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Optimized cleaning method for producing device quality InP(100) surfaces

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Abstract:

A very effective, two-step chemical etching method to produce clean InP(100) surfaces when combined with thermal annealing has been developed. The hydrogen peroxide/sulfuric acid based solutions, which are successfully used to clean GaAs(100) surfaces, leave a significant amount of residual oxide on the InP surface which can not be removed by thermal annealing. Therefore, a second chemical etching step is needed to remove the oxide. We found that strong acid solutions with HCl or H_2SO_4 are able to remove the surface oxide and leave the InP surface passivated with elemental P which is, in turn, terminated with H. This yields a hydrophobic surface and allows for lower temperatures to be used during annealing. We also determined that the effectiveness of oxide removal is strongly dependent on the concentration of the acid. Surfaces cleaned by HF solutions were also studied and result in a hydrophilic surface with F terminated surface In atoms. The chemical reactions leading to the differences in behavior between InP and GaAs are analyzed and the optimum cleaning method for InP is discussed.

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1. Introduction:

InP is an important III-V semiconductor for both electronic and photonic device applications. A clean and stoichiometric surface is critical for the performance of many devices, and it is also important for the growth of high quality epitaxial films. Different ways of cleaning InP(100) surfaces have been used [1-11]. Ion sputtering and annealing are typical cleaning methods for metals and thermally stable materials, but the relatively low decomposition temperature of InP (380°C) precludes effective annealing of the damage caused by ion sputtering [4, 5, 6, 7]. Sulfur passivation leads to stable surface termination, but the chemisorbed sulfur atoms cannot be removed completely by thermal annealing at temperatures below the decomposition temperature of InP [5, 6, 7]. The effectiveness of atomic hydrogen cleaning [1, 2, 3] is yet to be proven, and can result in the buildup and desorption of phosphine leading to an indium-rich surface [12].

Chemical cleaning offers an effective and practical method for cleaning semiconductor surfaces [8-11]. One group of chemicals widely used for cleaning InP(100)are hydrogen peroxide based solutions. These methods are effective in obtaining a clean GaAs(100) surface but its effectiveness on InP(100) was not completely clear from earlier studies.

HCl has also been used extensively on InP(100) surfaces, but mostly for etching [15 –20] rather than as a chemical cleaning method. Oxide and carbon contamination are reported on the surface after HCl etching [18]. This result should not be due to the chemical reactions of InP with the HCl, but rather environmental contamination after the etching, since these experiments were not done in a inert environment. As a result, the

surface quality of the InP(100) surface in those etching studies were not carefully controlled nor well-understood. It is not clear why HF had been used for InP cleaning in the first place. Being a weak acid, HF is not expected to perform as well as HCl in oxide removal. It is used for SiO_2 etching because of its unique property of dissolving SiO_2 to produce soluble SiF_6^{2-} but this is irrelevant for etching InP oxides. Nonetheless, it is interesting to look at the InP surface after treatment with an HF solution.

In this study, photoemission electron spectroscopy (PES) is used to study the chemical species remaining on the InP(100) surface after the different steps in the cleaning process. In order to reduce the number of variables, the chemical cleaning is done in an inert environment. In addition, synchrotron radiation (SR) is used as the excitation source for the PES because SR gives a tunable range of photons from 60eV to 600eV, yielding high surface sensitivity with a minimum electron escape depth of 5 Å. This work first studied the one step chemical cleaning process using hydrogen peroxide based solutions, which are typically used in the primary chemical etching step in the cleaning of GaAs surfaces. Although this process, when followed by vacuum annealing, will result in a clean, stoichiometric GaAs(100) surface [13], in the case of InP, this study shows that an additional chemical etching step is required to remove oxides remaining on the InP surface after etching. These oxides are not present in a typical GaAs clean, showing the importance of understanding the etching mechanisms specific to InP. In the second chemical cleaning step, different acids with different concentrations are investigated. It is found that the solution acidity is very important for surface oxide removal and if HF is used in the second step, a quite different surface termination is obtained.

2. Experimental:

The InP (100) wafers used are zinc doped, with a p-type carrier concentration of 5 $\times 10^{17} cm^3$. They are mirror-finished and manufactured by Wafer Technology, U.K. The chemical cleaning is done inside of a glove box purged with pure Argon. The glove box is directly connected to the load lock of the photoemission chamber, allowing immediate transfer after the chemical cleaning without any exposure to air. In this manner the cleaning environment is controlled to minimize the contamination from air.

Solutions used in cleaning are made from high purity chemicals purchased from Kanto Chemical Company. The concentration of H_2SO_4 is 96%, HCl, 36%, H_2O_2, 30% and NH_3, 30%, HF, both 49% and 1%.

For the first cleaning step, three hydrogen peroxide based solutions are studied.

(A) 4:1:100 H_2SO_4:H_2O_2:H_2O for two minutes

(B) 4:1:1 H_2SO_4:H_2O_2:H_2O for two minutes

(C) 10:2:100 NH_3: H_2O_2:H_2O for two minutes.

For the second step, the effectiveness of oxide removal by acid or base solutions with different concentrations is studied. Four different chemicals are investigated: HCl, H_2SO_4, NH_3 and HF. The NH_3 solution is found to be completely ineffective for oxide removal [14] so will not discussed further in this paper.

After the sample is dipped in the solution, it is rinsed with de-ionized water, blown dry with nitrogen, and immediately transferred into the load lock. The load lock is pumped down with a turbo-molecular pump and then the sample is transferred into the photoemission chamber for analysis. Lastly, the sample is vacuum annealed in the

photoemission chamber. The sample surface-temperature to heater-current relationship is periodically calibrated by touching the surface of a test sample with a chromel-alumel thermocouple. The time for vacuum annealing is normally 30 minutes unless stated otherwise.

The photoemission spectra are measured on Beam Line 8-1 (photon energy range of 30-190 eV) and 8-2 (photon energy range of 200-1300 eV) at the Stanford Synchrotron Radiation Laboratory (SSRL). The photon energy range of Beam Line 8-1 gives the best combination of surface sensitivity and energy resolution for the In 4d (E_b = 16.5eV) and P 2p (E_b = 135eV) core levels and the valence band which are measured at $h\nu$ = 70, 165 and 70 eV, respectively. Beam Line 8-2 must be used to access the core levels with higher binding energies such as the S2p (E_b = 162.5eV), Cl2p (E_b = 200eV), C1s (E_b = 284.2eV), O1s (E_b = 543.1eV) and F1s (E_b = 696.7eV). Surface concentrations of S and Cl were found to be negligible after etching and will not be considered further.

