

REAL-TIME MONITORING OF GaAs(100) ETCHING BY SURFACE PHOTOABSORPTION

JOSEPH ENG JR.*, HONGBIN FANG*, 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, NY 10027

ABSTRACT

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* via 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 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

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 involve monitoring light reflected from the surface, including ellipsometry, reflectance difference/anisotropy, differential reflectance, and surface photoabsorption/p-polarized reflectance spectroscopies. Each 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 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 Cl₂ 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 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.

EXPERIMENT

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 sec. 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.

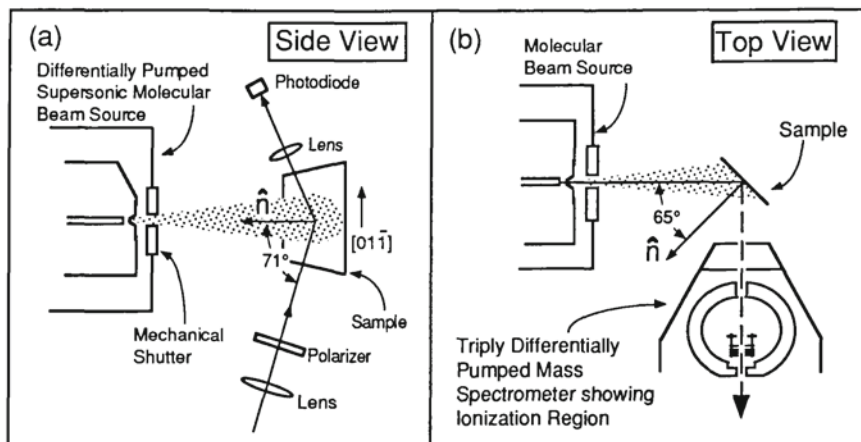


Figure 1. a) Schematic of the experimental set-up indicating the important geometrical parameters and optical elements in the SPA experiment. (The mass spectrometer has been omitted for clarity.) b) Orthogonal view of the experimental set-up showing the molecular beam scattering geometry. (The optical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

The HCl beam was incident onto 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 via 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 the procedure in Ref. [9].

Prior to insertion into the vacuum chamber, the wafer was degreased in chloroform, immersed in a 1:1 $\text{NH}_4\text{OH}:\text{H}_2\text{O}$ solution for 20 min, and rinsed with copious amounts of de-ionized (18.2 $\text{M}\Omega\text{-cm}$) water. It was then immersed in 4:1:1 $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ solution for 10 min., again rinsed with de-ionized water, and dried under nitrogen. The sample was mounted and inserted into the vacuum chamber in less than 10 min., and subsequently heated to 840 K while etching with HCl until a steady state etching rate was achieved [10].

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.

RESULTS

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 below 650 K, there is no appreciable etching of GaAs by HCl [9]. At temperatures above 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 ML/sec) 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

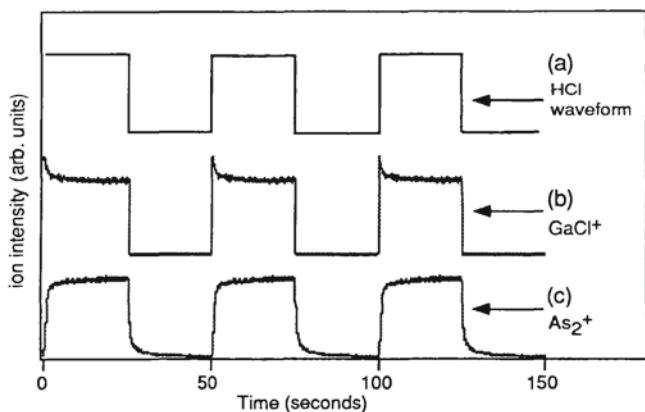


Figure 2: a) HCl waveform illustrative of that employed in all of the modulated molecular beam scattering studies in this work. b) The GaCl ($m/e^+ = 104$) signal corresponding to the HCl waveform in (a) for GaAs(100) etching at 840 K. c) The As_2 ($m/e^+ = 150$) signal for etching at 840 K. The plateaus 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.

alternately on and off for 50 seconds 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 As₂ 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 As₂ continues to desorb from the surface. This tail of As₂ 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 As₂) 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, since 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 the kinetic rate laws) are equal. This point as well as the modulation waveforms for GaAs etching by HCl are discussed more extensively in Ref. [9].

Since steady state etching of GaAs corresponds to equal rates of evolution for Ga and As, the mass spectrometer signals for GaCl and As₂ evolution in Figure 2 can be correlated on a per atom basis. Using such a correlation, the GaCl and As₂ 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 As₂ since there are two As atoms in each As₂ 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 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 [4] that for the experimental geometry in Figure 1, the surface reflectance at 488 nm is larger for Ga-terminated vs. As-terminated GaAs(100) surfaces. 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, As₂ 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 Ref. 4, for the same wavelength and incident azimuth. One reason for this 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, while in the HCl etching studies, the overall change in relative Ga to As surface coverage may be smaller during the modulated

