the Al–O family. One reason for the discrepancy with the Al–O

family could be that the coordination of aluminium in the aluminosilicate is different from its coordination in Al_2O_3 specimens: theoretical studies [13] indicate that the four-coordination of aluminium (AlO_4^{2-}) is not stable in pure alumina (which exhibits preferably the six-coordination AlO_6^{3-}) but can be stable in aluminosilicates. Thus, the aluminosilicate is more comparable, from the electronic structure point of view, to the silicates, which are also four-coordinates (SiO_4^{4-}), than to the alumina specimen.

This would mean, in the course of the present discussion, that the shift of $E_b(O)$ binding energy, between the Al–O and the Si–O families, could be partly attributed to a "structural" shift, i.e. an actual variation of the electronic structure of the valence band in agreement with Noller *et al.* [14], and partly attributed to a variation of the Fermi energy, as proposed by Mullins and Averbach [6, 7]. Considering the uncertainties of the experimental XPS measurements, it would be hazardous to quantify the respective value of each contribution. From the results obtained with the aluminosilicate, one may estimate that the "structural" contribution is not more than 0.5 eV.

With those interpretative restrictions, and thus as a first approximation, a general acidity–basicity scale may be proposed for all the specimens (Table IV). Because it is necessary to choose a reference value for the Fermi energy, the scale of Table IV is calculated by attributing arbitrarily the value $E_f = 3.6$ eV for pure monocrystalline Al_2O_3 , as explained in Section 3. It must be noticed that, by taking this reference, one obtains for pure silica a Fermi energy of 5.05 eV, also in agreement with the band gap of this compound, given by the literature as equal to 9–10 eV [11].

4.2. Brönsted acidity–basicity scale p.z.c. scale and correlations

Taking into account the preceding discussion, it becomes legitimate to extend the p.z.c. scale already proposed for the Al–O family (Table III) to the complete set of oxide surfaces. The p.z.c. values of the Si–O oxides are estimated by the same procedure: the experimental relation between E_f and p.z.c. proposed by Mullins [6] is applied to the E_f values of Table IV. The obtained p.z.c. scale is reported in Table V.

It has already been mentioned that the Lewis acidity–basicity scale obtained by XPS measurements and the Brönsted acidity–basicity scale obtained by rest-potential measurements coincides for the Al–O oxides (Section 3). It has been possible to measure the rest-potential, E_O , variation with pH for one specimen of the Si–O family: the silane coupling agent layer (J). This layer exhibits a "Nernstian" behaviour (Fig. 2e), which is independent of the substrate on which it is coated. The rest-potential for pH = 7 is, $E_O = -1.000$ V. With a Fermi energy of 3.6 eV (Table IV) and a deduced p.z.c. of 7.5, the silane coupling agent then appears to be well within both Lewis and Brönsted acidity–basicity scales. This correctly correlated position of the silane in both scales is thus a confirmation of the validity of the proposed interpretation of

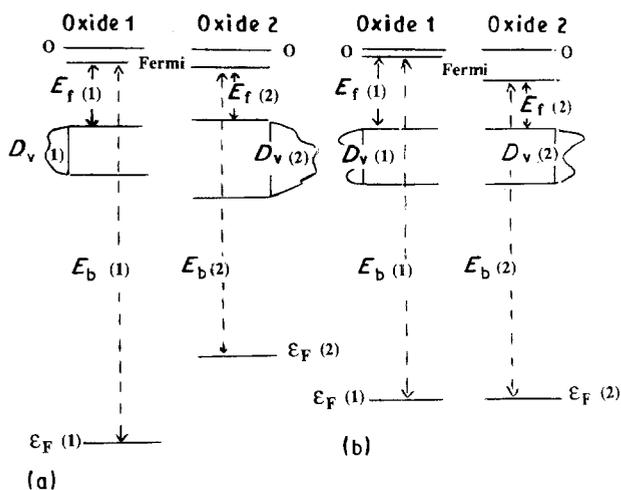


Figure 3 Interpretation of the measured binding energy variations. D_v = state density of the valence band, ϵ_F = Hartree-Fock potential. (a) General case: potential model of the "chemical shift": $E_b(1) > E_b(2)$, $D_v(1) < D_v(2)$, $\epsilon_F(1) > \epsilon_F(2)$. (b) Rigid band model: $E_b(1) > E_b(2)$, $D_v(1) = D_v(2)$, $\epsilon_F(1) = \epsilon_F(2)$, $E_f(1) > E_f(2)$

TABLE IV General classification of the studied oxide surfaces and relative variations of the Fermi energy, with only one reference (alumina O)

Surfaces	Type	ΔE_f (eV)	Uncertainty (eV)	E_f (eV) reference: O	
K	Silica aerogel	Si-O	- 0.50	\pm 0.30	3.1
O	Alumina monocrystal	Al-O	0	-	3.6
J	Silane coupling agent	Si-O	0	\pm 0.30	3.6
E	Chromic anodization	Al-O	+ 0.05	\pm 0.25	3.6
B	Sulphuric anodization-sealed	Al-O	+ 0.30	\pm 0.30	3.9
A	Sulphuric anodization	Al-O	+ 0.45	\pm 0.25	4.05
AS	Alumino silicate	Al-O	+ 0.45	\pm 0.30	4.05
		Si-O			
F	Massive alumina	Al-O	+ 0.50	\pm 0.25	4.1
I	Microscope slide	Si-O	+ 0.50	\pm 0.30	4.1
C	Phosphoric anodization	Al-O	+ 0.65	\pm 0.25	4.25
D	Sulphuric anod. excess sulphur	Al-O	+ 0.70	\pm 0.30	4.3
G	Floating glass-tin face	Si-O	+ 0.85	\pm 0.35	4.45
H	Floating glass-atmospheric face	Si-O	+ 1.10	\pm 0.20	4.7
L	Pure silica	Si-O	+ 1.45	\pm 0.25	5.05