The photoemission spectra are measured with a PHI (model 10-360) hemispherical energy analyzer with a multichannel detector. The spectra were fitted with Voigt functions, which are Gaussian broadened Lorentzian line shapes. The spin-orbit splitting is fixed at 0.86eV for P 2p and 0.855eV for In 4d.

3. Results and discussion:

3.1 Results of the one step chemical cleaning by hydrogen peroxide based solutions.

The InP(100) surfaces etched with hydrogen peroxide based solutions are hydrophilic. The P2p, In4d and valence band spectra cleaned by 4:1:100 H_2SO_4:H_2O_2:H_2O are shown in figure 1. Spectra labeled (A) are taken after the chemical etching. There is a chemically shifted P2p peak with kinetic energy 3.9 ± 0.2 eV lower than the bulk P2p peak (at 32.2eV). This is due to phosphorous oxide. The In4d spectrum can be decomposed into two components, the one on the right is the Indium bulk peak in InP, the one on the left, with kinetic energy 0.47 ± 0.03eV lower than the bulk peak, is due to Indium oxide. A strong feature exists around 60.5 eV in the valence band spectrum, which is related to the O2p level. Therefore, after this cleaning step, the surface has 0.23-0.5 ML of oxide, which most likely takes the form of Indium Phosphate [14]. Spectra labeled (B) are for samples cleaned with 4:1:100 H_2SO_4:H_2O_2:H_2O and annealed to 360°C. The phosphorous oxide peak moves to a kinetic energy 4.8 ± 0.2 eV lower than the bulk P2p peak, the Indium oxide peak is reduced, but a tail on the lower kinetic energy side implies that it not removed completely. The Valence band O2p feature splits into two peaks, at approximately 59 eV and 61eV. All these changes can be attributed to the conversion of Indium Phosphate to poly-phosphate or metaphosphate [14]. The vacuum annealing does not remove the oxide completely from the surface, but rather changes the form of the oxide.

For samples etched with the 4:1:1 H_2SO_4:H_2O_2:H_2O solution, there is more oxide (1 – 1.5 ML) left on the surface, as shown in figure 2 (a) and (b). For the P2p spectra, a peak labeled P’ is observed in addition to the bulk and oxide peaks. This peak can have contributions from either elemental Phosphorous or a sub-oxide. When the sample is annealed, the P’ peak disappears and the phosphorous oxide peak moves to lower binding

energy. At the same time, the In4d spectrum undergoes a line shape change. The tail on the lower kinetic energy side moves to even lower kinetic energy. This means that In4d components with higher binding energy appear when the sample is annealed. This is consistent with conversion of Indium Phosphate to poly-phosphate or metaphosphate. In poly-phosphate or metaphosphate, the charge density per atom is lower than in the phosphate group, so it attracts electron from Indium more strongly. As a result, Indium atoms in poly-phosphate or metaphosphate have lower charge density, causing a higher binding energy for the In4d photoelectrons.

Figure 2 (c) and (d) show the P2p and In4d spectra for InP(100) samples etched with a 10:2:100 $NH_3:H_2O_2:H_2O$ solution. Even more oxide is left on the surface. Similar changes in the oxide peaks are observed when sample is annealed. The valence band spectra for samples etched by solutions (B) and (C) are similar to solution (A) (shown in figure 1(c)).

It is known that solution (A) (4:1:100 $H_2SO_4:H_2O_2:H_2O$) is effective for GaAs(100) cleaning, where the surface is left with more than 2 ML elemental As and less than 0.2 ML suboxide after the chemical etching, which can be removed after annealing at 500°C [13]. The question that remains to be answered is: why are the chemical species so different for InP and GaAs? When GaAs is oxidized by H_2O_2, the products (excluding intermediate products) are Ga_2O_3, As_2O_5. When sulfuric acid is present in the solution, the Arsenic oxide exists as an acid like H_3AsO_4. The hydrolysis of GaAs in acid solution starts with the following reaction:

$$GaAs + H^+ \rightarrow Ga^{3+} + AsH_3 \qquad \text{(reaction 1)}$$

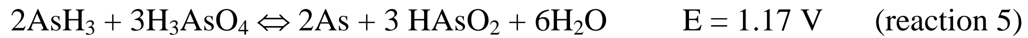
As in AsH_3 has an oxidation state of –3, while As in H_3AsO_4 has an oxidation state of +5. Can the latter oxidize AsH_3 to form elemental As, which has an oxidation state of 0? Let us look at the electro-chemical potential for the following half reactions:

$As + 3H^+ + 3e \Leftrightarrow AsH_3$ $\quad E_a^o = -0.61V$ (reaction 2)

$H_3AsO_4 + 2H^+ + 2e \Leftrightarrow HAsO_2 + 2H_2O$ $\quad E_a^o = 0.56$ V (reaction 3)

$HAsO_2 + 3H^+ + 3e \Leftrightarrow As + 2H_2O$ $\quad E_a^o = 0.248$ V (reaction 4)

Here, we can see that AsH_3 is a very strong reducing agent, while $HAsO_2$ and H_3AsO_4 are relatively strong oxidants. Therefore, the reactions below are very thermodynamically favorable due to large potential drop associated with the full reactions:



$2AsH_3 + 3H_3AsO_4 \Leftrightarrow 2As + 3\ HAsO_2 + 6H_2O$ $\quad E = 1.17$ V (reaction 5)

$AsH_3 + HAsO_2 \Leftrightarrow As + 2H_2O$ $\quad E = 0.858$ V (reaction 6)

The overall outcome is that elemental As is generated. It has to be pointed out that the system is not in an equilibrium state. H_2O_2 in the solution will continue to oxidize As and $HAsO_2$ to the final product H_3AsO_4, and fresh As will be produced as long as the GaAs substrate is still available. All the reactions compete with each other and form a balanced (not equilibrium) state, and a significant amount of elemental As is always present on the surface.

