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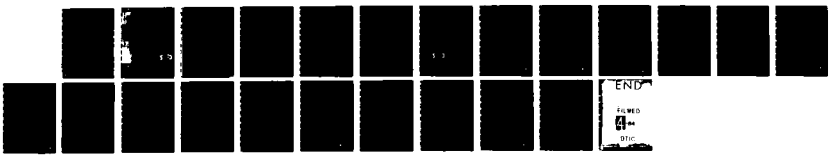

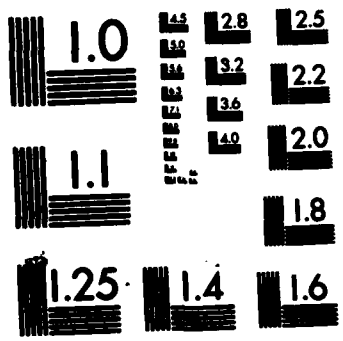

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Chemical Deposition of SiO_2 on InP

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Chemistry and Physics Laboratory
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The Aerospace Corporation
El Segundo, California 90245

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This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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Chemical deposition experiments were performed to determine how surface preparation and film deposition conditions influence insulator-semiconductor interface composition and chemical structure. Silicon dioxide layers were chemically deposited on indium phosphide by hydrolyzing silicon orthopropoxide. On unoxidized, etched surfaces, coverage was always patchy. On InP with approximately one monolayer of chemisorbed oxygen in a hydrated-phosphate-like environment, a continuous, ~60-Å-thick SiO_2 film was formed at

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room temperature. SiO_2 attached to the substrate through about one monolayer of Si-O-P bonds. Heating to 50°C during hydrolysis resulted in a mixed Si-In-P oxide, owing to simultaneous hydrolysis and oxidation processes.

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I. INTRODUCTION

Silicon dioxide is of increasing technological importance as a dielectric in high-speed electronic devices based on indium phosphide. The chemical characteristics (details of bonding and atomic arrangements) of the insulator-semiconductor interface profoundly affect device electrical properties.[1-3] The presence of many layers of native or mixed oxide at the interface causes trap states and electrical instabilities such as C-V hysteresis.[4] An ideal interface structure is one in which only a single monolayer of oxygen forms a "bridge" between the semiconductor and insulator phases without forming the true native oxide. Such an interface, which should have better electrical properties than structures with native-oxide interfacial layers, can be produced by low-temperature depositions on clean (i.e., appropriately etched) InP substrates. This report describes an oxide-deposition model, as well as x-ray photoelectron spectroscopy results that support the model's prediction that a thin, interfacial oxygen bridging layer is necessary for effective insulator-semiconductor bonding. Further experiments are needed to determine how such a layer affects interface electrical properties.

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II. INTERFACE MODEL

The initial product in room-temperature oxidation of InP is approximately one monolayer of oxygen attached to the surface phosphorus atoms and forming a hydrated-phosphate-like surface layer.[3,5] That layer forms after only a few minutes' air exposure, and further oxidation to a nonstoichiometric mixture of indium and phosphorous oxides with possibly some interfacial elemental P takes place slowly or with heating.[3] In many insulator deposition processes, such as chemical vapor deposition of SiO_2 on a heated substrate, oxidation of InP occurs during the processing itself, producing a relatively thick mixed-oxide layer with poor electrical properties. By eliminating the nonstoichiometric mixed oxide and elemental P and bridging the gap between semiconductor and insulator in only one monolayer (as appears to be the case in the Si-SiO_2 system[6]), interface state density should be reduced.

A chemical bonding model for native oxides on III-V semiconductors[7] indicates that phosphides are a better substrate than arsenides for nonnative oxide deposition in which native oxidation must be restricted to one monolayer. Phosphides have more covalent oxides than arsenides because terminal O's on P can form donor-acceptor bonds with the cations. This reaction is thermodynamically unfavorable for As-O bonds, so the native oxide on arsenides has more ionic bonds. The structure of the native oxide of InP, for example, is a diatomic analog of SiO_2 and should provide a good matching layer for SiO_2 deposition.

