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An X-Ray Photoelectron Spectroscopic and Chemical Reactivity Study of Routes to Functionalization of Etched InP Surfaces

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Although InP is widely used in optoelectronic applications,[1−3] little is known about the surface chemistry of this important semiconductor. Modification of the InP surface is potentially important as a route to introduce functional groups for the stabilization of InP photoelectrodes,[4] to control the surface recombination properties of InP-based electrical devices,[5,6] to study electron transfer from a solid to a redox-active donor at a fixed distance from the solid,[7,8] to control nucleation and growth of metals on semiconductors,[9] and for use in optically linked chemical-sensing applications.[10] To our knowledge, the only prior investigations of the derivatization of etched InP surfaces are the work of Gu et al.,[11] who coated the InP surface with overlayers of thiols through an unidentified binding mode, and that of Spool et al.,[12] who observed face-selective reactivity of InP with benzyl bromides and proposed that the reactivity of the P-rich, (111)B face of InP was dominated by the lone pairs of the terminal P surface atoms. We describe herein a new, apparently general strategy for functionalization of InP surfaces. We also present evidence that the reactions of this semiconductor surface are dominated by the reactivity of residual −OH functionalities on the InP surface.

Table 1 summarizes the X-ray photoelectron spectroscopic (XPS) data for a series of reactions performed with (111)B-oriented, n-type, single-crystal InP specimens having doping densities in the range $10^{15}-10^{18}$ carriers cm^{-3}. In our studies, etches and reactions were performed under anaerobic conditions. In accord with prior work under aerobic etching and reaction conditions,[12] exposure of (111)B-oriented InP to p-$CF_3C_6H_4CH_2Br$ yielded persistently attached F and fluorinated methyl C atoms (designated as C_F), as detected by XPS (Table 1). The atomic ratio C_F/F on the modified surface was found to be close to the expected value of 0.33 (Table 1). The limiting coverage of p-$CF_3C_6H_4CH_2$− groups was approximately 4×10^{14} cm^{-2}, as compared to a calculated P atom density of 6.7×10^{14} cm^{-2} on a perfect (111)B surface. Negligible C_F and F were observed on surfaces that had been exposed to p-$CF_3C_6H_4CH_3$ under the same conditions.

If the reaction involved alkylation of the surface through the P lone pair, a chemical shift to higher binding energy in the XPS of the surface P atoms would be expected as a result of the functionalization. In contrast, high-resolution XP spectra of etched InP (111)B faces showed negligible change in the P 2p region upon surface modification. Br^- (as a counterion) should also be present on the surface if a benzylphosphonium species had been formed, but only small amounts of Br were observed, with Br/F ratios <0.1 (Table 1). Attempts to exchange the putative surface anion with other anions, including $X^- = ClO_4^-$, Cl^-, or SbF_6^-, produced only traces of these species on the InP surface (Table 1). Titration of the etched, P-rich (111)B face with $(C_2H_5)_2O{\cdot}BF_3$, to probe the P lone-pair density on the surface, yielded negligible F detectable by XPS.

These experiments indicate that it is unlikely that P lone pairs are dominating the chemical reactivity of this InP surface. The lack of significant XPS signals on the etched InP (111)B surface other than those assignable to In, P, C, and O strongly suggests that residual hydroxyl groups are responsible for the surface chemistry. As support for this hypothesis, the reactivity of the two esters p-$CF_3C_6H_4COOC_{12}H_{24}Br$ and p-$CF_3C_6H_4COOC_{12}H_{25}$ with (111)B InP surfaces was investigated. Reaction of InP with the Br- or H-terminated alkyl esters yielded persistently attached CF_3 groups on the surface (C_F/F ratio from XPS = 0.43). These modified surfaces displayed essentially identical F/In intensity ratios to each other and to the surface obtained from reaction with p-$CF_3C_6H_4CH_2Br$ (Table 1). These data imply that essentially identical overlayer thicknesses, as probed by the F and In atom locations, were obtained from the three systems and provide strong evidence that the esters had been cleaved during reaction to produce persistently attached p-$CF_3C_6H_4COO$− groups on the InP surface (Table 1). A simple aliphatic halide also reacted with the InP surface to yield a surface-bound alkyl species. In addition, a fluorinated monochlorosilane reacted with the (111)B InP surface, yielding persistently attached Si atoms and fluoroalkyl groups, as detected by XPS (Table 1). This collection of chemical reactions is precisely that expected of −OH functionalities on the semiconductor surface.