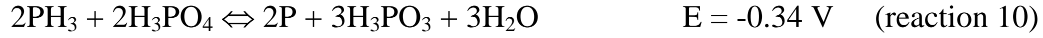
In the case of InP, the product of oxidation by H_2O_2 is phosphoric acid H_3PO_4. Similarly, we can look at the half reactions:

$H_3PO_4 + 2H^+ + 2e \Leftrightarrow H_3PO_3 + H_2O$ $\quad E_a^o = -0.28$ V (reaction 7)

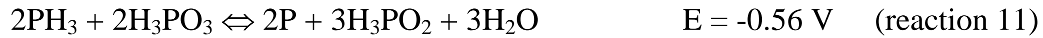
$H_3PO_3 + 2H^+ + 2e \Leftrightarrow H_3PO_2 + H_2O$ $\quad E_a^o = -0.50$ V (reaction 8)

$P(white) + 3H^+ + 3e \Leftrightarrow PH_3$ $\quad E_a^o = 0.06$ V (reaction 9)

Note that the following reactions are not thermodynamically favorable because potential drops for these reactions are negative!



$2PH_3 + 2H_3PO_4 \Leftrightarrow 2P + 3H_3PO_3 + 3H_2O$ E = -0.34 V (reaction 10)



$2PH_3 + 2H_3PO_3 \Leftrightarrow 2P + 3H_3PO_2 + 3H_2O$ E = -0.56 V (reaction 11)

As the result, although there might be some elemental Phosphorous as intermediate reaction product, or produced due to some special surface property, it is not likely that a significant amount of elemental Phosphorous can be built up on the surface. On the contrary, the surface chemical species are dominated by oxides, as shown in our experiments.

3.2. Results of the two step chemical cleaning with HCl or H_2SO_4 as the second step

After the sample is etched in the 4:1:100 H_2SO_4:H_2O_2:H_2O solution (first cleaning step), it is then dipped in a 1:3 HCl:H_2O solution for 30 seconds. The surface is hydrophobic after the second chemical cleaning step. The P2p spectra and In4d spectra after cleaning and annealing to different temperatures are shown in figure 3 and 4, respectively. The P2p spectrum after the second step etching in HCl can be decomposed into two components (figure 3(b)). The one on the right is P in InP. The one on the left with kinetic energy 1.35 ± 0.05eV lower than bulk peak (i.e. higher binding energy) is assigned as elemental Phosphorous in our early study [14], with coverage of about 0.4 ML. When sample is annealed in vacuum, the elemental P is first reduced (figure 3 (a)) and eventually removed at 330°C, as evidenced by the fact that only one component is needed to fit the P2p peak (figure 3 (c)). In figure 4, In4d starts with only one component. When sample is heated, a component appears on the higher kinetic energy side, labeled as

In' in figure 4 (a). Three components are used to fit the In4d peak after the sample is annealed to 330°C as shown in figure 4 (c). The lower binding energy component at 0.48±0.03eV to the right of the bulk peak (due to In in InP) is obvious from the line shape change in figure 4 (a). The higher binding energy component at 0.39±0.03eV to the left of the bulk peak it is required to obtain a good fit. The comparison of these results to prior InP(100) studies were discussed in reference 14.

Etching with the 1:1 H_2SO_4:H_2O in the second chemical cleaning step produced exactly the same results as for the HCl. This result leads to the belief that HCl is not unique for removal of oxides on the InP(100) surface and that other strong acids should also work as well.

In fact, the effectiveness of oxide removal by HCl or H_2SO_4 is strongly dependent on the concentration of the acid. If the InP sample is treated with a 1:15 HCl:H_2O solution, the surface is hydrophilic! The P2p and In4d spectra after a sample is cleaned by 1:15 HCl:H_2O are shown in figure 5 as well as the spectra for a sample cleaned by 1:3 HCl:H_2O for comparison. The amount of elemental P is less (0.2-0.3ML) compared to the 1:3 HCl:H_2O clean and there is about 0.1-0.2ML of oxide left on the surface. The result for sample cleaned by 1:10 H_2SO_4:H_2O is similar to the 1:1 H_2SO_4:H_2O, with a hydrophilic surface, less elemental P and about 0.1ML of oxide. However, this surface is not resistant to subsequent oxidation by water during the rinse, because more oxide is observed on the surface with increased rinsing time.

It is surprising that concentration of HCl or H_2SO_4 makes such a big difference here because a strong acid should remove oxide effectively, even if it is relatively dilute.

The underlying reason for this is that the more concentrated acid solutions can more effectively hydrogen-terminate the surface.

The hydrolysis of InP in an acidic solution takes place as follows:

$InP + H^+ \rightarrow In^{3+} + PH_3$ (reaction 12)

At the beginning of the reaction, H atoms bind to the surface phosphorous atoms, so the surface will have a hydrogen termination on the phosphorous sites after treatment with a strong acid solution. The hydrophobic surface caused by hydrogen termination is well known for Si surfaces because H-Si bond is almost non-polarized due to the small difference of their electron-negativity, and this appears to be also the case for InP(100) surfaces. Therefore, the "elemental" P component discussed earlier may not be really "elemental", but surface P atoms bonded to hydrogen instead. The concentration of H^+ must be high enough to successfully terminate the surface. When the H^+ concentration is too low, the OH^- groups in solution will compete with H^+ to terminate the surface sites, leading to a hydrophilic surface and an obvious oxidized Indium component, as shown in figure 5(b).

Not only is the hydrophobic surface resistant to oxidation by water, but it also results in less carbon contamination from the solution [14]. Therefore, to obtain a clean starting InP(100) surface, a strong acid solution with a high enough concentration must be used to achieve a hydrophobic surface. This is different than the case for the GaAs surface after the same chemical cleaning. There the surface has several layers of elemental As [13], which probably exist as molecules such as As_4. Therefore, there is no hydrogen termination for the GaAs surface and therefore it is not as hydrophobic as the InP.

3.3. Results of the two step chemical cleaning with HF as the second step

In contrast to the previous results, the InP(100) surfaces cleaned by HF in the second chemical cleaning step are hydrophilic, no matter what concentration is used.

Figure 6 shows the P2p and In4d spectra after InP(100) sample is etched in 1% HF for two minutes. There is no component due to elemental P, but a small oxide peak in the P2p spectrum is observed after the HF etch. The line shape change in the In4d spectra can be understood more clearly in figure 7, where the decomposition of the In4d peaks at different annealing temperatures is shown. After the second step etch in HF, the In4d can be decomposed into two components (figure 7(a)). The component on the right is due to In in bulk InP. The second component at 0.53 eV higher binding energy has a similar chemical shift as In oxide. However, as will be discussed below, this peak is actually due to surface Indium atoms bonded to Fluorine. This assignment is supported by the F1s and valence band spectra in figure 8.