An acceptable experimental test of the need for a single oxygen-atom bridging layer between InP and SiO_2 requires that the semiconductor surface be prepared, and the film deposited, with considerable care, to avoid excessive native-oxide formation. A room-temperature chemical (solution) deposition process was selected to provide the most benign oxidation conditions possible and maintain control over the surface chemical reactions. SiO_2 layers on InP were produced by polymerizing and hydrolyzing silicon orthopropoxide. Similar reactions have been used to produce mixed-oxide coatings on metals,[8] as well

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as single-component coatings on gallium arsenide.[9] A schematic representation of the complex silicon orthopropoxide deposition and polymerization process on InP is provided in the following reaction scheme:

$$InP + 1/2\ O_2 + H_2O \rightarrow InP(OH)_2 \tag{1}$$

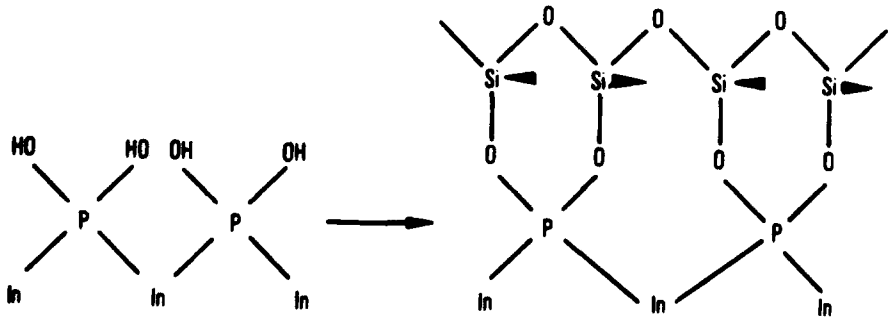
$$InP(OH)_2 + 2\ Si(OC_3H_7)_4 \rightarrow InP[O\text{-}Si(OC_3H_7)_3]_2 + 2\ C_3H_7OH \tag{2}$$

$$InP[O\text{-}Si(OC_3H_7)_3]_2 + 2\ H_2O \rightarrow InP[O\text{-}Si(OC_3H_7)_2OH]_2 + 2\ C_3H_7OH \tag{3}$$

$$InP[O\text{-}Si(OC_3H_7)_2OH]_2 + 2\ Si(OC_3H_7)_4 \rightarrow InP[O\text{-}Si(OC_3H_7)_2\text{-}O\text{-}Si(OC_3H_7)_3]_2 + 2\ C_3H_7OH \tag{4}$$

$$InP[O\text{-}Si(OC_3H_7)_2\text{-}O\text{-}Si(OC_3H_7)_3]_2 + 10\ H_2O \rightarrow InP(O\text{-}SiO_2\text{-}O\text{-}SiO_3)_2 + 10\ C_3H_7OH \tag{5}$$

Reaction (1) represents the room-temperature chemisorption of oxygen and water on InP to form a monolayer of a hydrated-phosphate-like compound, as observed in x-ray photoelectron spectroscopy (XPS). Reaction (2) is the initiation step of the alkoxide polymerization on the InP surface, and reactions (3) and (4) are the propagation steps of the polymerization. Reaction (5) is the termination step, a final hydrolysis removing the remaining organic components. The overall reaction can be pictured schematically as follows:



(6)

The actual polymerization reactions are complex, with many possible end-product structures, and reactions (1) through (6) are intended only as an illustration of the process. Detailed studies of the polymerization have been carried out for the analogous titanium alkyls.[10]

Conceptually, this sequence of reactions can produce a perfectly smooth, unmixed interface between insulator and semiconductor. X-ray photoelectron spectroscopy, combined with chemical-etch depth profiling, can determine whether the interface formed by such a process is actually smooth and unmixed. XPS can distinguish between oxidation states of elements, and chemical-etch depth profiling causes less damage to the interface than conventional ion sputter profiling.[11]

