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Real-Time Monitoring of the Etching of GaAs(100) by Surface Photoabsorption

Hongbin Fang,[†] Joseph Eng, Jr.,[†,‡] Chaochin Su,[†,§] Sujata Vemuri,[¶]
Irving P. Herman,[¶,*] and Brian E. Bent[†]

Columbia Radiation Laboratory and Departments of Chemistry and Applied Physics,
Columbia University, New York, New York 10027

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Surface photoabsorption (SPA) has been applied to monitor, in real time, the surface of GaAs(100) during chemical dry etching by a molecular beam of HCl. Changes in the HCl flux to the surface at a constant temperature (840 K) have been used to induce changes in the Ga:As ratio on the surface. These changes in surface stoichiometry have been detected *in situ* by SPA measurements of the transient fractional change in the reflectance of *p*-polarized, 488-nm light that is incident onto the surface near the pseudo-Brewster angle. On the basis of results from prior applications of SPA to the study of the atomic layer *deposition* of GaAs, the changes in the SPA signal as a function of the *etching* parameters can be correlated with changes in the relative surface densities of Ga and As. The findings are confirmed by independent determinations of the changes in surface stoichiometry made by measuring the time-integrated difference in the fluxes of Ga- and As-containing etching products evolved from the surface as a function of the HCl flux.

Introduction

This work developed from a conversation during lunch between Brian Bent and one of the authors (IPH). At the time, Brian was hotly pursuing a route to atomic layer-by-layer etching of GaAs using neutral beams and was interested in implementing new surface probes in his study; IPH was interested in developing new surface-sensitive optical probes and was more than happy to have a chance for a real collaboration with Brian. Writing on napkins, Brian outlined the aim of much of what is described here, which was to be but the first step in the collaboration.

Various optical probes have been developed that are capable of probing the surface and thin adlayers on the surface in real time during thin film processing.[1−3] Several of these probes involve monitoring light reflected from the surface, including ellipsometry, reflectance difference/anisotropy, differential reflectance, and surface photoabsorption/*p*-polarized reflectance spectroscopies. Each method has its relative strengths and weaknesses related to the completeness of the information derivable from experiment, the ease of implementation, and limitations on the types of processes that can be monitored successfully. In *p*-polarized reflectance spectroscopy (PRS) the (intensity) reflectance of light incident on the surface near the pseudo-Brewster angle is monitored as experimental conditions are changed, for example, by the alternation of reactant beams in atomic layer epitaxy (ALE). In the case of ALE, PRS has been applied using radiation that is both above[4,5] and below[6] the bandgap of the bulk material that is being deposited. In the former case, the technique has sometimes been termed surface photoabsorption (SPA).[4,5] In this paper, we present results on the application of SPA to monitor the chemical dry etching of a GaAs(100) surface by a molecular beam of HCl.

The chemical dry etching of GaAs(100) using neutral beams is of interest because of the potential for controlled layer-by-layer (digital) removal of material, with minimal concomitant damage. The digital etching of GaAs has been demonstrated previously for Cl_2 combined with electron beams[7] and HCl combined with ion beams,[8] but a purely chemical process that avoids the surface damage associated with charged particles has yet to be developed. The chemical criterion for controlled layer-by-layer etching is that the gas−surface reaction for each type of neutral beam used must be self-limiting (i.e., layer selective). Such an all-chemical digital etching cycle has been proposed[9] for GaAs(100) in which H atoms are used to remove As and HCl is used to remove Ga.

To date, the changes in surface composition that occur as a result of chemical etching of Ga and As from GaAs(100) have been monitored only indirectly via mass spectrometric detection of the Ga- and As-containing products that are evolved from the surface.[9] The aim of the current study is to demonstrate the utility of SPA for monitoring the relative Ga- or As-richness of the surface as the etching conditions are changed dynamically to induce changes in the surface stoichiometry. In these

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[*] To whom correspondence should be addressed. E-mail: iph1@columbia.edu.

[†] Department of Chemistry.

[¶] Department of Applied Physics.

[‡] Present address: Corporate Research Laboratories, Exxon Research and Engineering Corporation, Annandale, New Jersey 08801.

[§] Present address: Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan.