In figure 8 (a), F1s peak disappears when sample is annealed to 230°C, so does the dominant feature in the valence band at 58 eV, which is related to the F2p level. Based on the F1s intensity, the Fluorine coverage is calculated to be 0.48 ML before annealing and 0.31 ML after annealing at 180°C. In figure 7, we can see that the chemically shifted In component is reduced with the vacuum anneal. The coverage for this component is calculated to be 0.44 ML before annealing and 0.30 ML after annealed at 180°C. These values are very close to the F coverages calculated from the F1s intensity. This supports the conclusion that the chemically shifted In component is

primarily due to surface Indium atoms bonded to fluorine. Thus, after the HF treatment, the InP(100) surface is terminated with Fluorine on the Indium sites.

As shown in figure 8, fluorine is removed by annealing to 230°C. However, the chemically shifted In peak does not disappear completely because the becomes indium oxidized as also evidenced by an increase in the phosphorous oxide (note the P2p spectra in figure 6(a)). For this to happen, there must be a source of oxygen for this re-oxidation of the InP substrate. Indeed, the O1s core level spectrum shows that there is more than one monolayer of oxygen on the surface after the second step HF etch which is far greater than the amount of residual oxide left on the surface. This amount of oxygen is due to water molecules adsorbed on the surface. Even though the sample is blown dry before being loaded into chamber, the hydrophilic surface can still keep one layer of water on the surface. For Fluorine terminated surfaces, the binding of water to the surface is even stronger because the formation of hydrogen bonds between the very negatively charged fluorine atoms and the very positively charged hydrogen atoms in the water molecules. The energy for such hydrogen bonds can reach up to the order of 20 kJ/mol, which is very strong, compared to Van der Waals forces. The layer of water attached to the surface is tightly bound so they it not be removed by blow-drying. When the sample is heated, some water molecules leave the surface, but the rest attacks the substrate and causes re-oxidation.

HF solutions with other concentrations in the range from 10% to 1% were studied and with no significant dependence on the HF concentration. Furthermore, more oxide is seen on the surface with longer rinsing times after HF etching. This indicates that the fluorine termination does not protect the surface from oxidation in water.

It is interesting to ask the question why HF behaves so differently than HCl. The answer lies in the fact that HF is a weak solution with $K_a = 7.2 \times 10^{-4}$, while HCl is a strong acid. The H^+ concentration is very low even for concentrated HF solutions. From the earlier discussion, it is clear that the acidity of the solution plays the dominant role in the formation of "elemental" phosphorous and hydrogen termination on phosphorous sites. Therefore, it is understandable that the HF solution, with its very small concentration of H^+, is not able to form a hydrogen-terminated, hydrophobic InP(100) surface. On the other hand, the bonding between In and F is much stronger than the bonding between In and Cl, resulting in a fluorine termination is formed after HF treatment and retained after rinsing, whereas only a trace amount of Cl is seen on the surface after HCl etching.

3.4. Importance of the surface termination/passivation

Generally, chemical etching plays two roles in the overall cleaning process: first, it removes the surface contaminants; second, it prepares an appropriate starting surface (desirable passivation and termination) for the subsequent cleaning step, typically a vacuum anneal. A good chemical etching process must satisfy both criteria to ensure the cleanliness of the final surface. The second criterion is particularly important for materials that have low decomposition temperatures. Hence, in the development of an etching recipe that is based on the concepts of oxidation and dissolution, the third aspect of an appropriate surface termination must be considered as well. From our experience, a surface termination which results in a hydrophobic surface is typically the most desirable. Such a surface not only reduces the possibility of oxidation by residual water molecules

or contamination (especially by carbon) from solution but also eliminates the need for a drying step which can also introduce additional contamination.

Our results on InP demonstrate that a second etching step with a strong acidic solution containing a sufficient concentration of HCl or H_2SO_4 is required to created a hydrophobic, hydrogen terminated surface. Whereas, a weak acid such HF creates a hydrophilic, fluorine terminated surface. After the same vacuum annealing step, the hydrogen terminated samples produce a far superior final surface than those that are fluorine terminated. This is a direct result of the fact that the hydrophilic surface retains a layer of water molecules, which re-oxidize the surface when sample is heated. In this particular case, the binding of water to the surface fluorine atoms is fairly strong due to hydrogen bonding; however, it is not possible to generalize these conclusions to other hydrophilic surfaces without understanding the specific chemistry of those surfaces. For example, in the case of GaAs, although the surface is not hydrogen terminated after chemical cleaning, there are several layers of elemental As which act as a protective layer against reoxidation or contamination and are volatile upon heating. Therefore, in the GaAs case, the appropriate starting surface for subsequent vacuum heating can be the hydrophilic surface.

4. Conclusion:

Different chemical solutions were used to clean the InP(100) surface. In the one step chemical cleaning process, hydrogen peroxide based solutions were used and it was found that a significant amount of oxide is grown on the surface, which can not be completely removed by vacuum annealing. This requires the addition of a second

chemical cleaning step to remove the oxide. When a strong acid like HCl or H_2SO_4 solution is used, the oxide can be removed and submonolayer of hydrogen terminated P remains on the surface. However, the effectiveness of oxide removal and surface hydrogen termination is strongly dependent on the concentration of the acid. HF etching leaves the InP(100) surface terminated with fluorine on the Indium sites, which leads a hydrophilic surface with water molecules attached to F. The optimum chemical cleaning process in this study was found to be: 2 minutes etching in 4:1:100 H_2SO_4:H_2O_2:H_2O to remove the native oxide and 30s in 1:3 HCl or 1:1 H_2SO_4:H_2O to remove the chemical oxide grown by the hydrogen peroxide solution. This two step process can achieve a hydrophobic surface, which leads to less carbon contamination. Finally, the sample is annealed to the relative low temperature of 330°C which removes the elemental P and results in an atomically clean surface. We also concluded that the type of surface termination/passivation after the chemical treatment is very important for avoiding oxidation and contamination in the subsequent sample handling and treatment steps. This is an important point which must be considered when developing surface cleaning processes for any semiconductor surface.

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List of Illustrations:

Figure1. (a) P2p, (b) In4d and (c) VB spectra after the InP(100) sample is etched in 4:1:100 H_2SO_4:H_2O_2:H_2O solution. (A) After the chemical etch. (B) After etch and anneal at 360°C.

