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Etching AlAs with HF for Epitaxial Lift-Off Applications

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The epitaxial lift-off (ELO) process allows the separation of a thin layer of III/V material from the substrate by selective etching of an intermediate AlAs layer with HF. In a theory proposed for this process, it was assumed that for every mole of AlAs dissolved three moles of H₂ gas are formed. In order to verify this assumption the reaction mechanism and stoichiometry were investigated in the present work. The solid, solution and gaseous reaction products of the etch process have been examined by a number of techniques. It was found that aluminum fluoride is formed, both in the solid form as well as in solution. Furthermore, instead of substitution of constants, with 

\[ \frac{Dn}{3N} = \frac{1}{\pi \sqrt{Rh/2}} Dn \]  

where \( N \) and \( n \) are the molar concentrations of AlAs and dissolved H₂, respectively, \( D \) the diffusion constant of H₂ in the solution, \( R \) the radius of curvature of the film, and \( h \) the thickness of the AlAs release layer, which generally varies between 3 and 50 nm. Maeda et al. noted that, because of the diffusion coefficient in Eq. 1, \( V_{e,\text{max}} \) is expected to increase exponentially with temperature. This diffusion coefficient is given by

\[ D = D_0 e^{-E_a/RT} \]  

with \( D_0 \) the diffusion coefficient at infinite temperature, \( E_a \) the activation energy, and \( k \) the Boltzmann constant. Using \( E_a = 0.22 \text{ eV} \) and \( D(298 \text{ K}) = 4.8 \cdot 10^{-9} \text{ cm}^2/\text{s} \), \( D_0 \) is found to be 0.25 cm²/s. The combination of Eq. 1 and 2 and the substitution of constants, with

\[ N = 0.037 \text{ mol/cm}^2 \text{ and } n = 0.63 \cdot 10^{-6} \text{ mol/cm}^2 \]  

yield \( V_{e,\text{max}} \) as a function of the process parameters \( R, h, \) and \( T \)

\[ V_{e,\text{max}} = \frac{0.23}{\sqrt{Rh}} e^{-2551/T} \]  

with \( V_{e,\text{max}} \) in mm/h, \( R \) and \( h \) in mm, and \( T \) in K. By application of a weight-induced epitaxial lift-off process (WI-ELO), the relation between \( V_e \), the weight increase, the relevant process parameters, according to Eq. 3, has been investigated. As far as the dependence of \( V_e \) on \( h \) and \( T \) is concerned, good qualitative agreement between theory and experiment was found, but a qualitative discrepancy was encountered for the relation between \( V_e \) and \( R \). Furthermore, the lateral etch rate, as predicted by the model, showed a very large quantitative discrepancy with experiments. For a radius of curvature of 50 mm and a release layer thickness of 5 nm the model predicts a maximum attainable etch rate of approximately 3 µm/h at room temperature, while the experiments show values around 3 mm/h. From this it was concluded that the diffusion of hydrogen gas out of the etch crevice is not the limiting factor in the process, or that hydrogen may not even be a reaction product. This shows that for a correct description of the ELO process information about the actual etching reaction of AlAs with HF is essential.

The present study aims to clarify this reaction. For this purpose, layers of AlAs were etched with aqueous HF solution. The solid, aqueous, and gaseous reaction products were examined with a number of techniques. In previous WI-ELO experiments it was found that oxygen has an influence on the etch rate. For this reason the effect of ambient oxygen on the etch process has also been investigated.

Experimental

All samples used were grown on 2 in. undoped GaAs wafers with crystal orientation (100), 2 degrees off towards (110) using low-pressure metalorganic vapor-phase epitaxy (MOVPE) in an Aixtron 200 reactor. Source materials were trimethyl-gallium and trimethyl-aluminum for the group III and arsine for the group V elements. Disilane was used as the precursor of the n-type dopant silicon. The sample for the solid and aqueous reaction products

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analysis consisted of a layer of n-type AlAs of 50 μm thickness, capped with a 0.3 μm undoped GaAs layer. This cap layer was applied to prevent premature oxidation of the AlAs by oxygen in the air. The samples used for studying the gaseous reaction products and the influence of oxygen in the environment on the etch rate had a similar structure but an AlAs layer of only 5 μm thickness.