III. EXPERIMENTAL

The InP samples were polished (100) faces of p-type, Zn-doped material with a carrier concentration of less than 1×10^{18} cm^{-3}. The InP contained a Si impurity that was distinguishable from the Si in the deposited coating. All other chemicals used were reagent grade. The coupons were cleaned with acetone and methanol before coating deposition. Etched coupons (10s dip in a solution of 3% HF and 31% NH_4F by volume in water) were rinsed in methanol and kept covered with methanol during transfer to the coating solution, thus minimizing unintentional oxidation of the surface, although not completely eliminating it.[3] Some unintentional surface roughness might be produced by this step.

The coating solution contained 4% silicon orthopropoxide by volume in isopropanol and 0.5 wt% NaOH. A basic solution induces orthopropoxide polymerization, which would otherwise be slow. The InP coupons were placed in the coating solution and agitated for 1 min, then removed and allowed to hydrolyze in a horizontal position in room air. Most hydrolyses were conducted at room temperature, but one coupon was hydrolyzed on a hot plate at 50°C.

The spectra were taken on a GCA-McPherson ESCA-36 x-ray photoelectron spectrometer equipped with an electrostatic analyzer and a position-sensitive detector.[12] Chemical depth profiling was carried out in a N_2-filled glove bag attached to the spectrometer. The coupon was dipped into the etching solution (0.3% HF and 3.1% NH_4F by volume in water) for 1 sec, then removed immediately and rinsed with methanol. The etch rate of the deposited SiO_2 layers in this solution was approximately 20 Å/dip. After each dip the sample was inserted into the spectrometer for analysis. All binding energies reported have been referenced to a C(1s) binding energy of 285.0 eV to compensate for sample charging.

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IV. RESULTS

Initial experiments were conducted to determine the best preparation procedure for obtaining unoxidized and partially (~1 monolayer) oxidized InP. Semiconductor oxidation, reflected by the values of the XPS binding energies in Table I, is determined by the etchant used to prepare the surface.[3,5] H_2SO_4, HCl, and Br_2 etches left some native oxide on the surface, whereas an HF etch did not. Once the InP was etched free of native oxide with buffered HF, it was either kept free of oxidation by being stored in methanol or oxidized by exposure to ambient air to form approximately one monolayer of chemisorbed oxygen and water prior to processing in the coating solution. Although it contained NaOH, the coating solution used in these experiments did not remove the native oxide that had been formed intentionally on the semiconductor surface. When, to avoid polymerization, the coating solution was rinsed off in the glove bag immediately after the coupon was removed from the solution, a monolayer of phosphate remained on the surface.

TABLE I. XPS BINDING ENERGIES FOR InP

Treatment	P(2p) (eV)		In($3d_{5/2}$) (eV)	
	Substrate	Oxide	Substrate	Oxide
HF etch	129.0		444.4	
Concentrated H_2SO_4 etch	129.3	133.7	444.7	
HCl etch	129.6	133.7	444.8	
Br_2 etch	129.2	133.5	444.5	
RT[a] native oxide	133.6		444.5	
Heavily oxidized	133.8		444.5	445.7
SiO_2-coated, RT[a] hydrolysis	130.5		444.3	
SiO_2-coated, 50°C hydrolysis	130.5		444.1	445.8

[a]RT = room-temperature.

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Coupons that had been etched in buffered HF before being inserted into the coating solution did not form cohesive, uniform coatings. The SiO_2 formed small patches on the surface, and no oxidized forms of P were observable at the SiO_2-InP interface. Native oxide was present on the uncovered areas, as a result of the uncovered InP oxidizing during the hydrolysis step. Since the HF etch removed the native oxide, the uncovered areas were cleaned of oxidized P and In after the first dip of the chemical depth profile. However, the thicker patches of SiO_2 were not entirely removed. Each subsequent etch reduced the area as well as the height of the SiO_2 patches, and a depth profile with a nonabrupt interfacial region resulted (Fig. 1). No interfacial native oxide was observed during the depth profile. However, the area of the interfacial region available for analysis after each dip was small, probably only a ring of thinner oxide at the edge of each thick SiO_2 patch, and the spectrometer sensitivity might not have been high enough to observe the interfacial oxide if it were present.