Figure 2. Spectra after the InP(100) sample is etched with 4:1:1 H_2SO_4:H_2O_2:H_2O solution and annealed at different temperatures, (a) P2p, (b) In4d; and sample etched with 10:2:100 NH_3:H_2O_2:H_2O, (c) P2p, (d) In4d. Annealing temperatures are labeled on the spectra.

Figure 3. (a) P2p spectra after the InP(100) is etched in 4:1:1 H_2SO_4:H_2O_2:H_2O followed by a second etching step in 1:3 HCl:H_2O and then annealed (annealing temperatures are labeled on the spectra). (b) Fit for P2p after the chemical cleaning. (c) Fit for P2p after the chemical cleaning and annealing at 330°C

Figure 4. (a) In4d spectra after the InP(100) is etched in 4:1:1 H_2SO_4:H_2O_2:H_2O followed by a second etching step in 1:3 HCl:H_2O and then annealed (annealing temperatures are labeled on the spectra). (b) Fit for the In4d after the chemical cleaning. (c) Fit for the In4d after chemical cleaning and annealing at 330°C.

Figure 5. (a) P2p and (b) In 4d spectra for the InP(100) surface etched in 4:1:1 H_2SO_4:H_2O_2:H_2O followed by a second etching step in (A) 1:3 HCl:H_2O and (B)1:15 HCl:H_2O. The In4d spectrum is shown with the fit for case (B).

Figure 6. (a) P2p and (b) In 4d spectra for the the InP(100) sample etched in 4:1:1 H_2SO_4:H_2O_2:H_2O followed by a second etching step in 1% HF and annealed at different temperatures (temperatures are labeled on the spectra).

Figure 7. Numerical fitting of the In4d spectra for InP(100) etched in 4:1:1 H_2SO_4:H_2O_2:H_2O followed by a second etching step in 1% HF and annealed to different tmperatures: (a) After HF etch, before annealing, (b) 120°C. (c) 180°C, (c) 360°C.

Figure 8. (a) F1s and (b) valence band spectra for InP(100) etched in 4:1:1 H_2SO_4:H_2O_2:H_2O followed by a second etching step in 1% HF and annealed at different temperatures. (Temperatures are labled on the spectra).