The sample for the solid and aqueous reaction products analysis was broken into smaller pieces, which were placed in an airtight stainless steel container, together with two stainless steel balls. This container was mounted in a shaker machine (Retsch MM200) and after 3 min of milling at a frequency of 30 Hz, the wafer was ground up finely enough for further processing. The AlAs/GaAs powder mixture was transferred to a glass vessel, and a stirring magnet was added. The vessel was closed with a rubber septum to prevent escape of any poisonous gas, which could be produced during the etch process. 2 mL of an aqueous 12% HF solution was added to the glass vessel with a syringe through the septum. This amount of HF ensures that four moles of HF are present for each mole of AlAs in the powder. Therefore, all the AlAs could react with the HF while leaving only a small amount of HF, so that the glass of the vessel would hardly be etched. Note that, compared to AlAs, the reaction rate of GaAs with HF is 10^6 times lower.10 After the reaction was complete (1.5 h, as found in explorative experiments), the slurry, containing the fluid together with part of the fine solid remains of the wafer and some solid reaction products, was extracted and transferred to another glass vessel. This vessel was placed in a centrifuge for 5 min at 7000 rpm to separate the different fractions in the slurry. After the separation process, solid debris from the wafer, a white powder, a clear solution, and, floating on this solution, a thin film with a metal-like appearance were found from the bottom to the top of the vessel. The solution was examined using both aluminum nuclear magnetic resonance (NMR, Bruker Avance DRX500) and fluorine NMR (Bruker Avance DMX300) analyses. This NMR equipment was calibrated with an [Al(H₂O)₆]³⁺ solution and with trifluoro-acetic acid, respectively. The white powder and the metal-like film were taken from the vessel to be examined with scanning electron microscopy (SEM), combined with energy dispersive spectroscopy (SEM-EDS). Additionally, an X-ray powder diffraction spectrum was obtained from the white powder, using a Philips PW1820 automatic powder diffractometer.

For the gas-chromatography measurements, half a wafer with a 5 μm thick AlAs layer was milled for 3 min at 30 Hz and etched with 2.5 mL of an aqueous 0.5% HF solution in a closed vessel. This ensures that a sufficient amount of HF is present to etch all the AlAs. After the reaction was complete, a 10 μL sample from the gas phase above the solution was extracted through the septum using a syringe and fed into both a gas chromatograph/mass spectrometer (GC/MS, Interscience Polaris Q with a 30 m Rtx-1 column) and a gas chromatograph with a flame ionization detector (GC/FID, Hewlett Packard HP6890 Plus with a 30 m HP-1 column). The latter gives flame conductivity as a function of the retention time. To test whether or not AsH₃ is formed in the reaction, a sample of arsine gas, taken directly from the gas system of the MOVPE reactor, was also fed into both the GCs for comparison of the signals. To test whether or not hydrogen is formed during the etch process, a sample from the reaction gas and a hydrogen calibration sample were fed into a gas chromatograph with a thermal conductivity detector (GC/TCD, Hewlett Packard HP 5890A with a Porapack Q (80-100 mesh, Supelco) column), which is particularly suited for the detection of hydrogen gas.

In a final series of experiments, the gas composition in the glass vessel was varied to find out whether or not the oxygen of the ambient atmosphere plays an active role in the etch process of AlAs with HF. For this purpose, three samples, each consisting of half a wafer with 5 μm of AlAs, were processed. The first and third samples were ground and etched under pure nitrogen to prevent oxidation of the AlAs, while the second sample was processed in air and etched in a pure oxygen atmosphere. A syringe was used to apply 2.5 mL aqueous 0.5% HF solution to samples 1 and 2 through the septum, thereby preserving the atmosphere in the vessel. The third sample was etched with an HF solution that was placed in a nitrogen environment and through which nitrogen gas was bubbled for an hour. In this procedure, almost all the oxygen was removed from the solution and hardly any residual oxygen was expected to be present during the etching process. A titration measurement afterwards confirmed that the nitrogen bubbling procedure had not changed the concentration of the HF solution. For an overview of the samples and the processing conditions, see Table I.

