The Bandgap-Selective Photoelectrochemical Etching of GaAs/Al$_x$Ga$_{1-x}$As Heterostructures with Varying Mole Fraction

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ABSTRACT

We have demonstrated the highly selective removal of low aluminum (Al) mole-fraction Al$_x$Ga$_{1-x}$As layers from those with higher Al mole-fraction using the wet photoelectrochemical (PEC) etch process. AGaAs/Al$_x$Ga$_{1-x}$As semiconductor structure with layers of varying Al mole-fraction was examined. The sample was etched in a (1:20) HCl:H$_2$O electrolyte solution. A Ti/sapphire laser was used as the light source to tune the incident photon energy between the various bandgaps of the heterostructure layers. Relative etch rates >10^4:1 and >10^3:1 were found for mole fraction differences in x of 0.15 and 0.05, respectively. The selectivity was examined as a function of incident wavelength.

The GaAs/AlGaAs material system is extensively used in both electronic and optoelectronic semiconductor devices. Device fabrication processes often mandate the use of etches that are highly materials selective. Wet and dry etching techniques have been reported where GaAs is selectively etched with respect to Al$_x$Ga$_{1-x}$As.[1-3] In general, these selectivities result from differences in chemical reactivity of the materials or the relative volatility (dry etching) or solubility (wet etching) of the etch products. The intrinsic mechanism of wet photoelectrochemical (PEC) etching depends on the bandgap of the material being etched relative to the wavelength of the laser used to produce the etching. This bandgap-dependence, hence materials-composition dependence of PEC etching makes it a natural choice to produce highly selective etching. Brown *et al.* utilized an incident photon energy (corresponding to 0.85 μm wavelength) between the band edges of GaAs and Al$_{0.4}$Ga$_{0.6}$As to demonstrate extremely high etch selectivity between these two materials.[4] In this paper, we examine how well that material selectivity is preserved for Al$_x$Ga$_{1-x}$As/Al$_y$Ga$_{1-y}$As heterostructures having fairly thick layers (~1 μm) where the difference between x and y is as small as 0.05.

The PEC etch process is controlled by the transport of photogenerated carriers to the semiconductor/electrolyte interface.[5,6] The holes are consumed in the oxidative dissociation of the semiconductor, while the electrons participate in the reduction of the oxidizing agent. The Al mole-fraction for x < 0.45, is related to the (room temperature) bandgap of the material, E_g, and the corresponding wavelength, λ$_c$ as follows[7]

$$\lambda_c = \frac{hc}{E_g} = \frac{hc}{1.424 + 1.427x + 0.041x^2} \quad [1]$$

where c, the speed of light, is given in cm/s, h, Planck's constant, is given in eV-s, and E_g is given in eV. λ$_c$ is defined as the minimum wavelength for which the semiconductor is transparent, and therefore for which the photogeneration of electron-hole pairs will not occur. Thus, by using an incident photon wavelength, λ, such that λ$_c^{material\ 1}$ < λ < λ$_c^{material\ 2}$, it is possible to selectively etch material 2, stopping on material 1. To determine how well this principle holds for small differences in x, and hence in λ$_c$, we applied PEC etching to the structure shown in Fig. 1, which was grown by molecular beam epitaxy (MBE).

The layers of the structure were Si-doped n-type to 1×10^{17} cm^{-3} and grown on a (100)-oriented semi-insulating (SI) GaAs substrate. The Al mole-fraction progressively increases towards the substrate (x = 0, 0.15, 0.2), resulting in a progressively decreasing δx (δx = 0.15, 0.05) between the layers. Compositional control of the alloy x-value is achieved by careful calibration of aluminum and gallium growth rates by reflection high energy electron diffraction (RHEED) oscillation measurement, combined with optical evaluation of growth rates using quarter-wave AlAs/GaAs and AlAs/Al$_{0.50}$Ga$_{0.50}$As DBR mirror stacks. Reflectometry measurement of the stop band of these mirror stacks provides an accurate measure of the thickness and x-value of the distributed bragg reflector (DBR) mirror layers for quick confirmation of the RHEED oscillation measurements. These measurements provide the growth rates of each binary constituent to within 1%. The lowest x-value material in the stack was grown by standard analog alloy techniques, with both Ga

and Al shutters open continuously. The higher x-value layer was grown using a 20 Å period superlattice of AlGaAs/AlAs. Taking into account the accuracy of the shutter timing, the δx between the two Al$_x$Ga$_{1-x}$As layers should be correct to within 2.5%. All the Al$_x$Ga$_{1-x}$As layers have x < 0.45, and therefore have direct bandgaps. The MBE-grown layers were ~1-2 μm thick.