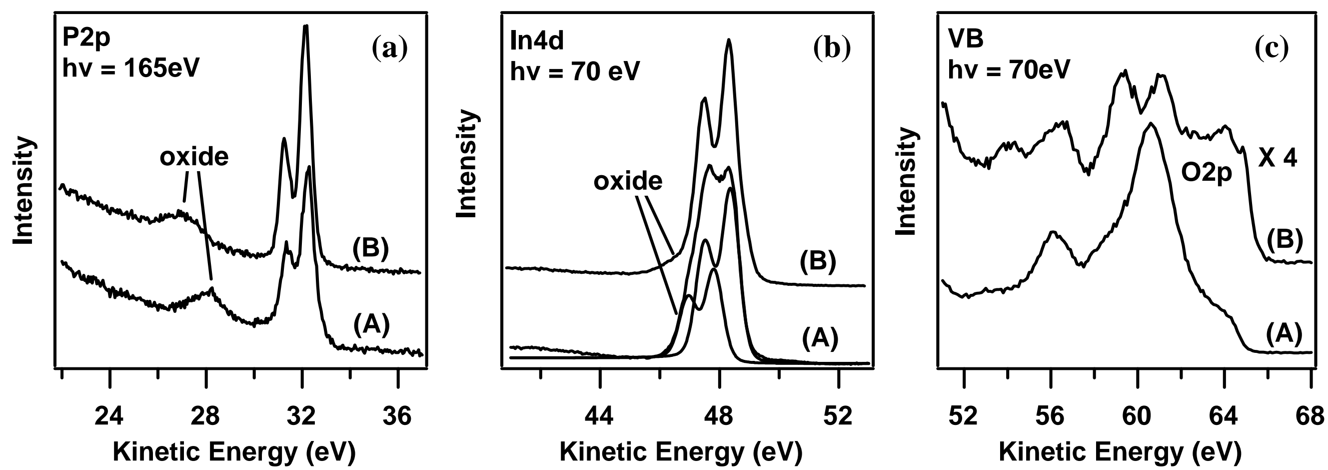

Figure 1

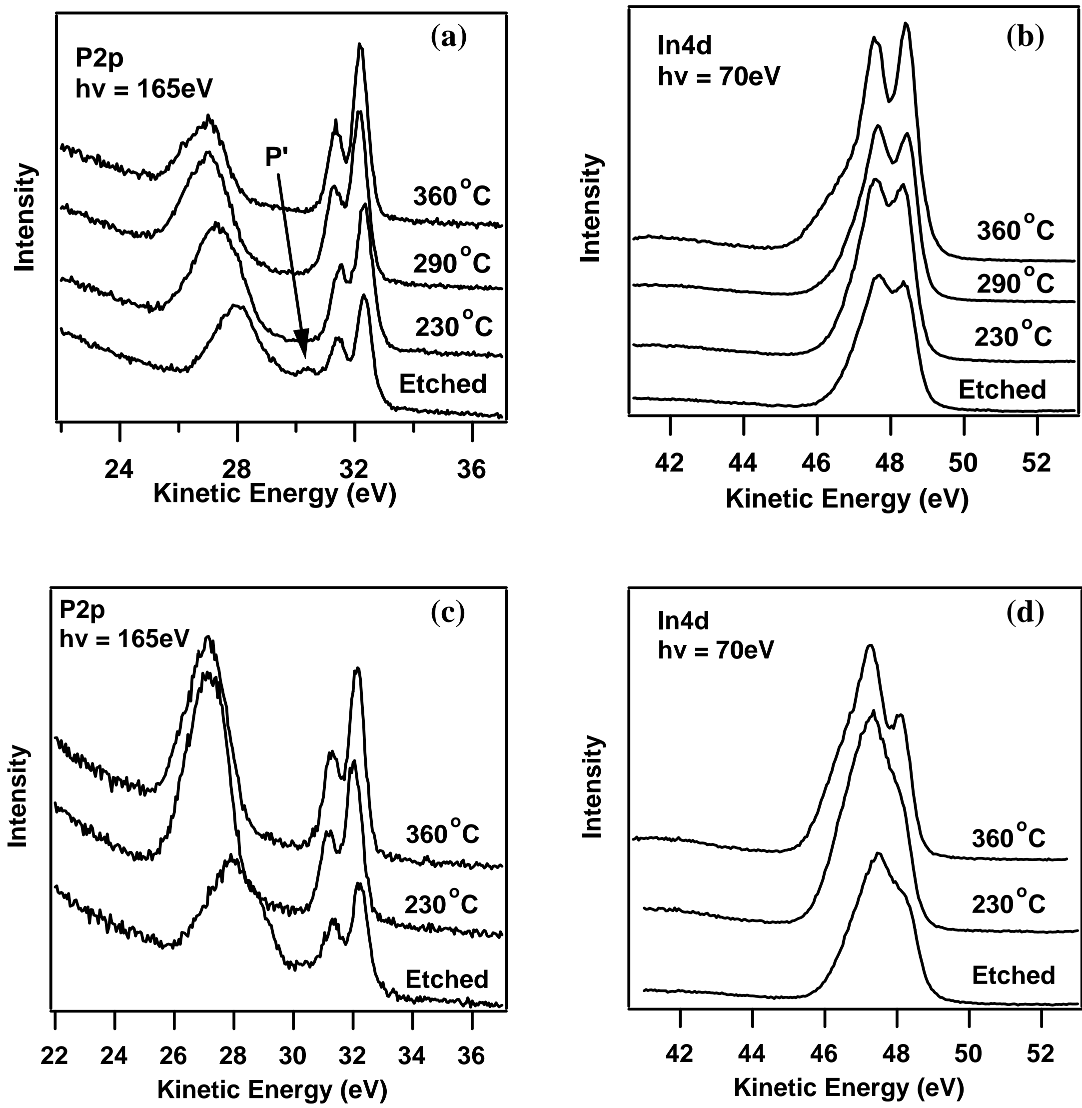

Figure 2

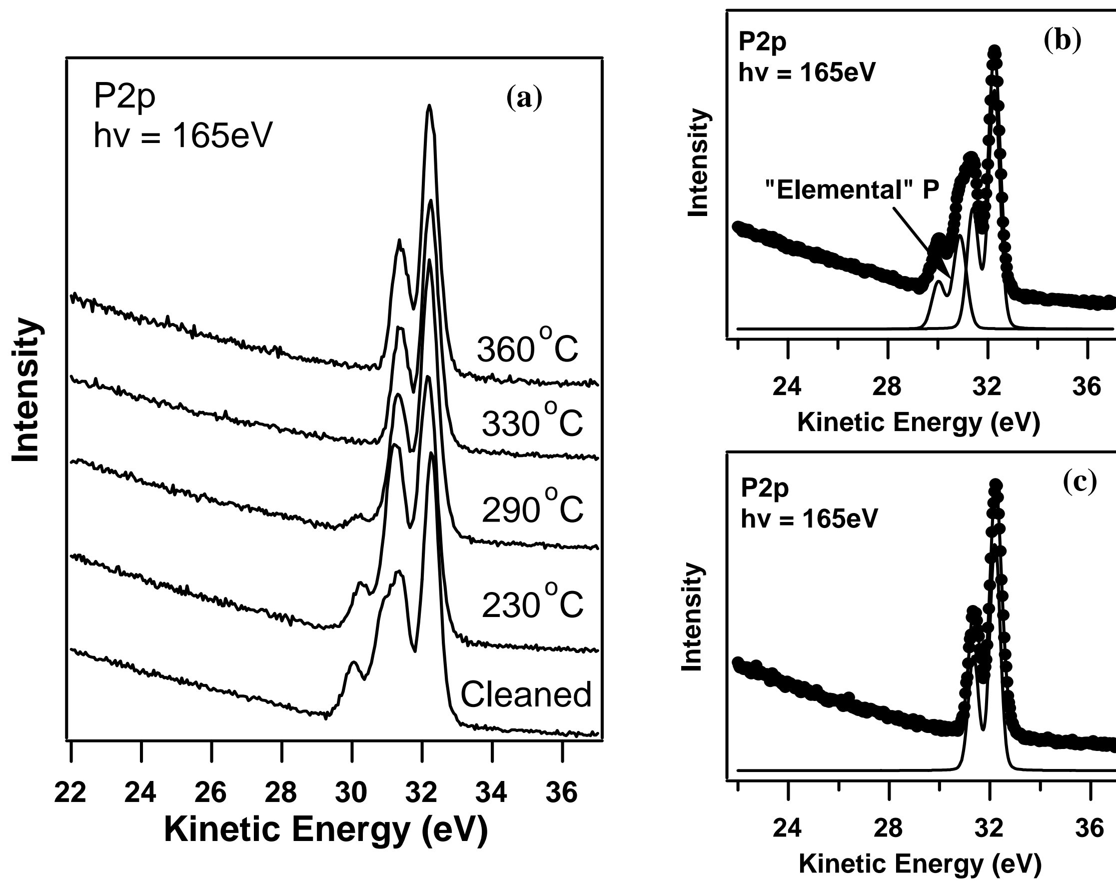

