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Arsenic-dominated chemistry in the acid cleaning of InGaAs and InAlAs surfaces

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The surface cleaning of InGaAs and InAlAs is studied using Synchrotron Radiation Photoelectron Spectroscopy. Thermal annealing at 400°C can not completely remove the native oxides from those surfaces. Elemental arsenic build-up is observed on both surfaces after acid treatment using HCl, HF or H_2SO_4 solutions, which is similar to acid-cleaned GaAs surface. Cleaned InGaAs surface is oxide free but small amount of aluminum oxide remains on cleaned InAlAs surface. The common chemical reactions between III-As semiconductors and acid solutions are identified and are found to be dominated by arsenic chemistry.

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The increasing need for higher speed and lower power consumptions has pushed the Si-based transistors to their performance limit. III-V compound semiconductors such as InGaAs and InAlAs, due to their high carrier mobility, are being actively investigated for a possible replacement of channel material of future metal-oxide-semiconductor devices.[1] Clean and stoichiometric III-V semiconductor surfaces are important for device fabrication. Thermal annealing is commonly used to remove the surface native oxide. Arsenic capping and atomic hydrogen cleaning of the InGaAs and the InAlAs surfaces have also been explored.[2-6] The study of the wet chemical cleaning of the InGaAs and the InAlAs surfaces can provide vital knowledge for the development of device fabrication processes. It is also very useful to look for the similarities and differences in the chemical cleaning of the InGaAs and InAlAs surfaces, and to compare them with the well-understood InP and GaAs surfaces.[7, 8] This can help us identify the common factors and trends in the chemical cleaning of III-V semiconductor surfaces, which can offer guidance for the search of effective cleaning methods for other III-V semiconductors. In this study, we find that after the acid cleaning, the InGaAs surface is completely oxide free but small amount of aluminum oxide still remains on the InAlAs surface. However, on both the InGaAs and the InAlAs surfaces, elemental arsenic build-up are observed, which is very similar to GaAs.[8] This similarity is due to the arsenic-dominated chemistry in the chemical reactions between the III-As semiconductors and the acids.

150 nm thick InGaAs (In:Ga=0.53:047) and InAlAs (In:Al=0.52:0.48) samples are grown on InP(100) substrates using molecular beam epitaxy (MBE). 2% HCl, 10% HCl, 2% HF, 10% HF and 5% H_2SO_4 solutions are used in the chemical cleaning, which are performed in an argon purged glove bag. Photoelectron spectra are collected at beam

line 8-1 of the Stanford Synchrotron Radiation Laboratory (SSRL). Unless stated otherwise, all spectra are collected at normal emission angle. Ga 3d, In 4d, As 3d, and Al 2p spectra are fitted with spin-orbit splitting of 0.44 eV, 0.855 eV, 0.70 eV, and 0.41 eV, respectively, using the fitting program developed by A. Herrera-Gomez.[9]

The As 3d, Ga 3d and In 4d spectra for an as-received InGaAs sample are shown as the bottom curves in figure 1(a) and (b). In figure 1 (b), the Ga 3d and In 4d core levels are very close to each other so numerical fitting is needed to deconvolve the spectra. The four components, from left to right, are Ga 3d of gallium oxide, Ga 3d of InGaAs, In 4d of indium oxide, and In 4d of InGaAs. Native oxides, as expected, are present on the as-received sample. The spectra for the InGaAs sample annealed at 400°C for 30 minutes in vacuum are plotted as the top curves in figure 1(a) and 1(b). In figure 1(a), arsenic oxide is completely removed. Gallium oxide and indium oxide are reduced, but significant amount of them still remains on the surface, as shown in figure 1(b). The residue oxide peaks, which can not be easily detected by conventional X-ray photoelectron spectroscopy (XPS), are obvious at photon energy of 100 eV because of the enhanced surface sensitivity due to the short photoelectron escape depth at this energy (~ 4-6 Å). Therefore, annealing at 400°C can not completely remove all the native oxide. Annealing at higher temperature is not tried to avoid the InP substrate decomposition.

The As 3d, Ga 3d and In 4d spectra for an InGaAs sample etched in 10% HCl solution for 2 minutes are shown as the bottom curves in figure 2(a) and (b). All the native oxides are removed by HCl treatment. Two components are needed to fit the As 3d spectrum. The component on the right is the As 3d of the InGaAs, while the one on the left, with a chemical shift of 0.6 eV from the bulk peak, is due to the elemental arsenic

build-up on the surface.[8] The thickness of the elemental arsenic is normally 4 – 10 Å, and strongly depends on the amount of initial native oxide. More native oxide before the cleaning generally leads to more elemental arsenic build-up, which is a natural result of the chemical reactions discussed later in this paper. After the sample is annealed at 200°C for 30 minutes in vacuum, the elemental arsenic is completely removed, while no change is observed on Ga 3d and In 4d spectrum, as shown by the top curves of figure 2(a) and (b).

