X-RAY PHOTOELECTRON SPECTROSCOPIC INVESTIGATIONS OF THE ACTIVATION OF FeTi FOR HYDROGEN UPTAKE

P. Selvam, B. Viswanathan, C. S. Swamy and V. Srinivasan

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

Abstract—Activation of FeTi alloy could either give rise to surface segregation and subsequent oxidation of titanium and the formation of iron clusters or the formation of metastable $TiFeO_x$ suboxide. The validity of either of the postulates could be gauged by monitoring the nature and concentration of each of the oxidation states of iron and titanium by depth profile analysis by XPS. These studies showed that fresh samples contained multiple oxidation states of iron and titanium though the concentrations of lower valent oxides are usually small. Sputtering studies showed that this oxide layer is of considerable depth and during activation, iron oxides are easily reduced to the metallic state as compared to the oxides of titanium. The chemical reaction induced, segregation may be the contributing factor for the enhanced concentration of titanium on the surface of these alloys.

INTRODUCTION

The intermetallic compounds explored for hydrogen storage applications have to be activated before they exhibit characteristic sorption properties [1–3]. The activation procedures employed depend on the nature of the alloy or intermetallics as well as on their preparation conditions. For example, FeTi alloys have been normally activated by heating them in hydrogen or in vacuum (10^{-2}Pa) at about 400°C [3]. The FeTi alloy is deactivated by exposing it to air for a relatively short time and reabsorbs hydrogen only after activation. Schlapbach and coworkers [4, 5] consider that this method of activation results in the surface layer Ti diffusion to the surface and precipitation of paramagnetic iron. This surface segregated Ti binds the impurities and leaves the iron in the metallic state where the dissociative activation of hydrogen takes place. Schober and Westlake [6] propose that the activation process results in the formation of metastable $TiFeO_x$ suboxides. AES and SIMS investigation of the activation by Zuchner and coworkers [7] seems to support the postulate of Schlapbach *et al.* [4, 5]. However, they propose the segregation of titanium to the surface depends on the experimental conditions (temperature, pressure) employed for activation since the titanium migration may be an activated process. Preferential segregation of one of the species (namely Ti in this case) either induced by oxygen chemisorption or by other effects like bonding and release of surface strain energy, has also been proposed as one of the effects of activation of the alloy. In spite of these extensive surface studies, the aspects on which further information is desirable include: (i) the nature, reactivity and chemical state of the various surface oxide species formed during activation, (ii) the cause of surface segregation and its role in activation and (iii) the identification of the actual catalytically active species (Ti and Fe) for the observed sorption characteristics. The purpose of this study is therefore to monitor the nature and concentration of titanium and iron species present on the surfaces of fresh as well as activated FeTi alloy by XP spectroscopic analysis as well as to evaluate the reactivities/stabilities of these species during activation.

EXPERIMENTAL

The FeTi alloy (HYSTOR-101) of MPD Technology Corporation New Jersey, U.S.A., was used as such or after activation by outgassing the alloy at 400°C for 24 h followed by cooling to room temperature in hydrogen at 70 atm in an autoclave. This hydriding and subsequent dehydriding at 200°C was repeated several times and this sample is termed as the activated alloy. The X-ray photoelectron spectra were recorded using a VG scientific ESCALAB mark II instrument with 50 eV pass energy and the peaks were deconvoluted using the iterative technique of Van Citteret [8], later modified by Jansson *et al.* [9] using an Apple II Europlus microcomputer. The samples were sputtered by argon ion source with a filament current of 60 μA and a voltage of 8 kV.

RESULTS AND DISCUSSION

The XP spectra of Ti ($2p$) region of the fresh FeTi alloy is shown in Fig. 1, together with the spectra obtained after various periods of sputtering. The inset shows deconvoluted spectrum of $Ti(2p_{3/2})$ region for the FeTi alloy. The data extracted from this figure namely the binding energy values of the peaks observed and the relative intensities of the peaks, $\Delta BE_{(1)}$ values, where $\Delta BE_{(1)} = 0 (1s) - Ti (2p_{3/2})$, for the various peaks as well as the full line width at half maximum height (FWHM) observed for various peaks in the fresh sample are given in Table 1. Normally in the case of FeTi alloys, it is