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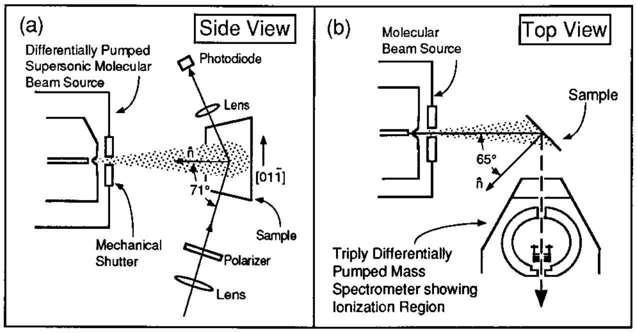

Figure 1. (a) Schematic of the experimental setup indicating the important geometrical parameters and optical elements in the SPA experiment. (The mass spectrometer has been omitted for clarity.) (b) Orthogonal view of the experimental setup showing the molecular beam scattering geometry. (The optical elements used in SPA have been omitted for clarity.)

studies, the changes in surface composition have also been determined via mass spectrometric detection of the relative fluxes of Ga- and As-containing products. The direct correlation between the SPA results and the integrated difference in the etching product fluxes suggests that changes in surface composition, as opposed to changes in surface structure, are the dominant contribution to the measured changes of the SPA signal as a function of etching conditions. A preliminary version of this paper was published previously.[10]

Experimental Methods

The experimental arrangement is shown schematically in Figure 1. A supersonic molecular beam of HCl (beam energy = 0.9 eV) was formed by expanding a 5% HCl/95% He gas mixture through a graphite nozzle with a nozzle diameter of 0.127 mm. The beam was collimated with a skimmer and then chopped with a mechanical shutter to produce a pulsed flux of HCl at the GaAs surface. In these studies, the beam was chopped to produce a train of square-wave pulses with equal on/off times of 50 s. This time scale was chosen to allow the surface etching reaction to decay to zero and then return to steady state during each period of the modulation.

The HCl beam was incident to the GaAs(100) surface at 65° from the surface normal (beam diameter = ~1 cm along the major axis of the ellipse on the sample surface), and the etching products were detected with a triply differentially pumped mass spectrometer located in the specular scattering plane and oriented at 25° from the surface normal towards specular reflection. Prior studies have shown that the product distribution is independent of the angle of detection, so the results at 25° are indicative of the angle-integrated product yield from the surface.[9] The relative product fluxes have been calibrated according to a previously published procedure.[9]

Prior to insertion into the vacuum chamber, the wafer was degreased in chloroform, immersed in a 1:1 NH_4OH:H_2O solution for 20 min, and rinsed with copious amounts of deionized (18.2 MΩ-cm) water. The wafer was then immersed in 4:1:1 H_2SO_4:H_2O_2:H_2O solution for 10 min, again rinsed with deionized water, and dried under nitrogen. The sample was mounted and inserted into the vacuum chamber in <10 min, and subsequently heated to 840 K while etching with HCl until a steady-state etching rate was achieved.[11]

In the SPA measurements, 488 nm radiation (several mW) from an air-cooled argon-ion laser impinged onto the GaAs(100) surface at 71° from the surface normal in a plane orthogonal to the HCl etchant. As shown in Figure 1, the SPA plane was oriented along the [01$\bar{1}$] azimuth of GaAs(100) to achieve maximum sensitivity of the SPA signal to changes in the surface stoichiometry.[4] The light was focused to a spot size (beam diameter) of ~1 mm at the sample surface, and placement of a linear polarizer immediately before the wafer ensured that the incident radiation was *p*-polarized. The incident light was modulated at 930 Hz, and modulations in the reflected light intensity were synchronously detected via a photodiode and lockin amplifier.

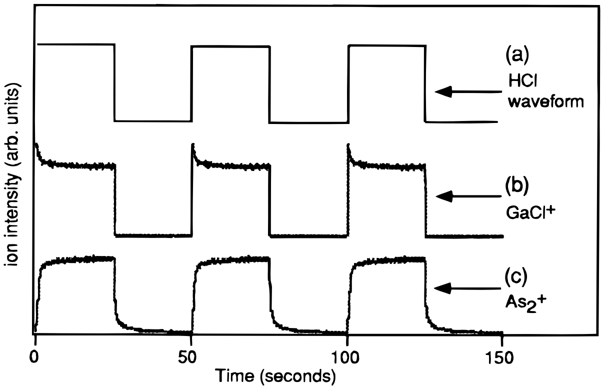

Figure 2. (a) HCl waveform illustrative of that employed in all of the modulated molecular beam-scattering studies in this work. (b) The GaCl ($m/e^+ = 104$) signal corresponding to the HCl waveform in (a) for GaAs(100) etching at 840 K. (c) The As_2 ($m/e^+ = 150$) signal for etching at 840 K. The plateaus in the GaCl and As_2 waveforms when the HCl beam is on indicate steady-state etching. The very different rates for GaCl and As_2 evolution when the beam is turned off and then, initially, after it is turned back on, correspond to the formation and removal of Ga-rich surface layers, respectively.

