

# Photoelectrochemical etching of *p*-GaAs

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A photoelectrochemical method for etching *p*-GaAs is reported. The method overcomes the apparent stability of GaAs to reductive decomposition by switching the potential of the *p*-GaAs between a value at which photogenerated electrons reduce the surface to Ga and  $\text{As}^{3-}$ , and a more positive value at which the majority carrier holes oxidize the Ga to  $\text{Ga}^{3+}$ . Etching has been observed in a variety of acidic and basic solutions in which  $\text{As}^{3-}$  and  $\text{Ga}^{3+}$  are soluble. With a 633-nm He-Ne laser beam having a peak intensity of  $0.75 \text{ W cm}^{-2}$ , a maximum etch rate of  $1300 \text{ \AA/min}$  has been obtained in a  $0.1\text{-M H}_2\text{SO}_4\text{-}0.1\text{-M NaSCN}$  solution. The rate of etching appears to be limited by the rate of dissolution and transport of the products away from the surface. The method is potentially useful for producing anisotropic etching in a variety of GaAs devices.

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Anisotropic etching to transfer mask patterns into an underlying semiconductor material is of much interest because of the need for high resolution etching techniques as the sizes of device structures become smaller. Anisotropic etching can be produced by light-induced decomposition processes for which etching only occurs on the illuminated portions of the surface. There have been a number of reports of semiconductor photoetching using decomposition reactions produced both by photogenerated minority carriers<sup>1-4</sup> and by photoactivated external agents.<sup>5,6</sup> The techniques using external agents have the serious drawback that they require a laser, generally in the UV, to produce the photoactivation and, therefore, have limited practicality for the rapid processing of large areas. The techniques using photogenerated minority carriers can use broadband incoherent light sources, since all photons with energies greater than the semiconductor band gap are effective in generating minority carriers.

Photogenerated minority carriers can induce decomposition at semiconductor surfaces in contact with an electrolyte because the absence of electrons in bonding orbitals, i.e., holes in the valence band, or the presence of electrons in antibonding orbitals, i.e., electrons in the conduction band, weakens the lattice bonds and subjects the semiconductor to attack by nucleophilic or electrophilic agents in solution.<sup>7</sup> Although there have been several reports of the use of photogenerated holes to etch *n*-type III-V semiconductors by oxidative decomposition, there have been no reports of the use of photogenerated electrons to etch *p*-type III-V semiconductors by reductive decomposition. In this letter we report on a method for photoetching *p*-GaAs by reductive decomposition.

Although there is both theoretical<sup>8,9</sup> and experimental<sup>10</sup> evidence that the reductive decomposition reaction for GaAs,



with the  $\text{As}^{3-}$  going into solution as  $\text{AsH}_3$ , should and does take place, illuminated *p*-GaAs surfaces at potentials at which Eq. (1) should occur show long-term stability. The reason for this stability is that the Ga remains on the surface

stabilizing it against further decomposition.<sup>11</sup> We have found that if, after forming this layer, the potential of the GaAs is made more positive in order to increase the hole concentration at the surface, it is possible to oxidize and dissolve the Ga layer more rapidly than the GaAs lattice itself. It is reasonable that this should happen, since the bonds between the Ga and the surface should be weaker than the bonds in the GaAs lattice. Therefore our method is a photoelectrochemical one in which the potential of the GaAs is periodically switched between a value at which photo-reduction occurs and a value at which oxidation occurs.

The experiments were done on samples of Zn:GaAs ( $p \approx 3\text{-}5 \times 10^{17} \text{ cm}^{-3}$ ) of [111] orientation. Electrical contact was made to the back side of the samples by means of ohmic contacts formed by the electrodeposition of gold. The samples were mounted so that the electrolyte could only contact the front surface of the GaAs when placed in a three-electrode electrochemical cell having an optical window. The potential of the GaAs was potentiostatically controlled with respect to a saturated calomel reference electrode (SCE) using a platinum counter electrode. The solutions were deoxygenated by bubbling  $\text{N}_2$  through them and stirred vigorously with a stirring bar. A spot on the GaAs surface was illuminated with a  $\text{TEM}_{00}$  beam of 633-nm He-Ne laser radiation having a beam diameter of approximately 0.5 mm. A spatial filter was used to eliminate higher-order transverse modes. The laser power was 0.75 mW yielding a peak intensity of  $0.75 \text{ W cm}^{-2}$ . The rates of etching were determined by measuring the depths of the holes formed with a Dektak surface profile measuring system.<sup>12</sup>

The Dektak profile of a photoetched hole is shown in Fig. 1. The dotted curve is a Gaussian distribution that has been fitted to the profile and has a diameter at the  $e^{-2}$  points of 0.56 mm. The good fit indicates that the etch rate was proportional to light intensity.