Table 1. Binding energies and FWHM of Ti $(2p_{3/2})$ core levels of fresh and activated FeTi alloys. The values reported for FeTi and Fe_2Ti_4O alloys as well as for Ti metal and its oxides are given for comparison

Material	State		Surface components	FWHM (eV)	$\Delta BE_{(1)}$* (eV)
(1) Fresh FeTi (unactivated)	(a) As received (Air exposed)	(i)	Ti	1.4	76.0
		(ii)	TiO	1.6	74.7
		(iii)	Ti_2O_3	1.7	73.6
		(iv)	TiO_2 (major component)	2.0	71.9
	(b) Sputtered sample (2310 s)	(i)	Ti (major component)	2.2	76.2
		(ii)	TiO	1.5	75.1
		(iii)	Ti_2O_3	1.6	73.9
		(iv)	TiO_2	1.6	72.2
(2) Activated FeTi	(a) As received (Air exposed)	(i)	Ti	1.5	76.0
		(ii)	TiO	1.7	74.6
		(iii)	Ti_2O_3	1.7	73.5
		(iv)	TiO_2 (major component)	2.1	71.8
	(b) Sputtered sample (1890 s)	(i)	Ti (major component)	2.2	76.1
		(ii)	TiO	1.6	74.7
		(iii)	Ti_2O_3	1.5	73.5
		(iv)	TiO_2	1.8	72.2
(3) FeTi [5]	Fractured in UHV		Ti	—	76.7
(4) Fe_2Ti_4O [5]	Fractured in UHV		Ti	—	76.4
(5) FeTi [10]	(a) As inserted		Ti	—	76.4 ± 0.1
	(b) Sputtered		Ti	—	76.4 ± 0.1
(6) Fe_2Ti_4O [10]	(a) As inserted	(i)	Ti	—	76.0 ± 0.1
		(ii)	TiO_2	—	71.5 ± 0.1
	(b) Sputtered	(i)	Ti	—	75.4 ± 0.1
(7) Ti film Electrode [11]	Electrochemical oxidation	(i)	Ti	—	77.0 ± 0.2
		(ii)	TiO	—	75.2 ± 0.2
		(iii)	Ti_2O_3	—	73.6 ± 0.2
		(iv)	TiO_2 (major component)	—	71.7 ± 0.2
(8) Ti metal [11]	Standard		Ti	—	77.0 ± 0.1
(9) TiO [11]	Standard		TiO	—	75.0 ± 0.2
(10) TiO_2 [11]	Standard		TiO_2	—	71.5 ± 0.1
(11) TiO_2 [12]	Single crystal		TiO_2	1.9	71.5 ± 0.2
(12) Ti foil [12]	Sputtered	(i)	Ti (major component)	1.9	77.0 ± 0.2
		(ii)	TiO	1.9	75.0 ± 0.2
		(iii)	Ti_2O_3	1.9	73.4 ± 0.2
		(iv)	TiO_2	1.9	71.5 ± 0.2

* $\Delta BE_{(1)}$ is binding energy difference $[O(1s) - Ti(2p_{3/2})]$.