For the InAlAs sample, the As 3d and In 4d core levels behave almost exactly the same as the ones of the InGaAs sample. After the as-received sample is annealed at 400°C for 30 minutes in vacuum, the native arsenic oxide is gone and the indium oxide is reduced but not completely removed. Indium and arsenic oxide removal and elemental arsenic build-up are observed after the sample is etched in 10% HCl solution for 2 minutes, as shown in figure 3(a) and (b). The amount of elemental arsenic is close to that on an HCl treated InGaAs surface if it has a similar amount of initial arsenic oxide. The elemental arsenic on the surface is removed by 200°C annealing.

Complete removal of aluminum oxide, however, proves very difficult, as shown by the Al 2p spectra plotted in figure 3(c). In figure 3(c)(i), only the Al 2p peak of the aluminum oxide can be seen, while the Al 2p signal from InAlAs is not observable. This indicates that there is disproportionally large amount of aluminum oxide on the as-received sample surface, probably because aluminum is very active and much more readily oxidized in air than indium and arsenic. This disproportional oxidation of the surface aluminum, arsenic and indium might pose a problem for device applications based on InAlAs because the surface stoichiometry is affected. Annealing at 400°C for 30

minutes in vacuum is not effective in removing the native aluminum oxide, as observed in figure 3(c)(ii). This demonstrates the ineffectiveness of thermal annealing as a cleaning method for InAlAs samples because the native aluminum oxide on the surface is thermally stable.

After the InAlAs sample is etched in 10% HCl solution, the aluminum oxide is greatly reduced, as shown in figure 3(c)(iii). A small oxide peak (<0.1 ML) still remains. Elongation of the argon purging time in the glove bag and/or the etching time in HCl solution do not seem to be able to make the surface completely free of aluminum oxide. This small amount of residue oxide is likely due to the re-oxidation of surface aluminum in the glove bag after the etching. Even if the ultra high purity argon (99.999%) used in the glove bag has only 1 ppb of oxygen, it still corresponds to about $1x10^{-6}$ torr and consequently one Langmuir per second of oxygen dosage on the InAlAs surface. The surface arsenic layer, which can offer some protection for the GaAs and the InGaAs surfaces against oxidation, is less effective for cleaned InAlAs surface because aluminum is very active. On the other hand, it is probably not essential to pursue a totally oxide free InAlAs surface for practical purposes because re-growth of aluminum oxide will almost certainly occur in the subsequent processes after the cleaning, due to the active nature of aluminum.

The annealing of HCl cleaned InAlAs sample in vacuum causes more aluminum oxide re-growth, as can be seen from figure 3(c)(iv) and (v), while indium and arsenic remain oxide free. Since the base pressure of the vacuum chamber is only $5x10^{-11}$ torr, we believe that the major sources of the oxygen for this oxide growth are the physisorbed water on the cleaned surface and/or the out-gassing of the sample holder. Those oxygen

sources, although not a concern for GaAs and InGaAs, pose a problem for InAlAs because aluminum is very easily oxidized. The amount of aluminum oxide after annealing is less than 1 ML, whether this oxide will cause a serious problem or not for InAlAs based devices is subject to further study.

The cleaning results of InGaAs and InAlAs are very similar to that of GaAs, in which the native oxide removal and the elemental arsenic build-up on the surface by acid treatment are well established.[7] Just like on GaAs, native arsenic oxide on the surface becomes arsenic acid in acid solution: $As_2O_5 + H_2O \rightarrow H_3AsO_4$, and the substrate reacts with acid to form AsH_3: $MAs + H^+ \rightarrow M^{3+} + AsH_3$ (M=Ga, In, Al). H_3AsO_4 and AsH_3 can react with each other to produce elemental arsenic through the following reactions, which are highly favorable thermodynamically because of the large electrochemical potential drop associated with the reactions:

$$2AsH_3 + 3H_3AsO_4 \Leftrightarrow 2As + 3\ HAsO_2 + 6H_2O \qquad E = 1.17\ V$$

$$AsH_3 + HAsO_2 \Leftrightarrow 2As + 2H_2O \qquad E = 0.858\ V$$

It is interesting to notice that those reactions are determined by arsenic chemistry, not by the group III metals in III-V semiconductors. Therefore, it is not a surprise that the chemical reactions on the InGaAs and InAlAs surfaces are very similar to those on GaAs. Previous work also demonstrates that InAs behaves in a similar manner.[10] We are tempted to extend this conclusion by speculating that, generally speaking, the reactions between cleaning acids and III-V semiconductors are mainly determined by the chemistry of group V elements. Of course, to what extent this speculation is true can only be substantiated by further cleaning experiments on various III-V semiconductor surfaces. We also want to point out that the same chemical reactions do not necessarily lead to the

same final cleanliness. The group III metals, although not active participants of the reactions in acid solutions, can significantly affect the final cleaning results, depending on how easy it is for them to re-oxidize and how stable their oxides are. This is well exemplified by the cleaning result of the InAlAs surface, where the active aluminum prevents the achievement of a complete oxide free surface.