Results and Discussion

Before presenting the SPA results, the modulated molecular beam-scattering protocol used in these studies is described to illustrate what is known about the chemical etching of GaAs by HCl. For temperatures <650 K, there is no appreciable etching of GaAs by HCl.[9] At temperatures >650 K, the steady-state etching of GaAs(100) by HCl occurs by removal of Ga as GaCl and removal of As as As_2. Figure 2 shows the kinetic behavior of these products, as observed by mass spectrometry, when a GaAs(100) surface is etched at 840 K by an HCl beam (flux, ~3.6 monolayer (ML)/s) that is modulated by a mechanical shutter. For reference, the HCl waveform is given at the top of the figure, and as shown, the HCl beam is alternately on and off for 50 s giving rise to a square wave modulation. Transients in the HCl flux during the opening and closing of the shutter are negligible on the timescale of the etching kinetics in these studies. Figure 2 also shows that after initial changes in the product signals when the HCl beam is first turned on, the GaCl and As_2 fluxes achieve constant values indicative of steady-state etching. When the HCl beam is then turned off, the GaCl flux immediately drops to zero while As_2 continues to desorb from the surface. This tail of As_2 evolution leads to a surface that is enriched in Ga. When the HCl beam is again turned on, the Ga-enrichment results in a burst of GaCl (the rate of GaCl formation is proportional to the surface Ga coverage), and the flux of Ga from the surface (as GaCl) exceeds the flux of As from the surface (as As_2) until a surface composition indicative of the steady state is again achieved. Note that the surface composition during steady state etching will not generally be As:Ga = 1:1, even though these two elements are being removed at equal rates at steady state. In other words, because the *rate constants* for Ga and As removal are not generally equal, the *rates* of their removal become equal only when the appropriate products of the rate constants and surface concentrations (as given by

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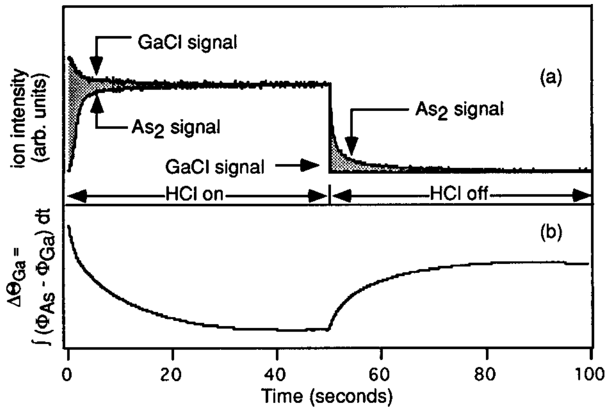

Figure 3. (a) Relative fluxes of Ga and As evolved during modulated beam etching of GaAs by HCl at 840 K. (b) The change in the surface coverage of Ga, $\Delta\Theta_{Ga}$, as a function of time.

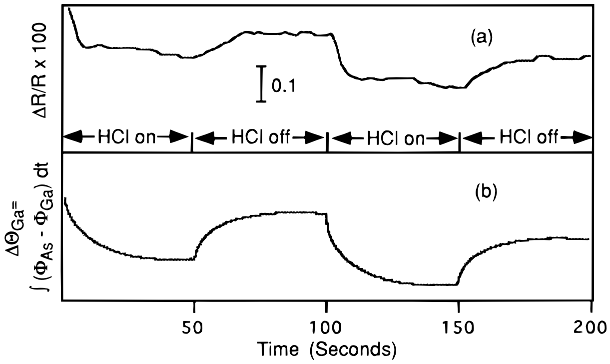

Figure 4. (a) The surface photoabsorption signal and (b) the integrated difference in the As and Ga product yields as a GaAs(100) sample is etched by HCl pulses at 840 K to induce changes in the surface composition.

the kinetic rate laws) are equal. This point as well as the modulation waveforms for GaAs etching by HCl are discussed more extensively in another publication.[9]

Because steady-state etching of GaAs corresponds to equal rates of evolution for Ga and As, the mass spectrometer signals for GaCl and As_2 evolution in Figure 2 can be correlated on a per atom basis. Using such a correlation, the GaCl and As_2 waveforms for a single modulation cycle are plotted in Figure 3a. Note that because the steady-state fluxes of Ga and As have been equated on a per atom basis, the relative flux of As shown is twice the relative flux of As_2 because there are two As atoms in each As_2 molecule. Note also that by taking the difference in the fluxes of As and Ga ($\Phi_{As} - \Phi_{Ga}$), one obtains the rate at which the surface becomes enriched in gallium. The integral of this rate, ($\int (\Phi_{As} - \Phi_{Ga})\, dt$), whose magnitude is given by the shaded areas in Figure 3a, indicates the extent of Ga enrichment or depletion ($\Delta\Theta_{Ga}$) relative to the Ga coverage on the surface during steady-state etching. This quantity, which is shown in Figure 3b as a function of time for etching at 840 K, is the quantity that can be probed directly by surface photoabsorption.