considered that the passivating layer consists of mainly segregated TiO_2 layers [4, 5, 7]. Sayers and Armstrong [12] have studied various standard titanium oxide materials (such as TiO, Ti_2O_3 and TiO_2) employing XPS and the binding energy values observed by them are also given in Table 1. It is seen that though major portion of Ti is present as TiO_2 on the surface of fresh FeTi alloy, discernable amounts of lower oxides of Ti are also present. The presence of metallic Ti could also be seen though to a lesser extent from the peak at 454.5 eV. It is observed from Fig. 1 that, with increasing time of sputtering there is an increase in the titanium metal
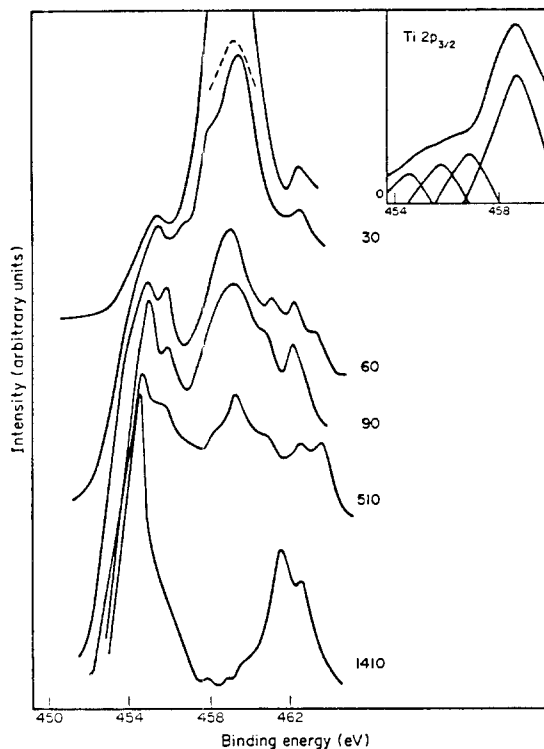
Fig. 1. X-ray photoelectron spectra of Ti($2p_{3/2}$) core levels in fresh (unactivated) FeTi and after different sputtering times (seconds). The inset shows the deconvoluted Ti($2p_{3/2}$) spectra of the air exposed sample. Ti($2p_{1/2}$) peak is also included.
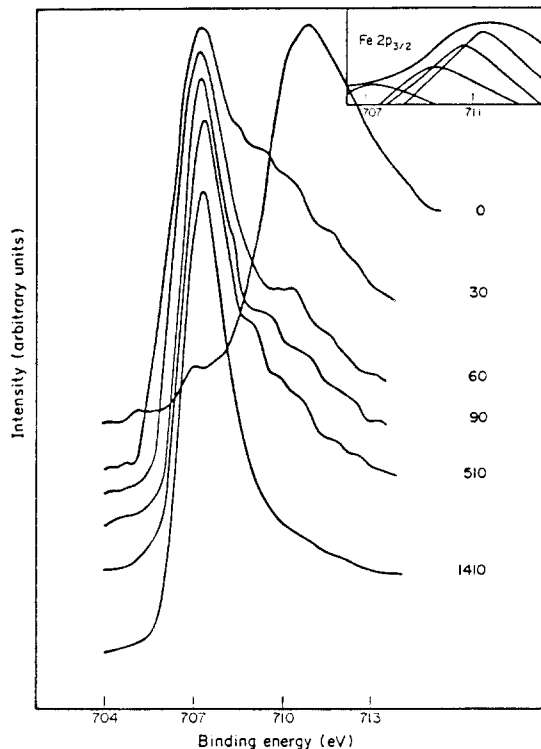

Fig. 2. X-ray photoelectron spectra of Fe($2p_{3/2}$) core levels in fresh FeTi and after different sputtering times (seconds). The inset shows the deconvoluted Fe($2p_{3/2}$) spectra of the air exposed sample.

content on the surface although other oxidation states of titanium are also present. This would indicate that (i) the oxide layer formed on FeTi alloy is of considerable thickness (ii) the suboxides formed are an inherent phenomenon of this alloy and are not concerned with partial oxidation of the surface layers. The situation is quite different in the case of iron.

It can be seen from Fig. 2 that iron is also present in different oxidation states on the surface of the alloy with majority of the iron being present as Fe_2O_3. However, sputtering this sample for 30 seconds resulted in considerable increase in the metallic component as seen from the spectra given in Fig. 2 showing that thick iron oxide layer is present only on the top few layers. The oxygen 1s peak could be resolved into two peaks with binding energy values of 530.5 and 531.6 eV. The higher energy peak disappears at early stages of sputtering showing that it arises from iron oxide. Even though majority of the iron oxides are sputtered away within 30 seconds, traces of iron oxide are still present even after sputtering for 510 seconds. The spectra obtained with the activated sample (Fig. 3) showed the presence of titanium as either Ti metal (to a lesser extent) or TiO_2. The metallic component increased with sputtering in the

activated sample. However, the presence of small amounts of lower oxidation state oxides could also be detected in the sputtered sample. Kim and Winograd [13] have postulated that ion bombardment can have reducing effect on all oxides whose free energy of formation $(-\Delta G^\circ_f)$ is less than 251 kJ mol^{-1}. TiO_2, which has $-\Delta G^\circ_f = 889$ kJ mol^{-1} (refer to Table 2) may be an exception to this general expectation. The same argument might also account for increased amounts of lower valent oxides observed as a result of sputtering in the case of fresh sample (Table 1). In the case of iron, the activated sample still contains Fe_2O_3 which could be completely removed by sputtering for 30 seconds (Fig. 4). At low sputtering times, the formation of lower oxides of iron discernable in the spectrum could have arisen from the effect of Ar$^+$ bombardment since the free energy of formation $(-\Delta G^\circ_f)$ of Fe_2O_3 is 742.2 kJ mol^{-1} (refer to Table 2). However, pure metallic state could be easily obtained by sputtering for greater than 90 seconds. The same effect could have been achieved if the alloy had been activated for few more cycles.