TABLE V Estimation of p.z.c. scale from the E_f scale of Table IV and the E_f versus p.z.c. correlation of Mullins and Averbach [6]

Specimen	p.z.c. (pH units)
K	8.9
O	7.5
J	7.5
E	7.4
B	6.6
A	6.2
AS	6.2
F	6.1
I	6.1
C	5.6
D	5.5
G	5.0
H	4.3
L	3.3

the whole set of results. The coincidence between both scales may be confirmed by comparing the E_f shifts of the Al-O and silane specimens to the rest-potential shifts at a given pH (Fig. 4) : The correlation is obviously observed.

5. Conclusions

This study on aluminium and silicon oxide surfaces was aimed at characterizing their electron donor/acceptor behaviour and their acid/base properties in aqueous solutions and to correlate both approaches. The following conclusions may be drawn.

1. Estimation of the electron donor/acceptor properties through XPS measurements of the binding energy shift for the anion and the cation can be done with reasonable accuracy, assuming that those shifts are, in this particular case, due to variations of the Fermi energy level of the surfaces.

2. The Lewis donor/acceptor scale obtained by this procedure can be correlated with the Brönsted acid/base scale established by measurements of the

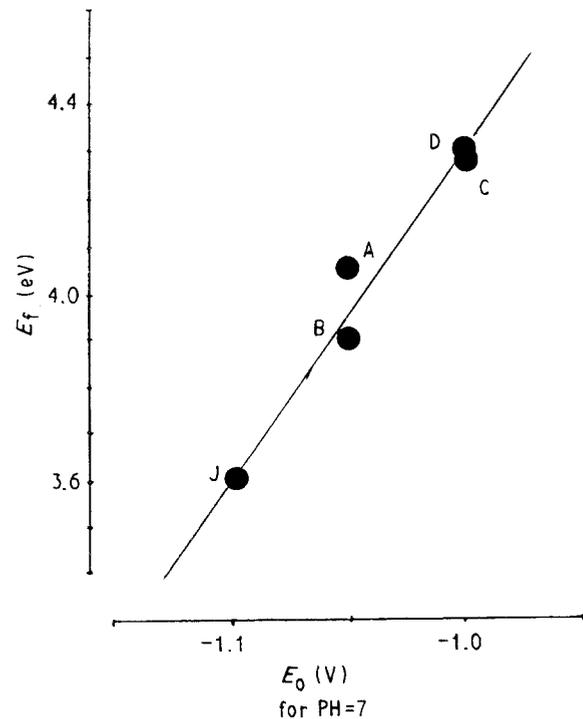


Figure 4 Correlation of the rest potential E_0 , for pH = 7 with the E_f variations for specimens of the Al-O bond family (A, B, C, D) and the silane coupling agent (J).

rest-potential of the surfaces in aqueous solution with various pH values. This correlation is a confirmation that the reactivity of those oxide surfaces is controlled by acid/base interactions.

3. The proposed approaches of surface reactivity could be generalized to other oxides, only if the base hypotheses are checked: parallel variations of the photoelectron binding energies of the anion and the cation, necessary in order to interpret those variations as shifts of the Fermi level; "Nernstian" behaviour of the rest potential in aqueous solutions leading to an acid/base behaviour in such solutions.

4. A more generalized approach to all types of substrate would need a precise knowledge of the electronic structure of their surface: valence band and

conduction band structure, band gap value. XPS and UPS techniques, coupled with electrochemical measurements are convenient tools for such investigations.

References

1. F. W. FOWKES, *J. Adhesion Sci. Technol.* **1** (1987) 7.
2. LIENG-HUANG LEE, *ibid.* **5** (1991) 71.
3. S. R. CAIN, *ibid.* **4** (1990) 333.
4. H. WINDAWI and F. F. L. HO (eds), "Applied Electron Spectroscopy for Chemical Analysis" (Wiley, 1982).
5. J. F. WATTS and E. M. GIBSON, *Int. J. Adhes. Adhes.* **11** (1991) 105.
6. W. M. MULLINS and B. L. AVERBACH, *Surf. Sci.* **206** (1988) 41.
7. *idem, ibid.* **206** (1988) 52.
8. M. CASAMASSIMA, E. DARQUE-CERETTI, A. ETCHERBERRY and M. AUCOUTURIER, *Appl. Surf. Sci.* **52** (1991) 205.
9. W. B. JENSEN, *J. Adhesion Sci. Technol.* **5** (1991) 1.
10. Y. MATSUMOTO, T. YOSHIKAWA and E. I. SATO, *J. Electrochem. Soc.* **136** (1989) 1389.
11. W. H. STRELOW and E. L. COOK, *J. Phys. Chem. Ref. Data* **2** (1973) 169.
12. J. A. TOSSEL, *J. Phys. Chem. Solids* **36** (1975) 1273.
13. *Idem, J. Amer. Chem. Soc.* **97** (1975) 4840.
14. H. NOLLER, J. A. LERCHER, H. VINEK, *Mater. Chem. Phys.* **18** (1988) 577.

*Received 2 January
and accepted 21 May 1992*