Other acid solutions, such as 2% HCl, 2% HF, 10% HF, 5% H_2SO_4 solutions are also investigated in the cleaning of the InGaAs and the InAlAs surfaces. The results are the same as that by 10% HCl, which indicates that the chemical cleaning explored in this work does not depend on the choice of acid or the concentration. This can be naturally explained by the chemical reactions mentioned above. The function of acids is to provide an acidic environment so that the reactions between As^{-3} and As^{+3}/As^{+5} can occur. Therefore, the choice of acid and concentration is not important as long as they can provide an acidic solution which is strong enough. For some III-V semiconductors, certain acids are not good options because they etch the substrate aggressively. In this case, other acids can be tried, which may lead to slower etch rates with similar cleaning results.

From the surface cleaning study of InGaAs and InAlAs, we can see that thermal annealing is not always effective in removing the surface native oxide. The chemical cleaning of InGaAs and InAlAs using acids are very similar to that of GaAs because the chemical reactions mainly involve arsenic, not the group III metals. However, the chemical properties of group III metals can play a substantial role in the final cleanliness of the III-V semiconductor surfaces.

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Figure captions:

Figure 1. (a) As 3d, (b) Ga 3d and In 4d spectra for a InGaAs sample. Bottom: as-received sample; Top: annealed at 400°C for 30 minutes. In (b), the dots are the experimental data and the solid lines are the numerical fitting results. The four individual components, from left to right, are Ga 3d of gallium oxide, Ga 3d of InGaAs, In 4d of indium oxide, and In 4d of InGaAs.

Figure 2. (a) As 3d, (b) Ga 3d and In 4d spectra for a InGaAs sample cleaned by 10% HCl solution. Bottom: right after the HCl cleaning. Top: annealed at 200°C for 30 minutes after the HCl cleaning. In (b), the dots are the experimental data and the solid lines are the numerical fitting results.

Figure 3. (a) As 3d, (b) Ga3d, and (c) Al 2p spectra for InAlAs samples. In (a), dots are experimental data and solid lines are fitting results. In (c), from bottom to top: (i) as-received sample; (ii) annealed at 400°C for 30 minutes; (iii) cleaned with 10% HCl solution; (iv) annealed at 200°C for 30 minutes after 10% HCl cleaning; (v) annealed at 400°C for 30 minutes after 10% HCl cleaning.