For each of the three samples, 10 μL gas samples were taken from the vessel in which the AlAs and HF were reacting, every 10 to 15 min during the first hour, and subsequently every 30 to 60 min, and fed into both the GC/MS and the GC/FID.

**Results and Discussion**

**Solid reaction products: SEM-EDS and powder diffraction.**—The SEM-EDS measurements revealed the presence of aluminum and fluorine in the white powder. Oxygen could not be detected with this particular SEM-EDS setup; it is therefore not possible to decide whether the powder consists of aluminum fluoride, aluminum oxide, or an oxyfluoride. The thin film contained gallium and arsenic. This is probably some very fine GaAs powder, which, due to surface tension, floated on the solution and thereby formed a film with a metal-like appearance.

X-ray powder diffraction analysis of the white powder revealed two different crystal forms of the compound AlF₃ · 3H₂O (rosen-bergite and aluminum fluoride hydrate). It can therefore be concluded that aluminum fluoride is the only solid reaction product.

**Aqueous reaction products; aluminum and fluorine NMR.**—The result of the Al-NMR measurement is given in Fig. 1. A sharp peak around 0 ppm, identical to the reference signal from the reference measurement is attributed to [Al(H₂O)₆]³⁺, the underlying wide band with a fwhm of ~650 Hz to either an [AlF₃(H₂O)₆-n]³⁻ with n = 0...3 or an [Al(OH)₃(H₂O)₃-n]⁺ with n = 0...4 compound.11 Comparing the tabulated data for the latter two compounds...
pounds, we conclude that the chemical shift (+2 to ±15 ppm for the fluoride and +3 ppm for the hydroxide) cannot be used to distinguish between the two. The tabulated line widths (550 Hz for the fluoride and 450 Hz for the hydroxide) indicate a better match of the fluoride with the measurements. Additionally, since the formation of a hydroxide compound in a strongly acidic environment (pH < 2) is rather unlikely, it can be deduced that the fluoride compound is the reaction product measured. Further evidence for this was found in the fluorine-NMR measurement (see Fig. 2). Several peaks are detected, and the peak at −79.6 ppm is attributed to an AlF$_3^-$ compound. From these results it is concluded that during HF etching of AlAs, solid aluminum fluoride hydrate (AlF$_3$•3H$_2$O) and dissolved aluminum fluoride compounds ([AlF$_6$$_{(n-3)}$$_{(n-3)}$] with $n = 0 \ldots 3$) are produced.

Gaseous reaction products; gas chromatography.—The GC/MS measurements yield a three-dimensional diagram showing retention time vs. mass number vs. intensity (counts). In a two-dimensional projection, as given in Fig. 3, the intensities for all mass numbers are added. The reaction gas signal appears to lie between 1 min, 38 s and 4 min. For further analysis, the average signal before injection of the reaction gas and after the reaction gas has passed the chromatography column is subtracted from the reaction gas signal in order to eliminate all possible background signals. Furthermore, only the signal collected between 2 and 2.5 min retention time is used, in order to obtain measurements that are as reproducible as possible. The mass spectrum for this time frame is given in Fig. 4a. Mass numbers below 35 are omitted, because some of the main peaks in this region (nitrogen, oxygen, and water) are so strong that they render the peaks of several of the reaction products virtually indistinguishable on the same scale. Figure 4b shows a spectrum for arsine gas, diluted in nitrogen, taken from the gas system of the MOVPE reactor. Arsine has a mass number of 78; the peaks at 79, 77, 76, and 75 are attributed to several ionized forms of AsH$_3$ (AsH$_4^-$, AsH$_2^-$, As$^-$, and As$^+$, respectively), which are easily formed in the mass spectrometer. The peaks around 150 and around 225 are attributed to arsenic dimers and trimers. A comparison of Fig. 4a and b shows that the arsine signature from Fig. 4b is predominantly present in Fig. 4a, indicating that arsine gas is a major reaction product in the reaction of AlAs with an aqueous HF solu-
arsenic compounds reaches the lowest level if the sample is etched with an oxygen-free HF solution (sample 3). The fact that an oxygen-containing species is still formed, although no oxygen whatsoever should be present, can be explained by possible small leaks in the rubber septum, resulting in very small amounts of oxygen diffusing into the vessel, and by the fact that it is not possible to remove all oxygen from the HF solution, simply by bubbling nitrogen gas through it. The lower intensity of the oxygen-related arsenic compounds in the case of sample 3 compared to sample 1 may partly be due to the fact that less oxygen is present, and therefore less of these compounds can be formed. Another effect is that, in case of sample 3, probably not all AlAs was etched in the reaction, as was observed in the intensity plots for arsine. As a result, less arsenic is freed and less of the compounds can be formed.