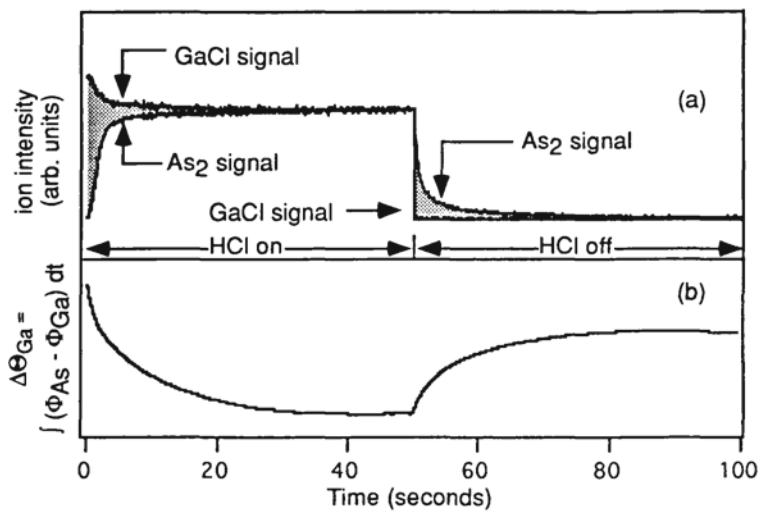


Figure 3: a) Relative fluxes of Ga and As evolved during modulated beam etching of GaAs by HCl at 840 K. b) The change in the surface coverage of Ga, $\Delta\theta_{Ga}$, as a function of time.

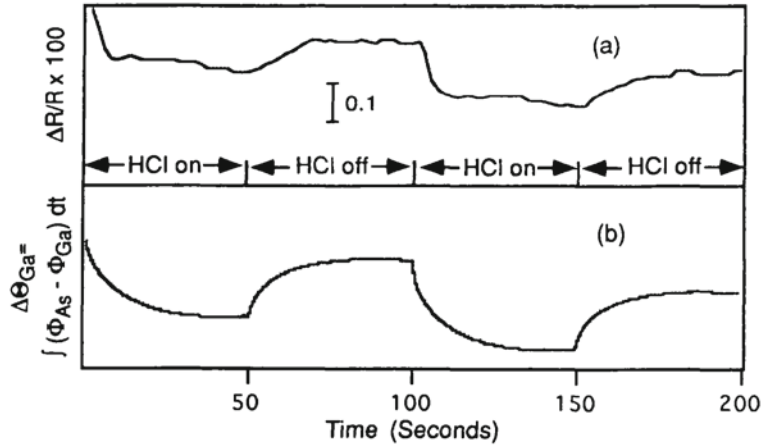


Figure 4: a) The surface photoabsorption signal and b) the integrated difference in the As and Ga product yields as a GaAs(100) sample is etched by HCl pulses at 840 K to induce changes in the surface composition.

studies here. Other possibilities include differences in 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 preliminary experiments. Finally, a gradual decrease in the reflectance is observed with increasing time in Figure 4a. This 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 $\Delta\Theta_{\text{Ga}}$, indicating that the surface may be slowly becoming As-enriched with each modulation cycle. Since an As-terminated layer has a smaller reflectance than a Ga-terminated layer, gradual enrichment in As may lead to a slow decrease in reflectance.

CONCLUSIONS

Surface photoabsorption (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. Future work will include spectroscopic monitoring of thin film processing with lower noise levels in the optical source.

ACKNOWLEDGMENTS

This work was supported by the Joint Services Electronics Program administered by the Columbia Radiation Laboratory (Contract No. DAAH04-94-G-0057 for IPH and BEB) and by National Science Foundation Grant DMR-94-11504 (for IPH).

REFERENCES

1. I. P. Herman, "Optical Dagnostics for Thin Film Processing" (Academic, San Diego, 1996).
2. J. F. McGilp, *Prog. Surf. Sci.* **49**, 1 (1995).
3. D. E. Aspnes, *Surf. Sci.* **307-309**, 1017 (1994).
4. N. Kobayashi and Y. Horikoshi, *Jpn. J. Appl. Phys.* **29**, L702 (1990); N. Kobayashi, T. Makimoto, Y. Yamauchi, and Y. Horikoshi, *J. Cryst. Growth* **107**, 62 (1991).
5. K. Nishi, A. Usui, and H. Sakaki, *Appl. Phys. Lett.* **61**, 31 (1992).
6. N. Dietz, A. Miller, and K. J. Bachmann, *J. Vac. Sci. Technol. A* **13**, 153 (1995).
7. T. Meguro, M. Hamagaki, S. Modaresi, T. Hara, Y. Aoyagi, M. Ishii, Y. Yamamoto, *Appl. Phys. Lett.* **56**, 1552 (1990).
8. Y. Aoyagi, K. Shimura, K. Kawasaki, T. Tanaka, K. Gamo, S. Namba, I. Nakamoto, *Appl. Phys. Lett.* **60**, 968 (1992).
9. C. Su, Z.-G. Dai, D.-H. Sun, W. Luo, M. Vernon, and B. E. Bent, *Surf. Sci.* **312**, 181 (1994).
10. J. Contour, J. Massies, A. Salètes, M. Outrequin, F. Simondet, J. Rochette, *J. Vac. Sci. Technol. B* **5**, 730 (1987).