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13. SUPPLEMENTARY NOTES

14. ABSTRACT Spectroscopic ellipsometry (SE) was used to study the effects of wet chemical etching and oxidation on GaAs and Al(0.3)Ga(0.7)As. Etch solutions were mixtures of citric acid, hydrogen peroxide, and water, with various volume ratios. Oxidation in both H ₂ O ₂ and H ₂ O was studied. Etch rates of GaAs and AlGaAs were determined from real time SE (RTSE) measurements during etching of heterostructures. The surface condition was also studied, with strong differences observed between fast-etch and slow-etch solutions. Use of RTSE as an etch-stop detector, either at the end of a layer or at a preselected depth within a layer, was demonstrated, with a precision of several nm during nonselective etching. Etch control was also demonstrated using focused-beam RTSE, in which the optical beam diameter was reduced from several mm to about 150 microns. Finally, application of RTSE to patterned surfaces yielded a surprising and useful interference effect which can be used to monitor etch depth into bulk material.

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Real Time Optical Monitoring of III-V Semiconductor Wet Chemical Etching

Final Technical Report

December 18, 2000

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Objectives

The etch rates of III-V semiconductors were to be accurately measured as a function of volume ratio of a citric acid/hydrogen peroxide etch solution. Spectroscopic ellipsometry (SE) was to be developed as an *in situ* real time end-point sensor.

Experimental

Ellipsometry measures the change in polarization of a monochromatic beam after reflection from a sample surface. The raw data are numerically fitted using a multilayer model to obtain useful information such as layer thicknesses, often with sub-nm precision. Commercial ellipsometry hardware and software were used, obtained from J.A. Woollam Co. An ex-situ system with scanning spectrometer covered the range 0.7-6.2 eV. A real-time system with polychromator and detector array measured up to several hundred wavelengths simultaneously over 1-5 eV. A simple Teflon chamber with fused quartz windows was designed for use with the RTSE.

Epi-ready wafers of bulk GaAs, and MOCVD grown heterostructures of GaAs/Al_{0.3}Ga_{0.7}As were purchased. The latter had AlGaAs layers 0.3 or 0.5 microns thick, and GaAs cap layers 500 or 30 nm thick. A sample about 1 cm² was cut and aligned on the sample holder. RTSE data were measured continuously as an etch (or oxidation) solution was poured into the top of the chamber.

Results

The first effort in the project was to study the surface condition caused by etching. In addition to layer thickness sensitivity, SE is also highly sensitive to the microscopic surface condition. Therefore it was necessary to understand the effects of etching on bulk surfaces, before studying heterostructures. A study of etched (100) GaAs surfaces was performed as a function of volume ratio of citric acid to hydrogen peroxide. Surface quality as characterized by ex-situ SE depended strongly on volume ratio. Low volume ratios ($\leq 2:1$), with corresponding low etch rates, produced a thin interfacial layer (perhaps due to microscopic roughness) beneath a porous oxide. The 2:1 ratio gave the optimum surface condition with minimal interface thickness. Higher volume ratios (\geq

3:1) associated with much higher etch rates produced qualitatively different overlayers which were optically absorbing and 4-6 nm thick. They appeared to contain a small percentage (~5-10%) of crystalline arsenic. Similar effects were seen in etched $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ surfaces. These results were published in [1].

We next moved to the real-time study of heterostructures. In order to analyze RTSE data the optical constants of all the materials, and the ambient, must be known. Each solution was therefore measured separately in order to obtain its optical constants. The optical constants of GaAs, $\text{Al}_x\text{Ga}_{1-x}\text{As}$, and the oxide were already available in the literature.

In this stage etch rates were measured, and end-point detection demonstrated, as described below. We also demonstrated that RTSE can be used to accurately and repeatably control the end-point of the etch, either at an interface or within a layer. In these studies a different etch solution was used: a (21:1:75) volume ratio of citric acid: hydrogen peroxide: de-ionized water which gave a nonselective etch of roughly 15-20 nm/min in GaAs and AlGaAs. A variable delay in the onset of etching was observed, related to varying surface cleanliness. Etch rates of 15.3 and 17.6 nm/min in GaAs and AlGaAs, respectively, were determined from the RTSE analysis. Real time monitoring was also used to control stopping of the nonselective etch after removal of the GaAs cap layer, as well as stopping the etch within the AlGaAs layer with 100 nm of AlGaAs remaining. These results were published in [2].

The above results were obtained on unpatterned surfaces, and required a large area (several mm^2) due to the relatively large diameter of the collimated optical beam. In the third year we used a focused beam to greatly reduce the surface area necessary for measurement, and began the study of patterned surfaces. Both steps move RTSE closer to practical applications in device fabrication. We also studied the oxidation of GaAs in H_2O_2 and deionized H_2O , in order to learn more about this fundamental process. The oxidation results have been accepted for publication [3].