Surface segregation is a common feature in most of these alloys. In addition to sputtering induced surface segregation, which could have been present in these

Table 2. Heats and Free energies of formation for titanium and iron oxides [14]

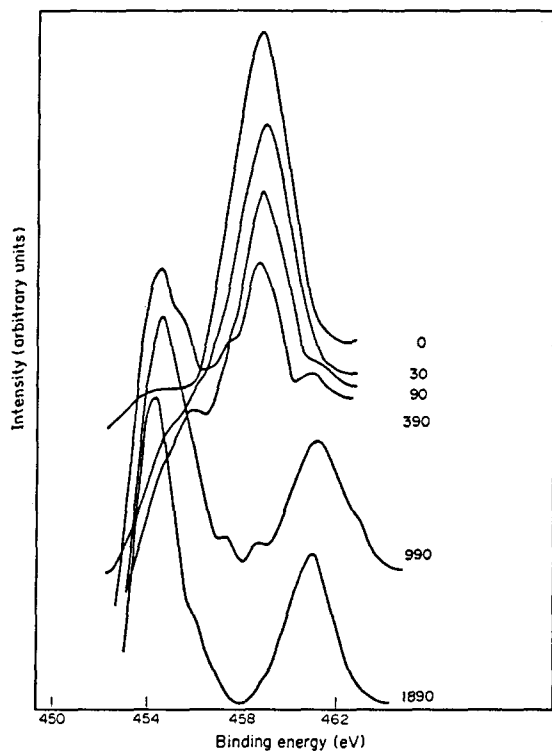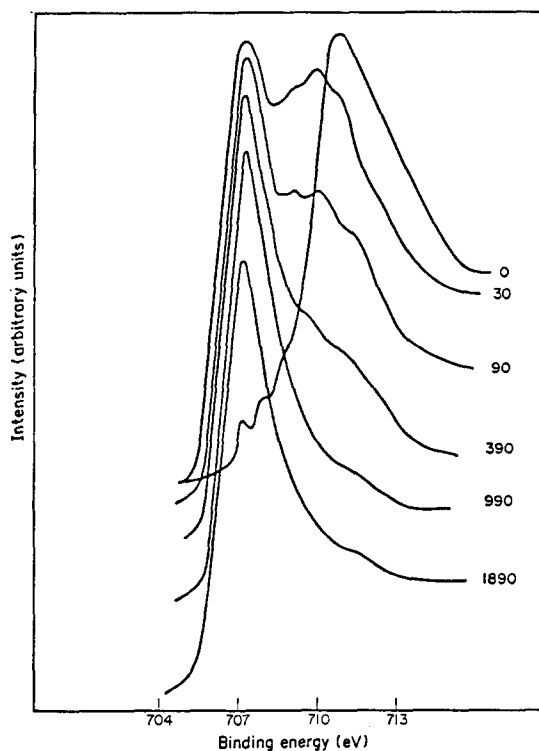| Thermochemical Data	Metal oxides					
	TiO	Ti_2O_3	TiO_2	$Fe_{0.95}O$	Fe_3O_4	Fe_2O_3
Enthalpy of formation at 298.15 K $(kJ\ mol^{-1})$	−522.6	−1520.9	−944.7	−266.3	−1118.4	−824.3
Free energy of formation at 298.15 K $(kJ\ mol^{-1})$	−495.0	−1434.3	−889.5	−246.4	−1015.5	−742.2

Fig. 3. X-ray photoelectron spectra of $Ti(2p_{3/2})$ core levels in activated FeTi and after different etching times (seconds). $Ti(2p_{1/2})$ peak is also included.

Fig. 4. X-ray photoelectron spectra of $Fe(2p_{3/2})$ core levels in activated FeTi and after different etching times (seconds).

