p-InP Photoetching

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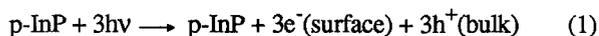
Introduction and Background

Anisotropic etching of III-V semiconductors for pattern transfer is of increasing interest as devices become smaller and more closely spaced. Also, etching processes which are selective to the composition or doping type of the semiconductor are of interest because they permit the monolithic integration of different devices. Photoelectrochemical processes are desirable because they are selective to the dopant type and band gap of the semiconductor.

Photogenerated minority carriers can decompose III-V semiconductors in contact with an electrolyte. The absence of electrons in the bonding orbital (holes in the valence band), or the presence of electrons in an antibonding orbital (electrons in the conduction band), weakens the chemical bond and makes it susceptible to nucleophilic or electrophilic attack by solution species (1). Holes at the semiconductor-solution interface directly lead to the anodic decomposition and dissolution of many semiconductors (2). Thus, p-type semiconductors can be etched under bias in the dark, and n-type semiconductors can be photoetched by hole-induced dissolution. This photoelectrochemical technique for n-type semiconductors has been used to etch integral lenses into light emitting diodes and gratings into semiconductor surfaces (2).

The stability of the p-InP surface is also important in its use as a photocathode for the production of hydrogen in energy conversion applications.

Although conduction band electrons destablize the semiconductor surface by reduction, the products are insoluble and not as well characterized (3). The photoelectrochemical etching of p-GaAs been shown to lead to the formation of arsine and gallium (4). Here, the first photoelectrochemical etching of (1 0 0) and ($\bar{1}$ $\bar{1}$ $\bar{1}$) p-InP is reported.

Since the photogeneration of minority carriers, Eq. 1, and reduction of the p-type semiconductor surface, Eq. 2, leads to insoluble products, a two step etching process is used.

$$\text{p-InP} + 3h\nu \longrightarrow \text{p-InP} + 3e^-(\text{surface}) + 3h^+(\text{bulk}) \quad (1)$$

$$\text{p-InP} + 3e^-(\text{surface}) \longrightarrow \text{In} + P^{3-} \quad (2)$$

The insoluble products are electrochemically etched in the second part of the process, Eq. 3.

$$\text{In} + 3h^+(\text{surface}) \longrightarrow \text{In}^{3+} \quad (3)$$

The potential is stepped from one where photogenerated electrons migrate to the surface (Eq. 1) to one where the con-

centration of holes in the valence band at the semiconductor-solution interface is large enough to carry out the anodic stripping (Eq. 3). The first half of the cycle is self limiting, and the cycle must be repeated for etching to proceed.

Results and Discussion

Holes were etched in (1 0 0) and ($\bar{1}$ $\bar{1}$ $\bar{1}$) p-InP crystals by stepping the potential between two values at which first photogenerated electrons and then holes were available to the semiconductor-solution interface. A He-Ne laser was used as the source of the illumination. Fig. 1 shows a surface profilometer trace of a hole etched in ($\bar{1}$ $\bar{1}$ $\bar{1}$) p-InP at 66°C by stepping the potential from -0.8V to 0.1V vs. a saturated calomel reference electrode (SCE). The period of the potential step was 0.1 ms, and the solution was 0.5M H_2SO_4. The duration of the experiment was 65 min, which corresponds to an etch rate of about 1 μm/min.

The etch rate for (1 0 0) p-InP was significantly less than for the ($\bar{1}$ $\bar{1}$ $\bar{1}$) face. The conditions in Fig. 1 produced an etch rate of 0.16 μm/min for the (1 0 0) face. The reduction of phosphorous on the surface, Eq. 2, is an important step in the process. The ($\bar{1}$ $\bar{1}$ $\bar{1}$) face has all phosphorous exposed to the solution, while the (1 0 0) face has half phosphorous and half indium exposed to the solution.

In addition to a higher etch rate, the etched ($\bar{1}$ $\bar{1}$ $\bar{1}$) surface was considerably smoother then the (1 0 0) surface. Etched holes in the ($\bar{1}$ $\bar{1}$ $\bar{1}$) face were usually specularly reflective while those in the (1 0 0) face were rough and dull in appearance. Roughness can be caused by preferential etching and exposing other, more reactive crystal planes. This again indicates that the (1 0 0) face is less reactive.

The rate of etching was dependent on temperature for both crystal faces and approximately doubled for every 10°C temperature increase from 22°C to 82°C. The room temperature etch rate for the (1 0 0) surface was 0.01 to 0.08 μm/min depending upon the applied potential of the reduction (eq. 2) and oxidation (eq. 3) reactions. The etched surface was rough and irregular.