To explore the oxidation state of the surface P atoms, XP spectra were recorded for chemically etched (111)B and (111)A surfaces and for (110) InP surfaces (a mixed face containing both P and In atoms) that had been prepared by cleavage of an InP crystal in ultrahigh vacuum (UHV). The latter two surfaces should both contain only lattice P signals,[13] in contrast to the P-rich (111)B face which also should display XPS signals from terminal surface P atoms. The P 2p region of the (111)A face and of the cleaved (110) face were essentially identical and were well-fit by a single spin−orbit-split doublet (Figure 1a). In contrast, the etched (111)B face showed an additional P 2p XPS signal at higher binding energy than the main peak, indicating P atoms in a higher oxidation state than those in the lattice. An additional peak at a similar binding energy was obtained for an etched (110) face, as displayed in Figure 1b. This signal of oxidized P was also present on the (111)B InP surface that had been functionalized with p-$CF_3C_6H_4CH_2Br$ under nominally anaerobic conditions. Thus, the lack of change in the P 2p XPS signal for etched (111)B samples during surface modification can be consistently ascribed to the rapid reactivity of the native (111)B surface with oxygen and/or water, producing a surface oxide/hydroxide that then participates in the subsequent surface

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(13) Although the (110) face is a mixed face containing both P and In atoms, terminal and bulk lattice P atoms are approximately equal on this face, because surface relaxation causes only minor changes in the surface structure (see: Woicik, J. C.; Kendelewicz, T.; Miyano, K. E.; Richter, M.; Karling, B. A.; Bouldin, C. E.; Pianetta, P.; Spicer, W. E. *J. Vac. Sci. Technol., A* **1992**, *10*, 2041), and no surface reaction was observed by XPS within 3 h after cleavage.

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Table 1. XPS Data for (111)B InP Surfaces

		atomic ratio[b]		intensity ratio	
	treatment[a]	C_F/F	X^c/F	$PO_x{}^d/P_{InP}$	F/In
1a	anaerobically etched InP			<0.05	
1b	aerobically etched InP			0.15	
2a	InP + p-$CF_3C_6H_4CH_2Br/(C_2H_5)_3N$ (0.2 and 0.02 M, resp., in CH_3CN)	0.36	<0.1	<0.05	0.38[e]
2b	InP + p-$CF_3C_6H_4CH_3$ (0.2 M in CH_3CN)			<0.05	<0.07
3a	InP + p-$CF_3C_6H_4CH_2Br$, then + 0.1 M $LiClO_4-CH_3OH$[f]	0.36	<0.02	<0.05	0.38
3b	InP + p-$CF_3C_6H_4CH_2Br$, then + 0.1 M $NaSbF_6-CH_3OH$[g]	0.36	<0.02	<0.05	0.38
4	InP + $(C_2H_5)_2O{\cdot}BF_3$ (0.1 M in hexanes/CH_2Cl_2, 10:1)			<0.05	<0.05
5a	InP + p-$CF_3C_6H_4COOC_{12}H_{24}Br$ (0.1 M in CH_3CN)	0.43	<0.02	<0.05	0.23[d]
5b	InP + p-$CF_3C_6H_4COOC_{12}H_{25}$ (0.1 M in CH_3CN)	0.43		<0.05	0.24
6	InP + $CF_3(CH_2)_3I$ (0.1 M in CH_3CN)	0.35	<0.1	<0.05	0.22[d]
7	InP + $CF_3(CH_2)_2Si(CH_3)_2Cl/(C_2H_5)_3N$ (each 0.1 M in CH_3CN)[h]	0.43	<0.02	<0.05	0.09