Focused beam RTSE only requires the addition of two lenses to the setup. The beam is about 150 microns in diameter at the sample surface. On an unpatterned surface the data are identical to those obtained using a collimated beam (about 3 mm diameter),

except that the signal to noise ratio is a little lower. Therefore all of the monitoring and control results reported previously can now be done using a much smaller area. One approach to etch control would be to use the focused beam to monitor a small unpatterned area, immediately adjacent to the patterned area where a device is being fabricated.

Another approach to etch control is to use RTSE directly on the patterned areas. This approach, studied in the fourth and final year, has the potential to provide direct information about the device area being etched. Furthermore, very little work has been published on ellipsometric analysis of patterned surfaces. Therefore almost any new information will increase current understanding. We began with simple linear grating patterns of photoresist on a GaAs/AlGaAs heterostructure, with grating periods of 10, 20, or 40 microns, made using a photomask and standard photolithography. Initially it appeared that the 40 micron pattern exhibited little difference from the unpatterned case, other than a reduced signal to noise ratio. But after etching for longer periods it became clear that the data continued to exhibit interference effects even after the AlGaAs layer was removed and etching had progressed into the GaAs bulk.

This was an unexpected and exciting discovery. Ellipsometry has been known from the beginning to be sensitive to layer thicknesses (this is a principal reason for its use), due to interference: a reflection from the surface interferes coherently with reflections from interfaces below it. However in this case the interference is between *lateral* regions. The E-field of the beam reflected from the photoresist-covered area adds coherently with that of the beam reflected from the neighboring area undergoing etching. This phenomenon is commonly seen in laser reflection measurements (though there it is observed only in intensity; SE also measures phase). To observe the effect here was initially surprising because SE does not use a coherent laser source, but rather a broadband lamp passed through a monochromator (*ex situ*) or a polychromator (real time). However a rough calculation of the coherence length based on the bandwidth of the spectrometer does give a value on the order of tens of microns, which is sufficient for lateral interference to occur in these gratings. The effect was also observed on patterned GaAs bulk wafers. Even after the photoresist was stripped off, leaving bare GaAs with

the line pattern profile etched into it, *ex situ* SE measurements showed very clear interference structure.

Furthermore, we were able to fit these data (though not in all cases) to determine the etch depth *into the bulk substrate*. This ability is unique to SE monitoring of patterned etching. In the unpatterned case SE can monitor etching through a thin film because of interference within the film itself. But once the film is gone and the substrate is reached, the interference ceases; though etching continues into the bulk, SE cannot monitor its progress. Patterning provides a reference point that allows interference to occur, even when there is no film.

What actually occurs due to patterning is a combination of diffraction and interference. Only the interference has so far been modeled. Inclusion of patterned interference required a relatively straightforward modification of the software, which was performed by the vendor (J.A.Woollam Co.). The computation time is only slightly longer than that required for unpatterned analysis, so the analysis can still be done in real time. Under certain conditions this limited modeling fits the data adequately to provide etch depth into the substrate. We have succeeded in real time data fitting during etching of bulk GaAs using 10, 20, and 40 micron grating period patterns, as well as 10 micron square patterns. Using the same patterns on GaAs/AlGaAs heterostructures, SE data exhibit features that still allow it to be used as an endpoint detector, signaling when the end of a layer has been reached. The data also continue to show interference effects while etching into the bulk. However, data from patterned etching of heterostructures have not so far been quantitatively fitted. In order to accurately model the data over a wider range of pattern shapes and sizes, and on multilayer samples, it appears that diffraction effects may have to be explicitly included in the model. This will probably require substantially more computation time. Results on patterned etching were reported at the 2000 AVS National Symposium, and will be submitted for publication.

Theses

The Masters thesis of Sang-Jun Cho was completed after the first two years of the project. It encompassed the work up to and including etch depth control on unpatterned

heterostructures summarized above (and in references [1] and [2]). A copy is available from the UNL library, or by contacting the P.I. Mr. Cho has continued work on the project as a Ph.D. student, and is expected to graduate in 1-2 years.

Personnel

Paul G. Snyder, Principal Investigator

Sang-Jun Cho, Graduate Research Assistant

Publications

1. P.G. Snyder, S.-J. Cho, "Investigation of citric acid-hydrogen peroxide etched GaAs and AlGaAs surfaces by spectroscopic ellipsometry," J. Vac. Sci. Technol. **B16**, 2680-2685 (1998)
2. S.-J. Cho, P.G. Snyder, "Real time monitoring and control of wet etching of GaAs/AlGaAs using real time spectroscopic ellipsometry," J. Vac. Sci. Technol. **B17**, 2045-2049 (1999)
3. S.-J. Cho, P.G. Snyder, "Study of GaAs oxidation in deionized water and hydrogen peroxide using spectroscopic ellipsometry," submitted to J. Vac. Sci. Technol. 6/9/00