Table 3. Physical characteristics of titanium and iron metals [15–17]

Metal	Melting point (K)	Surface tension (mJ m^{-2})		Surface Enthalpy at 0 K (mJ)		Latent heat of sublimation at room temp. (298 K) (kJ mol^{-1})	Latent heat of vaporization at boiling point (kJ mol^{-1})	Boiling point (K)	E^* (kJ mol^{-1})
		Solid at 0 K	Liquid at melting point	Solid	Liquid				
Ti	1943	2050	1500 (1700 at 1873 K)	0.92	0.86	469.3	425.8	3558	555
Fe	1809	2550	1830 (2200 at 1623 K)	0.92	0.82	398.6	340.4	3133	535

* The parameter E is related to the surface energy and heat of vaporization and is defined in equation (6) in ref. [16].

Table 4. Binding Energies and FWHM of Fe $(2p_{3/2})$ core levels of fresh and activated FeTi alloys. The values reported for FeTi and Fe_2Ti_4O alloys as well as for Fe metal and its oxides are given for comparison

Material	State	Surface Components		FWHM (eV)	$\Delta BE_{(1)}$* (eV)
(1). FeTi (unactivated)	(a) As received (Air exposed)	(i)	Fe	1.7	176.8
		(ii)	FeO	2.5	179.4
		(iii)	Fe_3O_4	2.9	180.1
		(iv)	Fe_2O_3 (major component)	5.0	180.9
	(b) Sputtered sample (2310)	(i)	Fe (major component)	2.2	176.7
		(ii)	FeO	3.0	179.3
		(iii)	Fe_3O_4	2.8	180.0
		(iv)	Fe_2O_3	3.5	180.7
(2) Activated FeTi	(a) As received‡ (air exposed)	(i)	Fe	1.6	176.9
		(ii)	FeO	3.0	179.3
		(iii)	Fe_3O_4	3.5	180.3
		(iv)	Fe_2O_3 (major component)	5.2	181.1
	(b) Sputtered sample (1890)	(i)	Fe (major component)	2.1	176.8
		(ii)	FeO	2.6	179.2
		(iii)	Fe_3O_4	2.8	180.0
		(iv)	Fe_2O_3	3.2	181.0
(3) FeTi [5]	Fractured in UHV		Fe	—	176.1
(4) Fe_2Ti_4O [5]	Fractured in UHV		Fe	—	176.3
(5) FeTi [10]	(a) As received		Fe	—	176.9 ± 0.1
	(b) Sputtered		Fe	—	176.9 ± 0.1
(6) Fe_2Ti_4O [10]	(a) As received		Fe	—	176.9 ± 0.1
	(b) Sputtered		Fe	—	176.9 ± 0.1
(7) Fe metal/ foil [10]	Standard cleaned		Fe	3.9	176.4 ± 0.2
			Fe	—	176.9 ± 0.2
(8) FeO [18]	Standard		FeO	5.0	179.5 ± 0.2
(9) Fe_3O_4 [18]	Standard		Fe_3O_4	4.0	180.5 ± 0.2
(10) Fe_2O_3 [18]	Standard		Fe_2O_3	5.0	181.7 ± 0.2
(11) Fe oxides [19]	As received (Air exposed)	(i)	FeO	4.5	179.1
		(ii)	Fe_3O_4‡	—	179.4 180.9
		(iii)	Fe_2O_3	4.5	180.9
(12) Fe film [20]	Oxidised	(i)	Fe	—	176.6
		(ii)	Fe_3O_4	—	180.3
		(iii)	Fe_2O_3	—	180.8

* $\Delta Be_{(1)}$ is binding energy difference $[O(1s)-Fe(2p_{3/2})]$.
† In addition, Fe^{2+} and Fe^{3+} were characterized by their satellite peaks at 715.1 and 719.7 eV respectively [19].
‡ Fe_3O_4 is tentatively considered as the product of one-third of Fe^{2+} and two-thirds of Fe^{3+}.

samples, the normal segregation of one of the components over the other could have arisen due to the following factors:

(i) The difference in the values of heats of sublimation,
(ii) the difference in the values of the surface tension of the components and
(iii) release of the bulk strain energy due to crystallographic mismatch between the components [15–17].

The data assembled in Table 3 show that the contribution of these factors to the observed segregation of Ti (Ti/Fe ratio in the fresh as well as activated samples are 2.3 and 2.5 respectively) may be negligible as compared to the chemically induced segregation of reactive titanium. The possibility that the oxidation of titanium could occur even in deep layers may be one of the reasons for its preferential segregation to the surface.