The experimental setup, which consists of a simple electrochemical cell and a light source, has been described in detail elsewhere.[8] The sample, which serves as the anode, is mounted on a Teflon holder and electrical contact is made to it by a Ti-Au coated glass slide; a platinum wire serves as the cathode where the reduction reaction occurs. The two electrodes are immersed in a (1:20) HCl:H$_2$O solution which has a negligible dark etch rate. An Argon-ion laser is used to optically pump a Ti/sapphire laser which has a tuning range of 690 nm < λ < 830 nm. The linewidth of the laser is quite sharp at less than 1 Å. The wavelength calibrations were done using an optical spectrum analyzer. The incident wavelength is tuned by a micrometer which tilts the Ti/sapphire crystal and provides a wavelength control of ~1 nm. The laser beam is focused through a lens resulting in a diameter of ~0.5 mm at the sample surface. The etched depth is measured using a surface profilometer (accuracy ~200 Å) from the center of the Gaussian etched pit to the flat surface.

Consider the values λ$_c$ shown in Fig. 1. The tuning range for etch selectivity between the x = 0 and x = 0.15 layers is ~115 nm while the range decreases to ~32 nm between the x = 0.15 and x = 0.20 layers. The samples were etched at a power intensity of 25.5 W/cm^2. Figure 2 is a plot of the etched depth as a function of etch time for two incident laser wavelengths of 827 and 767 nm. As predicted, the etched depth saturated at ~1 μm for λ = 827 nm, terminating on the Al$_{0.15}$Ga$_{0.85}$As layer. Interestingly, the λ = 767 nm light which is 24 nm above the λ$_c$ of the x = 0.15 layer, has an etched depth saturation of ~2 μm, terminating on the Al$_{0.20}$Ga$_{0.80}$As layer and not on the Al$_{0.15}$Ga$_{0.85}$As layer. This behavior will be commented on later in the text. The limiting etched depth in the first case is achieved within the first minute of the etch, and in the second case,

1 μm n-GaAs	x= 0.0	λ$_c$ = 872 .47 nm
1 μm n-AlGaAs	x=0.15	λ$_c$ = 758.04 nm
2 μm n-AlGaAs	x=0.20	λ$_c$ = 726.11 nm
SI GaAs substrate		

Fig. 1. The MBE-grown layers are Si-doped n-type to 1×10^{17} cm^{-3} on a (100)-oriented SI GaAs substrate.

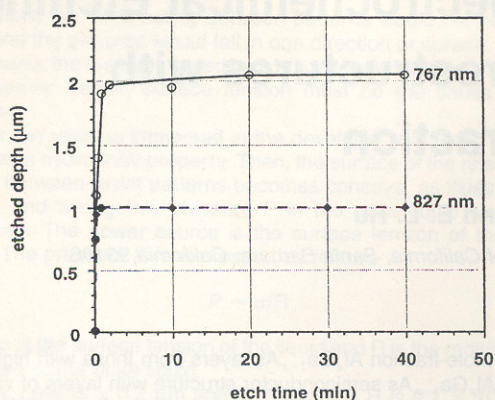**Fig. 2. Etched depth as a function of etch time for laser wavelengths of 827 and 767 nm. The laser intensity is 25.56 W/cm².**

Fig. 3. Etched depth after 20 min of etching as a function of wavelength. I = 25.5 W/cm² (diamonds), and I = 2.55 W/cm² (circles).

with the first two minutes. In both cases, over-etches were carried out for 40 min. These data suggest a very high selectivity has been achieved, but we shall attempt a more quantitative definition as follows. We define the etch selectivity as the bulk etch rate of the top layer, divided by the bulk etch rate of the desired etch stop layer. We assume that the "bulk" etch rate is the one observed for a thick layer of the material, relatively far from the underlying interface with the etch-stop layer. The etch rate of the top layer will diminish as the etched surface approaches the interface, hence for layer 1, we use the average etch rate in the first five seconds of etching (0.75 μm/5 s = 9 μm/min). Assuming an error in etched depth determination of a few hundred angstroms for ~40 min of over-etch, the selectivity of layer 1:layer 2 is >10^4:1. To compute the selectivity of etching layers 1 and 2 at λ = 767 nm with respect to the etch stop layer 3, we use an average etch rate through the two layers, (1.4 μm/0.5 min = 2.8 μm/min), rendering a selectivity of layer 2:layer 3 of >10^3:1. The etched pits are initially Gaussian in shape, but proceed to flat-bottomed pits with continued etching. In their selective PEC etching of GaAs from $Al_{0.40}Ga_{0.60}As$, Brown *et al.* reported a residual layer of GaAs, 200 Å thick, that persisted after prolonged etching. We have not confirmed the presence of a similar residual layer.