Oscilloscope traces of the current flow through the cell during one cycle of potential change are shown in Fig. 2. Trace (a) was taken with the sample in the dark, and trace (b) was taken with the He-Ne laser beam illuminating part of the sample. In the dark, the cathodic current is very small because of the low electron concentration. There is a small

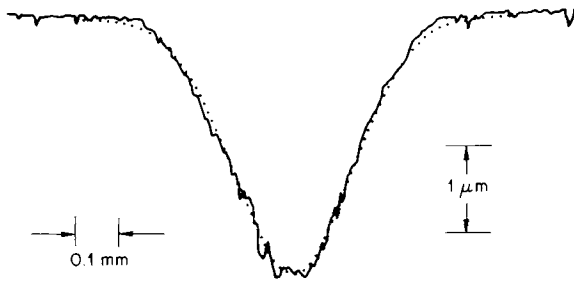
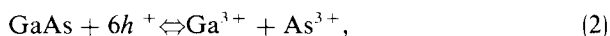


FIG. 1. Dektak profile of a hole photoetched with a Gaussian  $TEM_{00}$  He-Ne laser beam in a 0.2-M NaOH + 0.1-N EDTA<sup>3+</sup> solution. The dotted curve is a Gaussian distribution fitted to the profile.

anodic dark current due to the oxidative decomposition of the GaAs by the reaction<sup>1,3</sup>



which occurs over the entire surface of the sample. Under illumination much larger cathodic and anodic transient currents flow. During the cathodic portion of the cycle the photogenerated electrons drive Eq. (1). It is also possible that some of this current results from the reduction of  $H^+$ . Although the steady-state  $H^+$  reduction is very small at this potential, the condition of the GaAs surface changes during this transient period. During the anodic portion of the cycle, the Ga formed in Eq. (1) should be oxidized according to the reaction



where the subsequent complexation of the  $Ga^{3+}$  is dependent upon the pH of the solution.<sup>8</sup>

Only a fraction of the photocurrent in Fig. 2 results in material removal because of competing reactions. Some of the  $As^{3-}$  formed can be oxidized to GaAs, As, or  $As^{3+}$  during the following anodic interval and some of the  $Ga^{3+}$  formed can be reduced during the following cathodic interval. Also, if hydrogen is produced during the cathodic interval, then some of the anodic current could be due to the

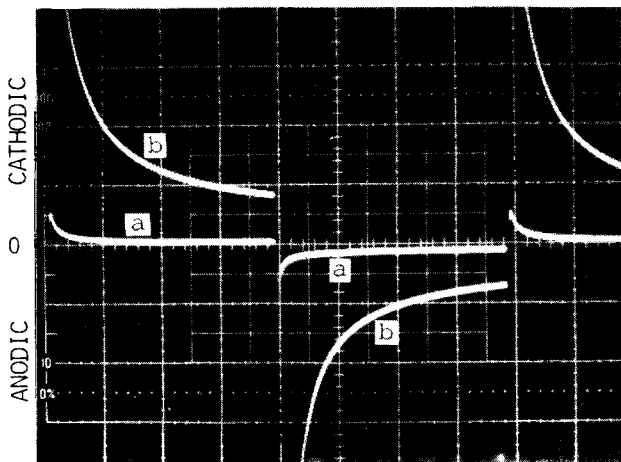


FIG. 2. Oscilloscope traces of current vs time when the potential is switched between  $-0.20$  and  $+0.25$  V vs SCE in a 0.1-M  $H_2SO_4$  solution. Trace (a) is with the sample in the dark and (b) is with the sample illuminated with a 0.75-mW He-Ne laser beam. Vertical scale =  $20 \mu A$ /division; horizontal scale =  $0.5$  ms/division.