The XPS data presented showed that Ti is present as TiO_2 and iron as metallic Fe in the surface layers of the activated alloy. The metallic Fe particles at the surface and the metallic species in the subsurface layers of the intermetallic compound could promote the dissociative adsorption of hydrogen. Schlapbach et al. [4, 5] consider that the preferential segregation and oxidation of titanium protects iron from oxidation. It is not clear how far this explanation is valid especially in view of the observation that iron is also present as iron oxides in the fresh and activated samples (the binding energy data for $Fe(2p_{3/2})$ peak for this sample are presented in Table 4 together with the corresponding data from literature). Probably the presence of increased amounts of metallic iron on the surface of the activated sample as compared to the fresh sample accounts for its hydrogen sorption capacity. Repeated activations could have increased the amount of surface metallic iron (as even with 30 seconds sputtering the amount of metallic iron on the surface increased several-fold) resulting from preferential reduction of the iron oxides as comparted to titanium oxide.

CONCLUSION

The main points that arise from this study are:
(i) In the fresh FeTi alloy, both iron and titanium are present on the surface in various oxidation states, the concentrations of lower oxides being always small.
(ii) Activation of this alloy resulted in the increase of the metallic iron component on the surface. The titanium is preferentially segregated to the surface probably by chemical reaction induced process and was present mostly as TiO_2.

REFERENCES

1. J. H. N. Van Vucht, F. A. Kuijpers and H. C. A. M. Burning, *Philips Res. Rep.* **25**, 133 (1970).
2. J. J. Reilly and R. H. Wiswall, *Inorg. Chem.* **6**, 2220 (1967); **7**, 2254 (1968).
3. J. J. Reilly and R. H. Wiswall, *Inorg. Chem.* **13**, 218 (1974).
4. L. Schlapbach, A. Seiler and F. Stucki, *Mater. Res. Bull.* **13**, 1031 (1978) and L. Schlapbach, A. Seiler, F. Stucki and P. Zurcher, *Z. Phys. Chem. N.F.* **117**, 205 (1979).
5. L. Schlapbach and T. Riesterer, *J. Less—Common Metals* **101**, 453 (1984).
6. T. Schober and D. G. Westlake, *Scripta Metall.* **15**, 913 (1981).
7. H. Zuchner and G. Kirch, *J. Less—Common Metals* **99**, 143 (1984) and H. Zuchner, U. Bilitecoski and G. Kirch, *J. Less—Common Metals* **101**, 441 (1984).
8. P. H. Van Citteret, *Z. Physik* **69**, 298 (1931).
9. P. A. Jansson, R. H. Hunt and E. K. Plyler, *J. Opt. Soc. Am.* **58**, 1665, (1968).
10. M. Polak, M. Hefetz, M. H. Mintz and M. P. Dariel. In T. N. Veziroglu, W. D. Van Vorst and J. H. Kelley, eds, *Hydrogen Energy Progress IV, Proc. 4th World Hydrogen Energy Conf.*, Pasadena, California, June 13–17, 1982, Vol. 3, p. 1307, Pergamon Press, Oxford (1982).
11. N. R. Armstrong and R. K. Quinn, *Surface Sci.* **67**, 451 (1977).
12. C. N. Sayers and N. R. Armstrong, *Surface Sci.* **77**, 301 (1978).
13. K. S. Kim and N. Winogard, *Surface Sci.* **43**, 675 (1974).
14. *CRC Handbook of Chemistry and Physics*, 64th Edition, CRC Press, Florida, (1983–84).
15. A. R. Miedema and R. Boom, *Z. Metallkde.* **69**, 183 (1978) and A. R. Miedema, *Z. Metallkde.* **69**, 287 (1978).
16. A. R. Miedema, *Z. Metallkde* **69**, 455 (1978).
17. *Smithells Metals Reference Book*, 6th Edition, Butterworths, London (1983).
18. P. Mills and J. L. Sullivan, *J. Phys. D: Appl. Phys.* **16**, 723 (1983).
19. C. R. Brundle, T. J. Chuang and K. Wandalt, *Surface Sci.* **68**, 459 (1977).
20. J. K. Gimzewski, B. D. Padalia, S. Affrossman, L. M. Watson and D. J. Fabian, *Surface Sci.* **62**, 386 (1977).