Figure 3

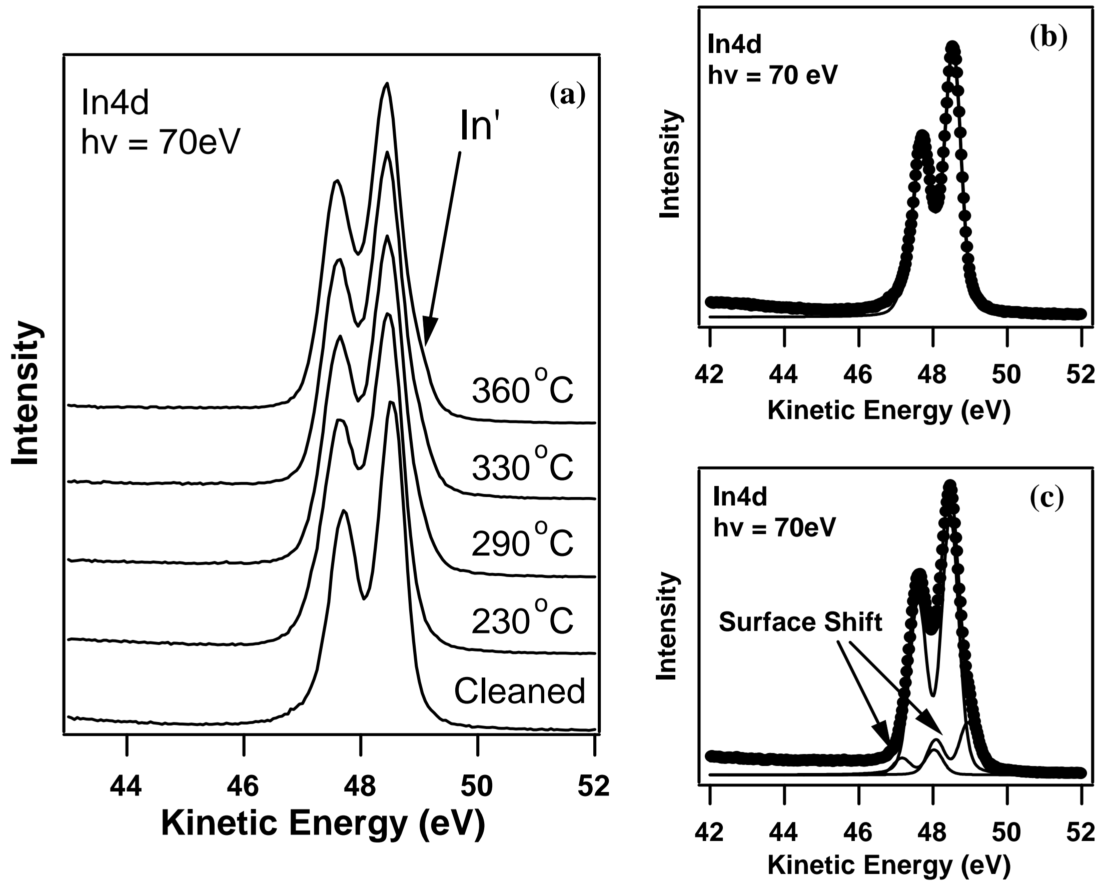

Figure 4

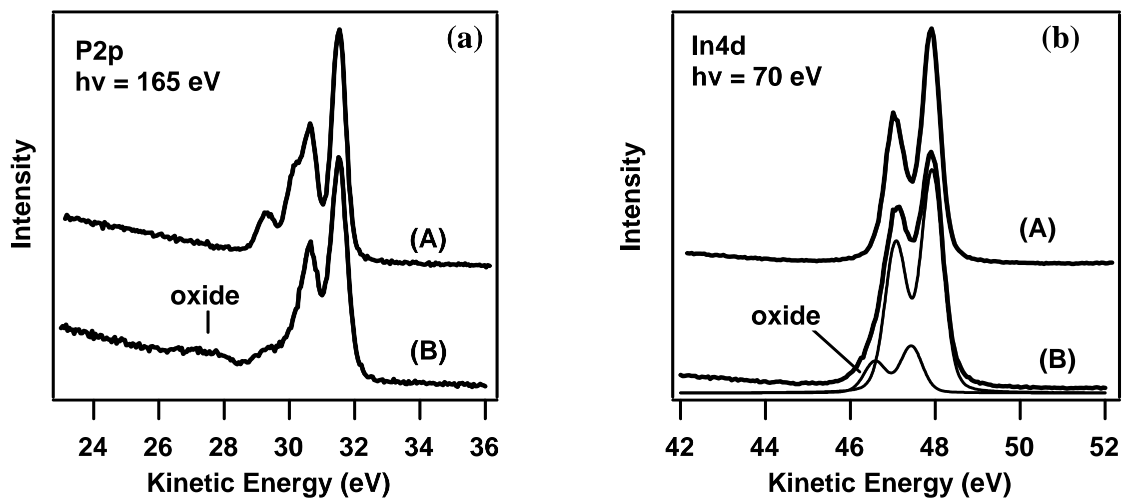

Figure 5