Results of SPA measurements during modulated beam etching of GaAs(100) by HCl at 840 K are shown in Figure 4. In Figure 4a, the transient fractional change in the reflectance *R* of the *p*-polarized 488 nm light impinging near the pseudo-Brewster angle is plotted as the HCl beam is modulated with the waveform shown in Figure 2a. Note that the reflectance is larger when the HCl beam is off than when it is on. Prior applications of SPA to study atomic layer epitaxy of GaAs(100) have shown that for the experimental geometry in Figure 1, the surface reflectance at 488 nm is larger for Ga-terminated versus As-terminated GaAs(100) surfaces.[4] Thus, the increase in reflectance when the HCl beam is off suggests Ga-enrichment. This enrichment is corroborated by determining $\Delta\Theta_{Ga}$ from mass spectrometric measurements of the scattered ion intensities during etching, as shown in Figure 4b. During steady-state etching, the rate of Ga atom removal is equal to the rate of As atom removal, and there is virtually no change in reflectance. When the HCl beam is turned off, As_2 continues to desorb, leaving the surface relatively rich in Ga. This Ga-enrichment appears as an increase in the SPA signal. When the HCl is turned on again, a sharp increase in the GaCl signal in the mass spectrometer is seen, indicating an increased As surface coverage and a subsequent decrease in reflectance. The characteristic times for these transient changes probed by mass spectrometry are consistent with those seen in the SPA trace.

The magnitude of the fractional change ($\Delta R/R$) of the reflectance *R* in Figure 4a is ~0.1%, which is less than the ~2% observed during GaAs ALE in the studies of Kobayashi et al.,[4] for the same wavelength and incident azimuth. One reason for this difference is that during ALE the surface is probably almost completely Ga-terminated after each Ga-deposition cycle and almost completely As-terminated after each As-deposition cycle, whereas in the HCl etching studies, the overall change in relative Ga-to-As surface coverage may be smaller during the modulated studies here. (This simplified picture of the surface being either Ga- or As-terminated after alternating steps in ALE is in question;[12] still, the relative change during etching can be much smaller than that during ALE.) Moreover, the dielectric function of the surface, and consequently *R*, may not change linearly with the Ga or As content of the surface and may depend on the details of the surface reconstruction. Other possibilities for the smaller SPA response include differences in the angles of incidence in the ALE and etching experiments and also the possibly small (although not negligible) *s*-polarized component in the incident beam used in these experiments.

Figure 5 shows the time dependence of the surface coverage using the kinetic model developed by Su et al.[9] When the HCl beam is turned on, the Ga coverage decreases from 1.0 to 0.6, as the As coverage increases from 0 to 0.4 (Figure 5a); when the HCl beam is turned off, the respective steady-state coverages return to 1.0 and 0. Figure 5b shows that the model predicts that the steady-state $\Delta\Theta_{Ga}$ ($= \Theta_{Ga} - \Theta_{As}$) varies between 1.0 and 0.2 as the HCl beam is alternately turned off and on. ($\Delta\Theta_{Ga} = -1.0$ for an As-covered surface.) This result suggests that the surface is always rich in Ga and that the change in the relative concentration of Ga on the surface between cycles (40%) is indeed less than that expected during atomic layer epitaxy. Also note that the transient behavior seen in Figure 5, as the beam is turned on and off, is similar to that seen experimentally.

A gradual decrease in the reflectance is observed with increasing time in Figure 4a. This decrease may result from continued surface roughening and the concomitant decrease in specularly reflected light reaching the detector. Additionally, Figure 4b shows a gradual decrease in $\Delta\Theta_{Ga}$, indicating that the surface may be slowly becoming As-enriched with each modulation cycle. Because an As-terminated layer has a smaller reflectance than a Ga-