InP with a monolayer of chemisorbed O in a hydrated-phosphate-like environment formed a uniform SiO_2 coating when treated with silicon orthopropoxide. The depth profile and representative spectra for a typical sample are given in Fig. 2. The coating is thin (~60 Å thick) and is entirely SiO_2. A small amount (~1 monolayer) of a slightly oxidized form of P is present at the SiO_2-InP interface. The P has a lower binding energy than the original native oxide (Table I), and therefore is not as electron deficient. The broad feature at about 104 to 105 eV in the 5-dip spectrum is caused by the Si impurity in the InP.

Heating the coupon to 50°C during hydrolysis resulted in a mixed-oxide layer (Fig. 3). Oxidized In is present in the surface layers (Table I), and the interface is much broader than for a room-temperature hydrolysis, although the thickness of the film is approximately the same.

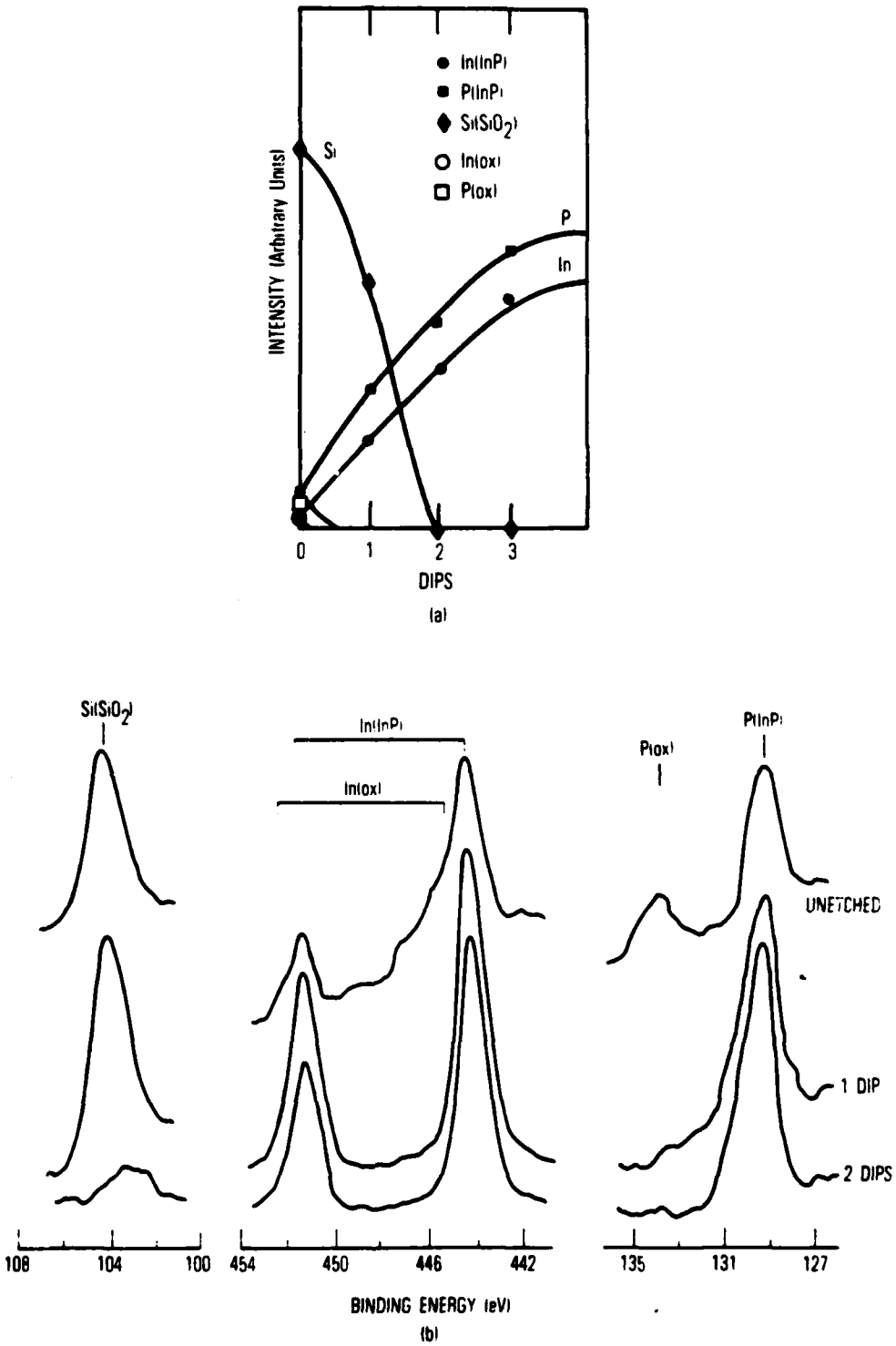
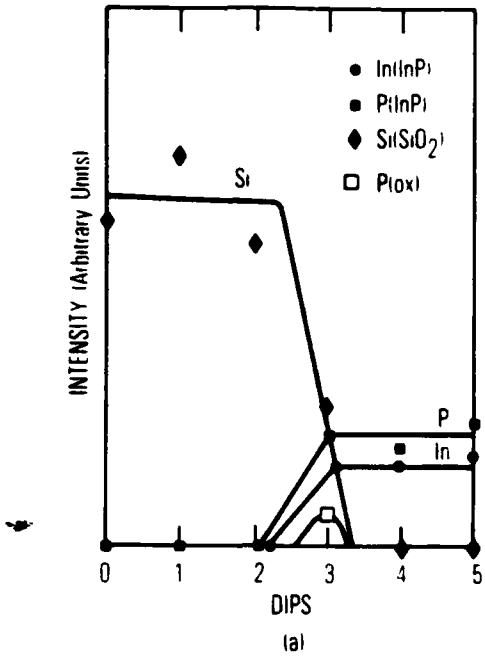