For all experiments, except that of sample 3, GC/FID measurements show two peaks at retention times of 2 min, 6 s and at 2 min, 9.6 s, respectively. For the gas retrieved from the etching of sample 3, only one peak at a retention time of 2 min, 6 s is observed. Injection of pure arsine from the gas system of the MOVPE reactor also resulted in one peak at 2 min, 6 s. From these results it can be concluded that arsine is formed in all cases. For samples 1 and 2, processed with a significant amount of oxygen, the formation of one other component is detected. This is most likely the set of oxygen-related arsenic compounds with mass numbers 91, 92, and 107. For sample 3 the concentration of oxygen-related arsenic species, which according to GC/MS measurements is half of that obtained by sample 1, is obviously below the detection limit of the GC/FID equipment.

The analysis of the gaseous reaction products clearly shows the formation of arsenic (AsH₃) gas. A number of oxygen-related arsenic compounds, such as AsO, AsOH, and AsO₂⁻, are also detected at low concentrations with the GC/MS, if oxygen is not excluded during the preparation of the samples. From the analysis of gaseous reaction products, formed in the etching process under different atmospheres, it can be concluded that (i) no hydrogen is formed in etching AlAs with HF and (ii) the presence of oxygen is necessary for completing and maintaining the reaction.

Etching of AlAs in HF solution with the formation of AsH₃ seems similar to the etching of InP in concentrated HCl solution. In the latter case chemical attack by undissociated HCl on InP surface bonds gives rise to the formation of PH₃ and InCl₃.

InP + 3HCl → InCl₃ + PH₃

[4]
H₂O (step 3). If the remaining back bonds to As and Al react in the same way as in steps 1 to 3, then AsH₃ and either AlF₃ or Al(H₂O)₃⁺ will be formed. Alternating attack on a surface Al atom by F⁻ and H₂O will give rise to a mixed fluoro-aqua complex [AlFₓ(H₂O)ₙ₋₃₋ₙ⁺]ⁿ⁻, with n = 1...3. In principle, attack on a surface Al-As bond by the undissociated acid, as occurs for InP in HCl, is also possible (see Fig. 6b). The result will be the same as for step 2 of Fig. 6a. Subsequent reactions with F⁻ or HF and/or H₂O will lead to the same products.

The results of the present work clearly show that the AlF₃ product is only sparingly soluble. The formation of an insoluble trifluoride (which may be in the hydrates), as also predicted by the NMR results can explain the passivation, which is observed in this system. The fact that passivation does not occur if AlAs is etched with HCl resulting in AlF₃ and AlCl₃ shows that arsenic hydride is unlikely to be responsible for the termination of etching. Also the AlCl₃ formed in this case will rapidly hydrolyze and dissolve (similar to HCl etching of InP). From the results obtained in aerated and deaerated solutions it is clear that oxygen plays a role in the surface chemistry. Direct oxidation of AlAs by oxygen can occur to a limited extent (this would explain the As₂O₃ detected in the GC/MS experiments). The presence of adsorbed oxygen is expected to influence the etching steps, as shown in Fig. 6. The results suggest that passive film (AlF₃) formation is hindered; why this is so is not clear at present.