[a] InP samples were etched prior to surface modification by applying a two-step procedure, using Br_2-CH_3OH and NH_3-CH_3OH solutions.[15] Surface modifications were carried out at 62 °C, except for procedure 3, which was performed at room temperature. Once the reaction was completed, samples were removed from the derivatization solution, thoroughly rinsed with clean CH_3CN (62 °C), and blown dry with N_2. The entire surface preparation was carried out under anaerobic conditions, unless otherwise noted. [b] The atomic ratios were derived from the measured XPS intensities (see, e.g., Seah[16]). Sensitivity factors were taken from Wagner et al.[17] The measured binding energies of C_F, F, PO_x, P_{InP}, and In were 292.7, 688.3, 133.3, 128.6, and 665.7 eV, respectively. [c] X = Br (69.1 BeV) for reactions 2, 3, and 5, I (619.4 BeV) for reaction 6, and Cl (269.2 BeV) for reaction 7. [d] PO_x represents indium phosphate(V). [e] The absolute number of p-$CF_3C_6H_4CH_2-$, p-$CF_3C_6H_4COO-$, and $CF_3(CH_2)_3-$ units on the surface was calculated to be 4.3×10^{14}, 2.6×10^{14}, and 2.9×10^{14} cm^{-2}, respectively, using a standard overlayer−substrate model.[18] The p-$CF_3C_6H_4CH_2-$ and p-$CF_3C_6H_4COO-$ overlayers were estimated to be 8.7 Å thick, and the $CF_3(CH_2)_3-$ overlayer was estimated to be 6.4 Å thick. Escape depths were taken from Laibinis et al.,[19] and sensitivity factors were taken from Wagner et al.[17] [f] No Cl was detected by XPS. [g] No Sb nor additional F was detected by XPS. [h] The Si 2p peak was observed at 102.3 BeV. Also, no reaction was observed in the absence of $(C_2H_5)_3N$, whereas reaction 2a proceeded without $(C_2H_5)_3N$ but reached the reported limiting coverage more rapidly in the presence of this base.

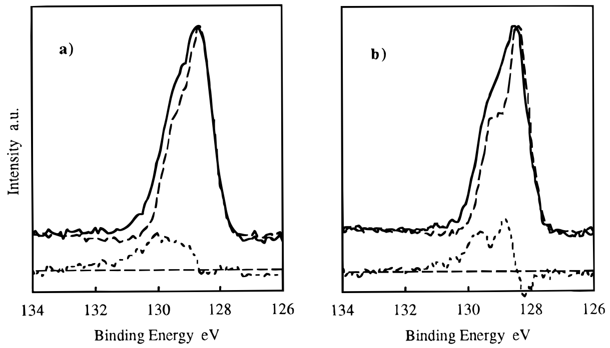

Figure 1. XPS spectra of the P:2p region for various InP samples. (a) Solid line, etched (111)B InP; dashed line, etched (111)A InP. (b) Solid line, etched (110) InP; dashed line, (110) InP cleaved in UHV. The dotted lines are difference spectra for the signals in each panel, in each case showing the presence of additional, high-binding-energy signals for the etched (111)B and etched (110) surfaces. The spectra were recorded with focused and monochromatized Al $K\alpha_{1,2}$ irradiation ($h\nu$ = 1486.6 eV) and a pass energy of 54 eV. The peaks were normalized after background subtraction.

reaction chemistry. The low reactivity of the In-rich (111)A face toward functionalization with benzyl halides is then readily explained by the differences in nucleophilicity between the acidic P−OH groups exposed on the (111)B face and the basic In−OH groups exposed on the (111)A face of etched InP crystals.

In summary, the reactivity of the (111)B face of etched InP appears to be dominated by classical -OH group reactivity. This surface-bound functional group can be exploited using a variety of conventional reaction pathways to yield persistently bound alkyl chains, benzyl groups, silyl groups, and other functionalities on the InP surface. The presence of −OH groups and their role in the chemical functionalization reaction are beneficial in the case of InP, because surface modification is thus possible without destroying the strong InP−O interaction that produces the excellent electrical properties of the etched, air-exposed InP surface.[5,14] Characterization of the monolayer properties of these InP surfaces to effect deliberate modification of surface oxidation processes, as well as electrical studies of these surfaces to modify their surface recombination velocity, will be reported subsequently.

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