Fig. 1. **SiO_2 film on InP that had previously been etched to remove all native oxide: (a) depth profile; (b) typical XPS spectra taken during depth profiling.**



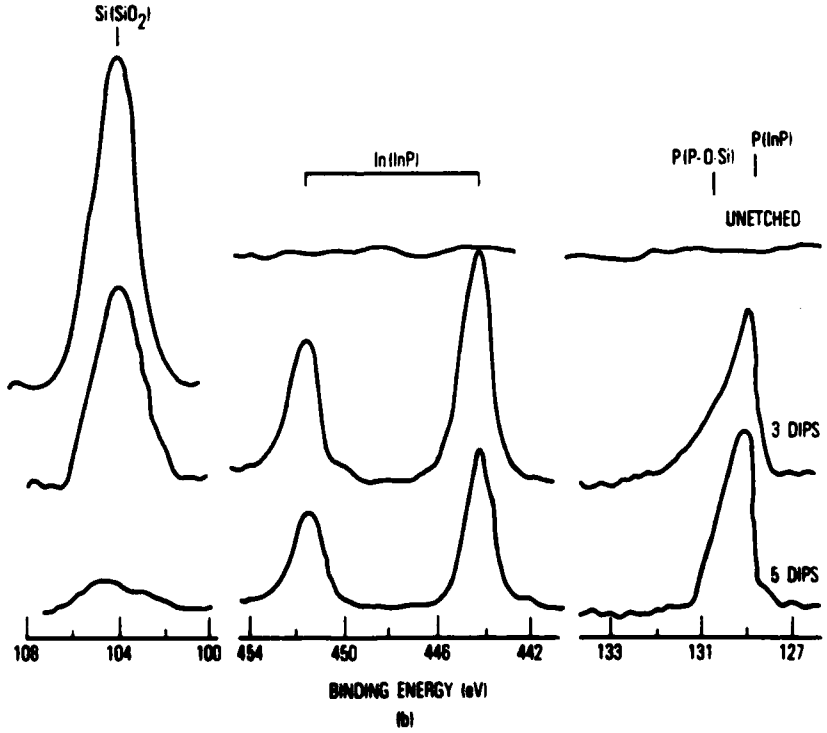
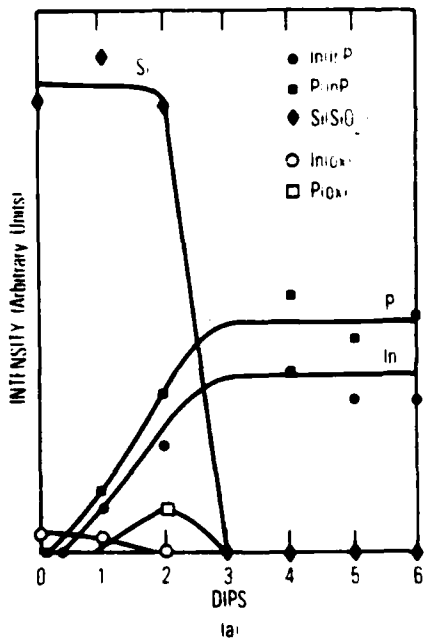