The selectivity resulting from the 767 nm light led us to investigate the role of wavelength, with the fixed etch time of 20 min. In particular, we wished to establish the selectivity of the PEC etch when the photon energy would be close to the bandgap of the materials being etched. Those data are shown in Fig. 3. The solid horizontal lines represent the expected etched depth assuming a sharp absorption cutoff for photon energies below the material bandgap. The thickness of the solid lines indicates the range of values expected due to experimental uncertainty in determination of the etched depth and wavelength. The data are taken at two incident intensities: 25.5 W/cm² (diamonds), and 2.55 W/cm² (circles). In general, for λ much greater than $\lambda_c^{material\,i}$, high etch selectivity is obtained, with the etch terminating on material i. As λ approaches $\lambda_c^{material\,i}$, the selectivity is degraded. The wavelengths which were higher than ~65 nm from the λ_c of the $Al_{0.15}Ga_{0.85}As$ layer, displayed excellent selectivity. As the wavelength was adjusted within ~24 nm of the λ_c of the $Al_{0.15}Ga_{0.85}As$ layer, the selectivity was lost. Note however that these wavelengths were still significantly far above the λ_c of the $Al_{0.20}Ga_{0.80}As$ layer, resulting in high etch selectivity as observed in Fig. 2 for the 767 nm light. Again, as the wavelength was adjusted within ~25 nm of the λ_c of the $Al_{0.20}Ga_{0.80}As$ layer, the selectivity was lost. The etched depth saturation of ~4 μm observed at the two lowest excitation wavelengths results from the doping-selectivity of the n^+ GaAs com-

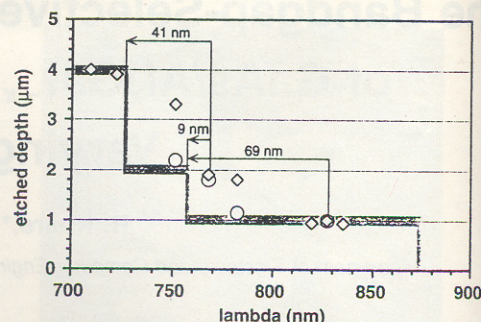pared to the SI GaAs.[8] We believe this reduction of selectivity results from the absorption curve not having a sharp cutoff at λ_c. Calculations have shown that at photon energies 44 meV (~25 nm) below the bandgap of GaAs (and similarly for AlGaAs layers) the material has reduced but significant absorption (α = 25 cm⁻¹).[9] This finite absorption results in a slow but steady etch rate which increases with incident laser intensity at a given wavelength.

We have shown that the wet PEC etch process can be a highly sensitive technique for the selective etching of n-type heterostructures due to its intrinsic bandgap-dependence. Mole-fraction differences as low as 0.05 were resolved with selectivities exceeding 10^3:1. These results cannot be extrapolated to p-type heterostructures due to the limited PEC etch rates in such materials.[8] We have also found that the selectivity is diminished as the incident wavelength approaches λ_c of the underlying semiconductor layer. In the structure described in this work, the MBE-grown layers were thick (>1 μm) and the x-values increased towards the SI GaAs substrate. We have found that when the layers become thinner, holes generated in underlying low-bandgap material can drift/diffuse to the surface and promote etching in layers other than which they are generated. This phenomenon will be discussed in more detail elsewhere.[10]

Acknowledgment

REFERENCES

1. C. M. Knoedler and T. R. Kuech, *J. Vac. Sci. Technol. B,* **4**, 1233 (1986).
2. G. C. DeSalvo, W. F. Tseng, and J. Comas, *This Journal,* **139**, 831 (1992).
3. E. Yablonovitch, T. Gmitter, J. P. Harbison, and R. Bhat, *Appl. Phys. Lett.,* **51**, 2222 (1987).
4. R. T. Brown, J. F. Black, R. N. Sacks, G. G. Petersen, and F. J. Leonberger, *Mat. Res. Soc. Symp. Proc.,* **75**, 411 (1987).
5. F. Kuhn-Kuhnenfeld, *This Journal,* **119**, 1063 (1972).
6. J. van de Ven and H. J. P. Nabben, *ibid.,* **137**, 1603 (1990).
7. D. Huang, G. Ji, U. K. Reddy, H. Morkos, F. Xiong, and T. A. Tombrello, *J. Appl. Phys.,* **63**, 5447 (1988).
8. R. Khare and E. L. Hu, *This Journal,* **138**, 1516 (1991).
9. H. C. Casey, Jr. and M. B. Panish, *Heterostructure Lasers, Part A: Fundamental Principles,* Academic Press Inc. (1978).
10. R. Khare, D. B. Young, and E. L. Hu, *Appl. Phys. Lett.* **62**, 1809 (1993).