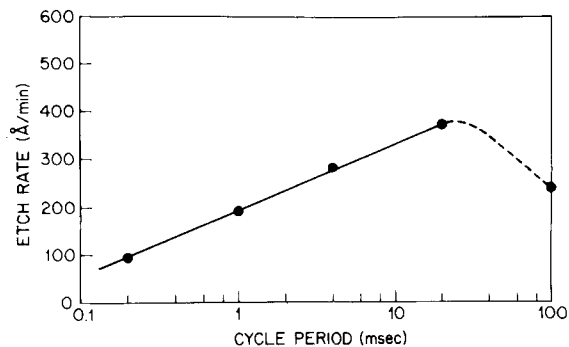


FIG. 3. Plot of the rate of photoetching vs the cycle period in a 0.2-M NaOH + 0.1-M oxalate solution. Cathodic ( $-0.95$  V vs SCE) and anodic ( $-0.49$  V vs SCE) intervals were equal and the total duration of etching for each period was 1 h.

oxidation of the  $H_2$  formed. The fraction of the photocurrent in Fig. 2 that resulted in material removal can be estimated since the actual etch rate corresponding to Fig. 2 was determined to be  $640 \text{ \AA}/\text{min}$ . From Fig. 2 the cathodic charge per cycle and the anodic charge per cycle are both approximately equal to  $8 \times 10^{-8}$  C. Assuming that the current distribution follows the Gaussian laser beam distribution, the charge density at the center of the spot is  $8 \times 10^{-5} \text{ C cm}^{-2} \text{ cycle}^{-1}$ . The charge density required for  $As^{3-}$  or  $Ga^{3+}$  formation by Eqs. (1) and (3) respectively can be expressed as  $5 \times 10^{-5} \text{ C cm}^{-2} \text{ \AA}^{-1}$ . If all of the charge resulted in material removal, the etch rate would have been  $1.6 \text{ \AA}/\text{cycle}$  or  $2.4 \times 10^4 \text{ \AA}/\text{min}$ . Since the actual etch rate was  $640 \text{ \AA}/\text{min}$ , only about 2.7% of the current resulted in etching. Therefore the rate of etching appears to be limited by the rate at which the products can be solvated and transported away from the surface. In agreement with this was the observation that etching was very much slower if the solution was not stirred.

From the anodic dark current in Fig. 2 an estimate can be made of the rate of dark etching. The dark anodic charge per cycle is approximately  $8 \times 10^{-9}$  C. This charge was spread over the entire area of the sample,  $0.135 \text{ cm}^2$ , giving a charge density of  $6 \times 10^{-8} \text{ C cm}^{-2} \text{ cycle}^{-1}$ . The charge density required for the removal of GaAs by Eq. (2) can be expressed as  $10^{-4} \text{ C cm}^{-2} \text{ \AA}^{-1}$ . Therefore the dark etch rate should be  $6 \times 10^{-4} \text{ \AA}/\text{cycle}$  or  $9 \text{ \AA}/\text{min}$ . This is approximately 70 times slower than the photoetching rate of  $640 \text{ \AA}/\text{min}$ .

The reoxidation and rereduction that can occur affects the dependence of the etch rate on the cycle period. When the period is very short, there is little time for dissolution and

TABLE I. Summary of etching results in various solutions.

Solution	Cycle time (msec)	Etch time (min)	Etch rate ( $\text{\AA}/\text{min}$ )
0.2-M NaOH	4	60	190
0.2-M NaOH + 0.1-M Oxalate	20	60	375
0.2-M NaOH + 0.1-N EDTA <sup>3+</sup>	10	120	250
0.1-M $H_2SO_4$	4	15	640
0.1-M $H_2SO_4$ + 0.1-M NaSCN	10	12	1300

transport of the products away from the surface. The products are then reoxidized or rereduced and very little material is removed from the surface. On the other hand, when the period is very long, the products escape from the surface but, since the amount of  $\text{As}^{3-}$  which is formed in one cycle is limited, the amount of material removed per unit time decreases as the period increases. This leads to an optimum period which is illustrated by the experimental results in Fig. 3.

Etching has been observed in a variety of acidic and basic solutions. A summary of some of these results is given in Table I. The highest etch rate that has been observed is 1300 Å/min in a solution of 0.1-M  $\text{H}_2\text{SO}_4$  and 0.1-M NaSCN.

In conclusion, it has been found possible to photoetch *p*-GaAs by a photoelectrochemical method in which the potential of the GaAs is switched between a value at which photoreduction occurs and a value at which oxidation occurs. With He-Ne laser light at an intensity of 0.75 W cm<sup>-2</sup> an etch rate of 1300 Å/min has been achieved, which compares favorably with plasma etch rates. A light intensity equivalent to this laser intensity can be readily achieved with

well-collimated light from a broadband incoherent source such as a tungsten lamp. This method should also be applicable to other III-V semiconductor compounds.

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