Fig. 2. SiO_2 **film on InP prepared with room-temperature hydrolysis: (a) depth profile; (b) typical XPS spectra taken during depth profiling.**



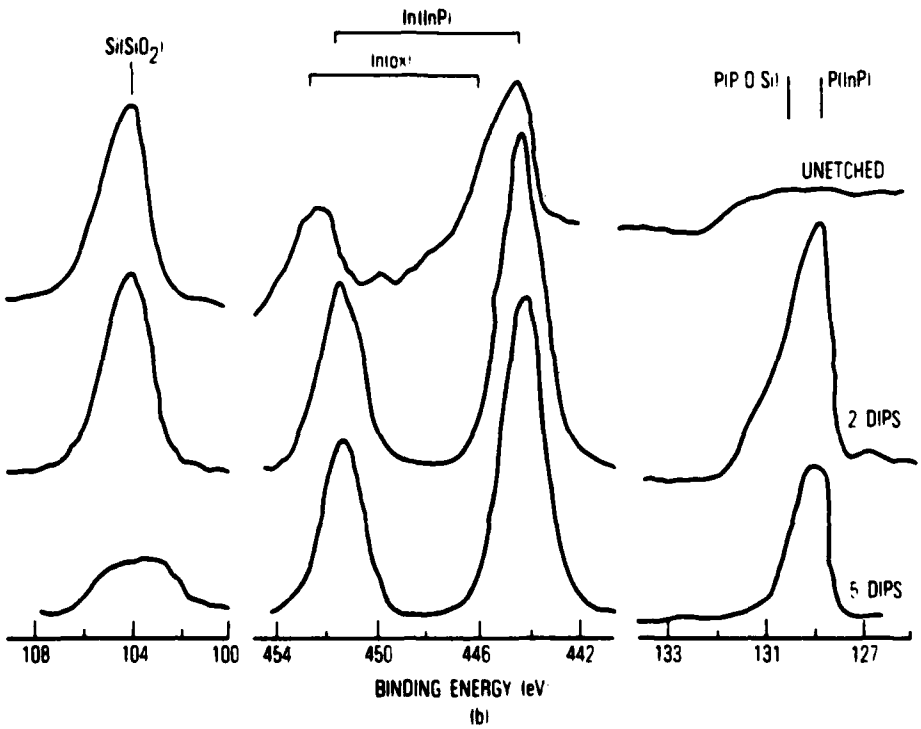


Fig. 3. **SiO_2 film on InP prepared with 50°C hydrolysis: (a) depth profile; (b) typical XPS spectra taken during depth profiling.**