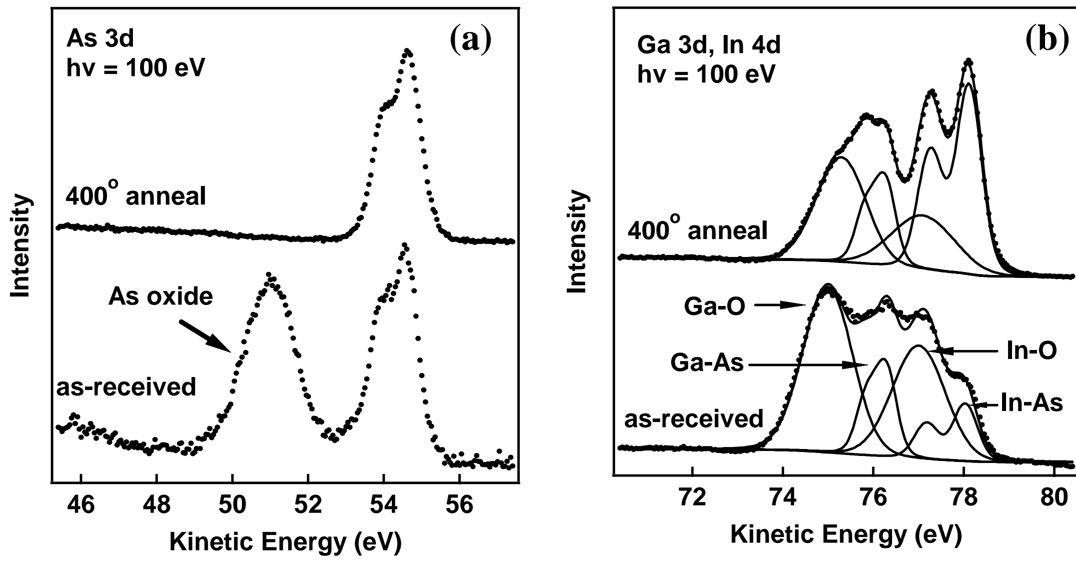

Figure 1

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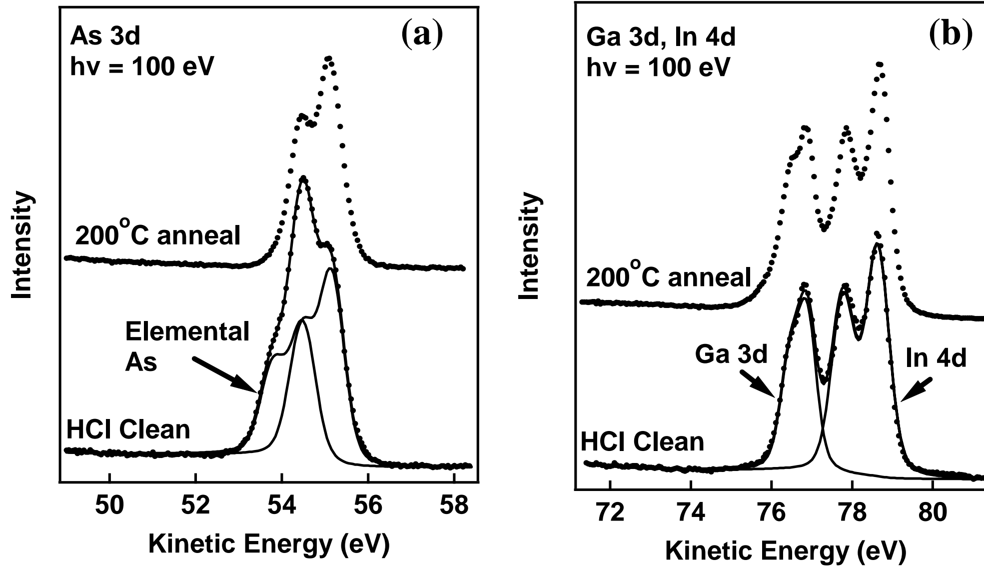

Figure 2.

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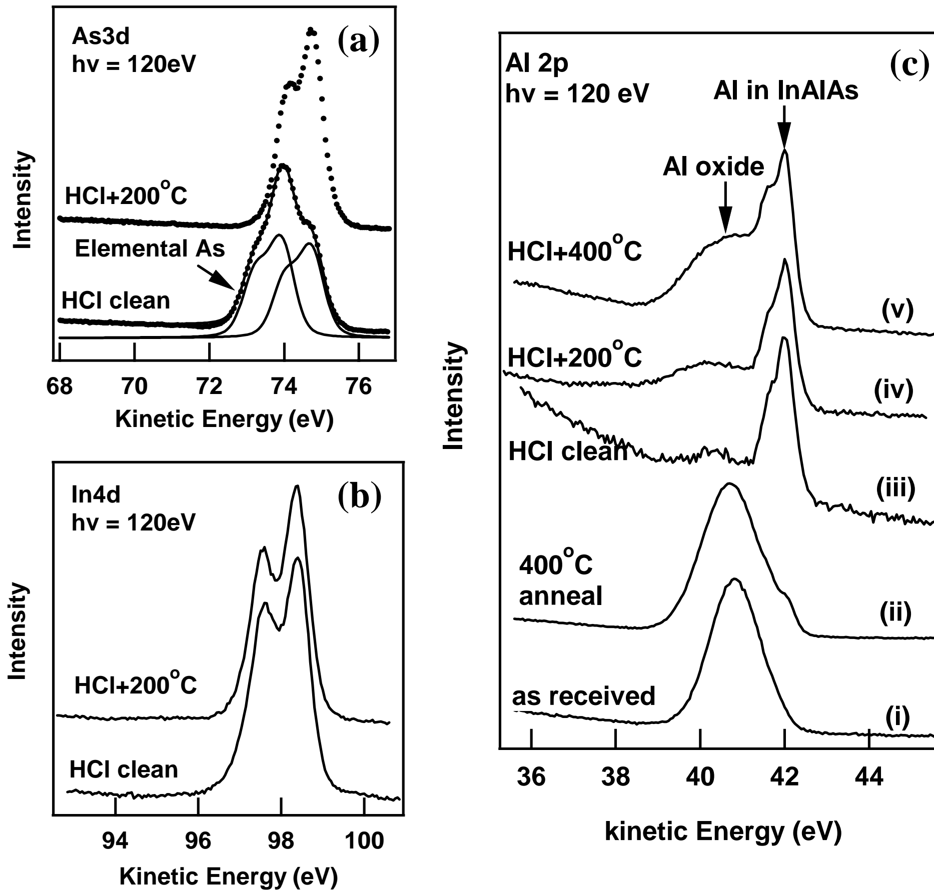

Figure 3

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