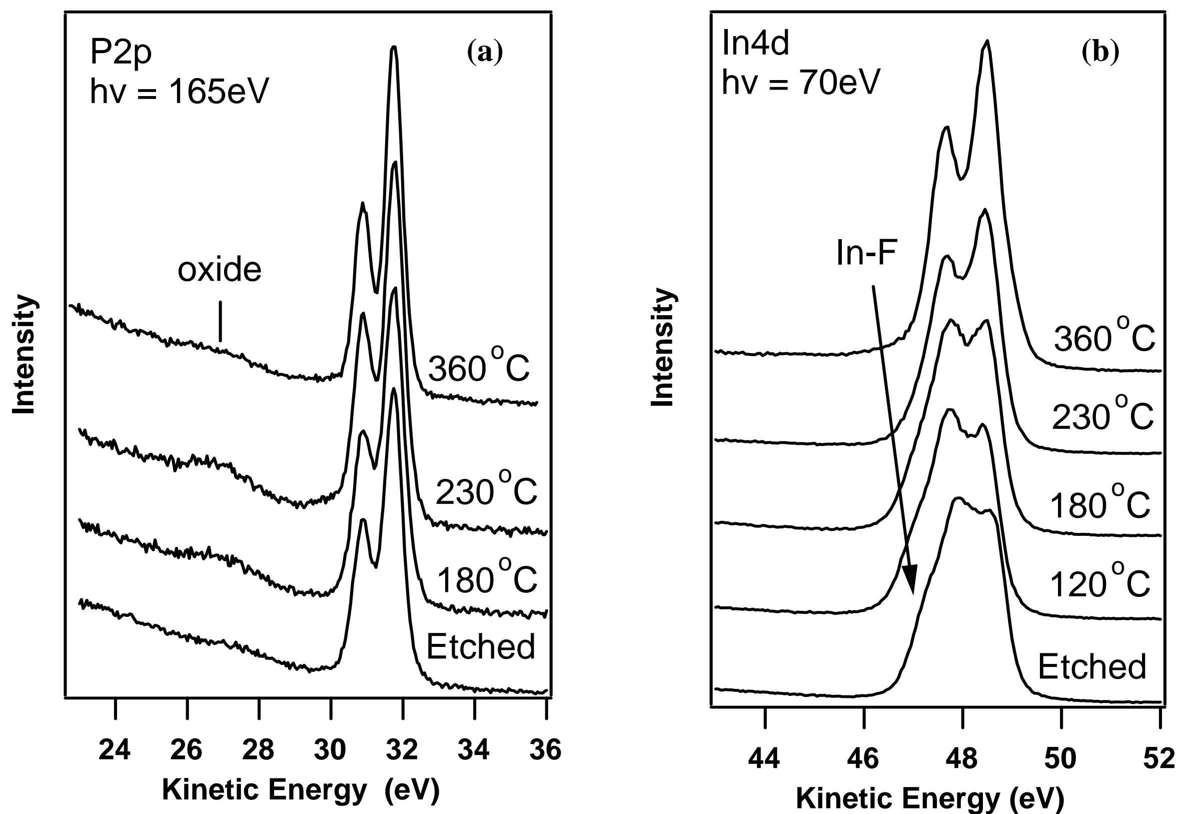

Figure 6

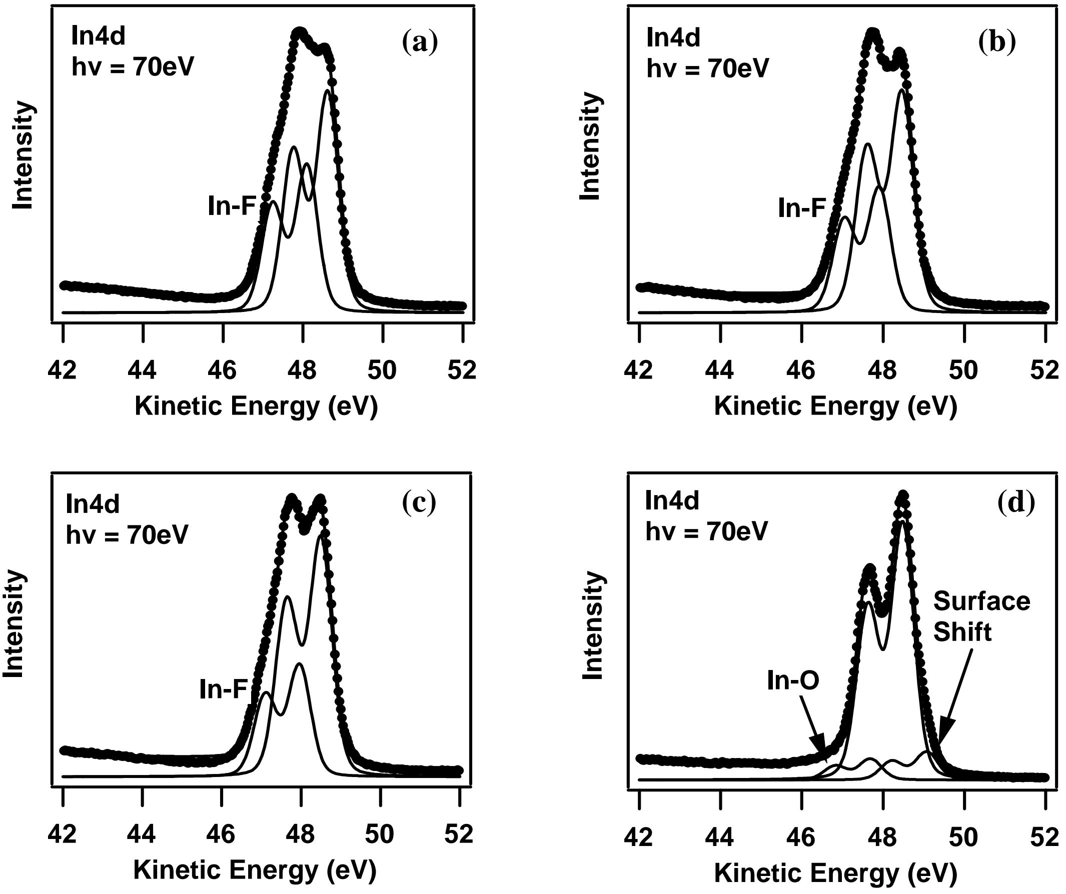

Figure 7

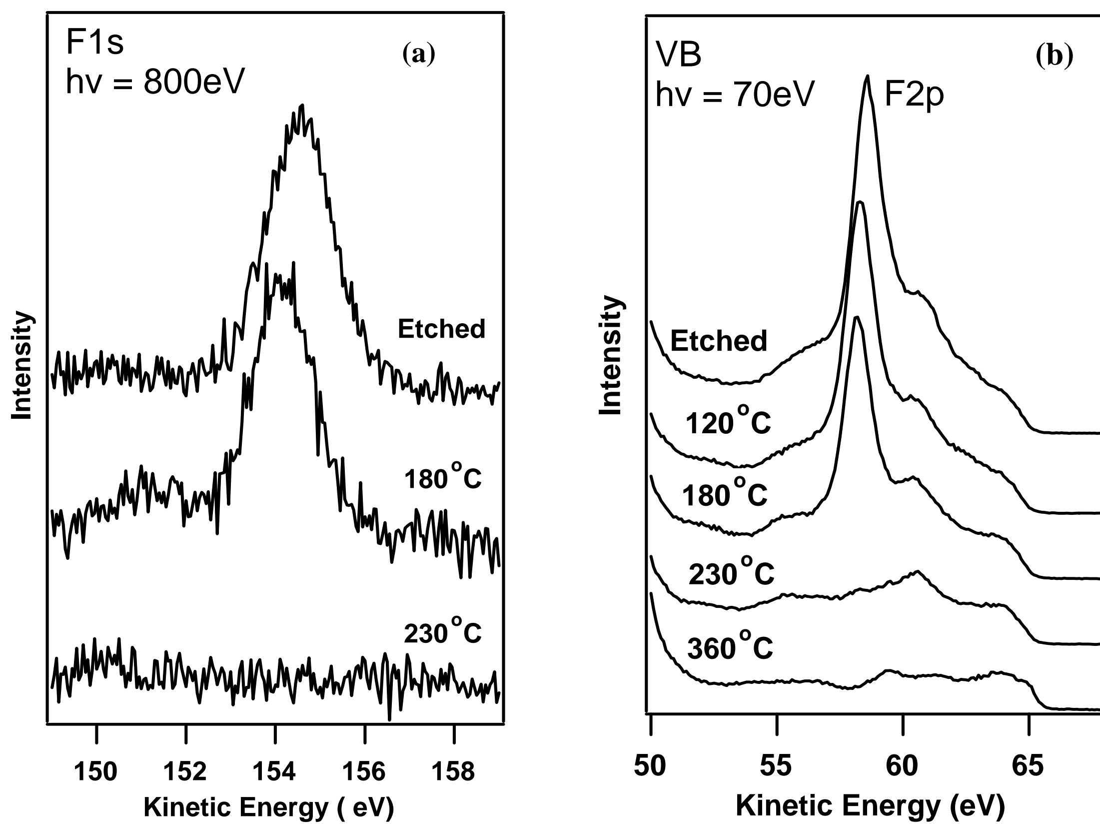

Figure 8