Another possible explanation for the observed passivation is the formation of solid arsenic at the surface. The oxygen, which is present in the solution, might oxidize the arsenic to form As₂O₃ as detected in the GC/MS and thus prevent passivation and maintain the etch process.

**Conclusions**

In previous reports on the epitaxial lift-off process it was assumed that in etching AlAs with HF solution three moles of hydrogen are formed for each mole of AlAs. In the present study, this has been investigated by a structural analysis of all reaction products, solid, in solution, and gaseous. SEM-EDS and X-ray diffraction measurements show that a white powder, formed during the etching, is an aluminum fluoride compound. Aluminum and fluorine NMR experiments in the solution showed the presence of the aluminum species [AlFₓ(H₂O)ₖ₋₃₋ₙ]ⁿ⁻, with n = 1...3 and [Al(H₂O)ₖ]⁺. Gas chromatography measurements with GC/MS and with GC/FID show the formation of arsenic and oxygen-related arsenic compounds like AsO, AsOH, and As₂O₃. The latter compounds are probably formed when As₂O₃ decomposes in the GC/MS, an assumption that is supported by the fact that the GC/FID shows only one peak for these compounds. The GC/TCD experiments refute the assumption that hydrogen gas is formed in the etch process. Consequently, the out-diffusion of hydrogen through the narrow etch slit cannot be the limiting step in the etch rate of the epitaxial lift-off process.

Oxygen is shown to play a significant role in the ELO etch process. During an in situ measurement in an aerated solution it is found that the amount of arsine gas increases faster to its maximum, if a sample is etched in an oxygen atmosphere. If the process is performed in a nitrogen atmosphere, the same maximum value is reached, but the time needed to reach this value is considerably longer. If, in addition, the oxygen dissolved in the HF solution is first removed, the arsenic concentration reaches its maximum considerably faster, but this maximum value is much lower than that found in the presence of oxygen.

From experiments in which AlAs was etched with both concentrated and diluted (10%) HCl, it was found that the dissociated acid is capable of dissolving AlAs. The mechanism describing the etching of AlAs with aqueous HF solution is therefore similar. In a first step, the proton attack on the As leads to a rupture of the As-Al bond and an As-H bond is formed. The positively charged Al is at the same time complexed by either F⁻ or H₂O. The remaining Al and As back bonds may react in a similar way to form AlF₃ or Al(H₂O)₃⁺ compounds. Alternating attacks on a surface Al atom by F⁻ and H₂O will give rise to a mixed fluoro-aqua complex [AlFₓ(H₂O)ₖ₋₃₋ₙ]ⁿ⁻, with n = 1...3. Etching of AlAs by undissociated HF is in principle also possible. The reaction mechanism is then similar to the etching of InP in concentrated HCl and the process yields the same reaction products as for the etching of AlAs in a dissociated HF solution.

The AlF₃ compound that is formed in the reaction is shown to be sparingly soluble in water. The formation of this compound at the surface can therefore explain the passivation, as observed in this process. Another possible passivating agent is solid arsenic at the surface. The oxygen in the solution might oxidize the arsenic to form As₂O₃ as is detected in the GC/MS and thus prevent passivation.

The model, as described above, is confirmed by examination of the ELO process in its normal implementation. In that case, the release layer is extremely thin (~5 nm), so that blocking of the AlAs surface plays an extremely important role. In experiments, it was found that this process comes to a premature halt, when absolutely no oxygen is present during etching. With oxygen present, the process continues and the III/V films are freed from their substrate.

It should be clear that an understanding of the epitaxial lift-off process requires more than knowledge of the reaction mechanism and stoichiometry. Interesting points for further investigation in-
clude the influence of stress and strain on the lateral etch rate and the escape of the gaseous reaction products.

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