V. DISCUSSION

The presence of a monolayer of chemisorbed oxygen at the InP surface is clearly a crucial factor in the chemical deposition of SiO_2 grown by silicon orthopropoxide polymerization: a 60-Å-thick film of SiO_2 forms with an O-bridge layer; without an O-bridge layer, a continuous film does not form. In addition, coating formation causes the environment of the interfacial P to change. The P(2p) binding energy is lower for the P at the SiO_2-InP interface (~130 eV) than for the original native oxide (133.6 eV). The lower binding energy indicates that the P is in a much less electron-withdrawing environment at the SiO_2-InP interface than in the native oxide. The local environments proposed in reactions (5) and (6) satisfy this condition, as the following Sanderson method electronegativity arguments show.

The Sanderson method assigns electronegativities, or stability ratios (SRs), to groups of atoms. The values are the geometric means of the stability ratios of the elements forming the group. The charge on an atom in a group can be calculated as the difference between the SR of the free atom and that of the group, divided by a normalization factor. This method of atomic-charge calculation yields values that agree well with XPS data for a variety of compounds.[13]

InP is a tetrahedrally bonded solid, in which each P has four In nearest neighbors. At the surface, two of the neighbors are missing, and OH groups can bond to the P in their place to form the hydrated-phosphate-like surface of Eq. (1). After reaction with silicon orthopropoxide as in Eqs. (2) through (5), the two OH groups are replaced by OSi groups. The stability ratios of OH and OSi are 4.30 and 3.69, respectively, implying the much greater electron-withdrawing power of the OH group. To calculate the charge on the interfacial P, we used a simple model in which only the bonds that change are considered. Thus the local environments of interest are PIn_2 (bulk InP), $P(OH)_2$ (native oxide), and $P(OSi)_2$ (SiO_2-coated InP). The calculated charges Q_p are listed in Table II.

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TABLE II. SANDERSON METHOD ATOMIC CHARGES

Treatment	Q_p	P(2p) binding energy (eV) Measured	Calculated
HF etch	-0.086	129.0	
RT[a] native oxide	0.16	133.6	
SiO_2-coated, RT[a] hydrolysis	0.058	130.5	130.1

[a]RT = room-temperature.

In general a linear correlation exists between the atomic charge calculated by the Sanderson method and XPS binding energies.[13] Using the calculated Q_p's and the measured binding-energy values for InP and the native oxide, we calculated the binding energy of interfacial P in SiO_2-coated InP to be 130.1 eV, which agrees well with the measured value of 130.5 eV. This result supports the proposed model of SiO_2 connection to InP through P-O-Si bonds for the room-temperature oxides and thus the presence of a single monolayer of bridging O atoms.

The high-temperature oxide, on the other hand, contains In-O bonds and P-O-Si bonds in the bulk of the oxide film, and has a broad oxide-semiconductor interface. In this case, the hydrolysis reaction is combined with further, thermally enhanced oxidation of the semiconductor, resulting in a mixed Si-In-P oxide. No true InP thermal oxide is present, as evidenced by the lack of a P 2p peak at 133.6 eV. The P in this oxide is thus coordinated to Si through P-O-Si bonds in the bulk of the mixed oxide.

These experiments demonstrate how surface preparation and film deposition conditions influence the resulting insulator-semiconductor interface composition and chemical structure. A single bridging layer of chemisorbed oxygen is necessary for effective insulator-semiconductor bonding. In chemical deposition of SiO_2 on InP, high-temperature hydrolysis produces a mixed oxide; room-temperature hydrolysis produces a single-component oxide. In addition, the

insulator-semiconductor interface is abrupt in the latter case, perhaps as abrupt as one monolayer, which we suggest is because of a P-O-Si bridge layer between the InP and SiO_2. High temperatures and other oxidation-promoting conditions should be avoided when depositing nonnative insulators on InP if elimination of native or mixed oxides is desired. Benign deposition conditions can lead to an abrupt interface that should lack the chemical and structural defects that are implicated as electron traps.

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