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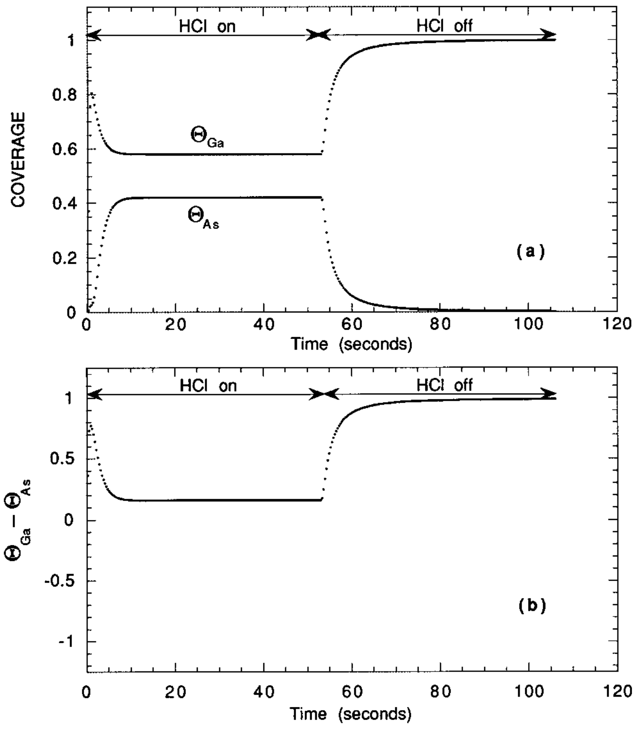

Figure 5. (a) Ga and As coverage during the HCl pulse cycle at 840 K using the kinetic model in ref 9; and (b) the net Ga coverage ($\Delta\Theta_{Ga} = \Theta_{Ga} - \Theta_{As}$) during the same cycle. (The oscillation in the Ga coverage at the beginning of the cycle is an artifact arising from a limitation in the model.)

terminated layer, gradual enrichment in As may lead to a slow decrease in reflectance.

The monitoring of the etching of GaAs(100) surfaces can be improved in several ways. Lower noise sources can be used, and the signal can be corrected for fluctuations in the source intensity. One way this can be done is by monitoring the difference between the detected reflected signal and the signal from a split-off portion of the beam incident on the surface, which can been attenuated to nearly null the difference. The photon wavelength and angle of incidence can be optimized, as described by Eryigit et al.[13] (Eryigit et al.[13] also show that it may be preferable to optimize ΔR instead of $\Delta R/R$, and that SPA analysis is not always optimal near the pseudo-Brewster angle.) Spectroscopic monitoring can also improve analysis and understanding.

Experimental evidence of only the relative Ga or As concentration on the surface has been discussed here. A more absolute value for the surface concentration can be obtained by comparing the reflectance during the etching cycles with that after preparation of the GaAs(100) under well-controlled conditions where the surface structure is known[14] or can be measured.

The possibility of surface roughening and its impact on SPA monitoring can be examined by using two wavelengths, one at λ_1 for which there is a large SPA response and one at λ_2 for which there is a small (if any) SPA response. The loss of reflectance at λ_2 due to elastic laser light scattering will indicate surface roughening, and can be used to correct the reflectance at λ_1. Because any change in reflectance at λ_2 is due to the total integrated scatter, which varies as $1/\lambda^2$, the correction of ΔR at λ_1 due to laser light scattering is $(\lambda_2/\lambda_1)^2$ times ΔR at λ_2.[1]

The digital etching cycle proposed by Su et al.[9] involves steps to remove As with H atoms and to remove Ga with HCl. In using SPA to probe the alternating cycles, the reflectance can change both because of the change in surface composition due to the process and, if the temperature required for each cycle is different, the change in temperature. The temperature dependence is not an issue if both cycles occur at the same temperature, as in the 600−650 K range proposed by Su et al.[9] However, other routes to digital etching may be optimized with the alternating cycles occurring at different temperatures. Estimates using the known temperature dependence of the dielectric function of bulk GaAs (for example see the references cited in ref 1) suggest that the change in ΔR due to the different temperatures of the cycles is negligible. Although the temperature dependence of the surface dielectric function for GaAs is not known, it is unlikely that it would have a significantly stronger dependence than that of the bulk. However, if the surface undergoes a change in reconstruction due to this change in temperature, a significant part of the change in the reflectance during alternating cycles could be due to this effect, which must be included in the analysis.

Finally, SPA can be used to kinetically monitor the surface. Although Figure 4 shows that the characteristic times for the transient changes probed by SPA and mass spectrometry are approximately the same, more detailed studies may lead to further insight.

Conclusions

SPA measurements have been used to monitor the relative Ga and As surface coverages in real time during the etching of GaAs(100) by a modulated supersonic molecular beam of HCl. The observed changes in reflectance agree with changes in the surface coverage, as determined indirectly by mass spectrometric detection of the desorbing etching products. To our knowledge, these results represent the first demonstration of SPA for monitoring changes in surface composition as a result of a surface etching process.

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