Several series of chronoamperometic experiments were carried out to investigate the formation of the insoluble products formed in Eq. 2 and their temperature dependence. Fig. 2 shows the anodic current after the potential had been stepped from -0.8V to +0.1V vs. SCE. In Fig. 2A, the p-InP electrode was kept in the dark for 60s at -0.8V. In the dark, no pho-

toreduction, Eq. 2, is expected. The anodic current is primarily due to the non-faradaic charging of the semiconductor depletion region. In Fig. 2B, the electrode was illuminated for 0.1s with a 5mW He-Ne laser during the first few seconds while biased at -0.8V. The electrode was then allowed to sit in the dark just as in Fig. 2A so that any soluble products formed during the photoreduction could diffuse away. The capacitive charging of the semiconductor is the same in both cases, and the illuminated area was about 10% of the exposed surface area. It is clear that insoluble products were formed on the surface of p-InP during the photoreduction, and these can be stripped off during excursions to more positive potentials.

The anodic stripping current shown in Fig. 2 becomes larger as the potential becomes more positive. This represents an increased rate of photoeletrochemical etching. However, the potential of the anodic stripping reaction is bounded by the direct dissolution of p-InP, as shown in Eq. 4.

$$p\text{-}InP + 6h^+ \longrightarrow In^{3+} + P^{3+} \tag{4}$$
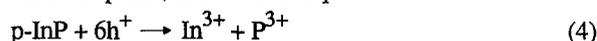
When the stripping potential was held at 0.5V vs. SCE, the rate of dark etching became unacceptably high compared to the rate of photoetching.

It was found that the anodic stripping current increased with temperature just as the etch rate did in Fig. 1. The etch rate per unit time, as measured in $\mu m/min$, was not significantly affected by the cycle time of the potential step. That is, increasing the cycle time from 0.1 ms to 10 ms did not significantly affect the removal rate. The removal rate per potential step cycle was of course directly related. This can be seen in Fig. 2 where the anodic stripping current has not decayed to background levels even after 20 ms. The chemical dissolution of the reduction and oxidation products is slow and probably responsible for the temperature dependance.

The current efficiency can be calculated by comparing the InP removal rate to the anodic stripping current. When the (1 0 0) p-InP was etched by cycling the potential between -0.8V and 0.4V vs. SCE at 49°C with a 10 ms period, the etch rate was 0.36 $\mu m/min$ or 0.6 Å/cycle. The chronoamperometric net current, i(light)-i(dark), was integrated for the same 10 ms cycle time, and the charge was 1.78 x 10^{-7} coulombs. If this were the amount of In stripped off the surface as a result of Eq. 3, then the removal rate for each 10 ms cycle would be 1.0 Å/cycle.

Conclusion

The ability to etch p-InP photoelectrochemically in a controlled and selective manner has been demonstrated by switching the potential between a value at which photoreduction of the surface occurs and a value at which oxidation occurs. The rate of etching and the resulting surface topography are dependent upon the orientation of the crystal, the temperature, and the cathodic and anodic potentials.

References

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4. F.W. Ostermayer, Jr., and P.A. Kohl, Appl. Phys. Lett., 39, 76 (1983).

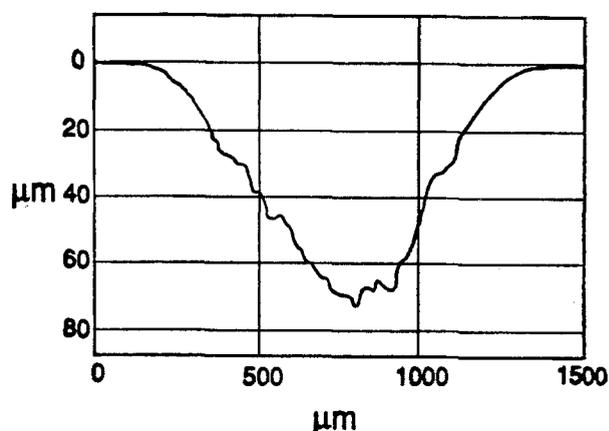**Fig. 1.** Profile of a photoelectrochemically etched hole in $(\bar{1}\,\bar{1}\,\bar{1})$ p-InP H_2SO_4 at 66°C with the potential cycled from -0.8 to 0.1V vs. SCE at a frequency of 10 kHz.
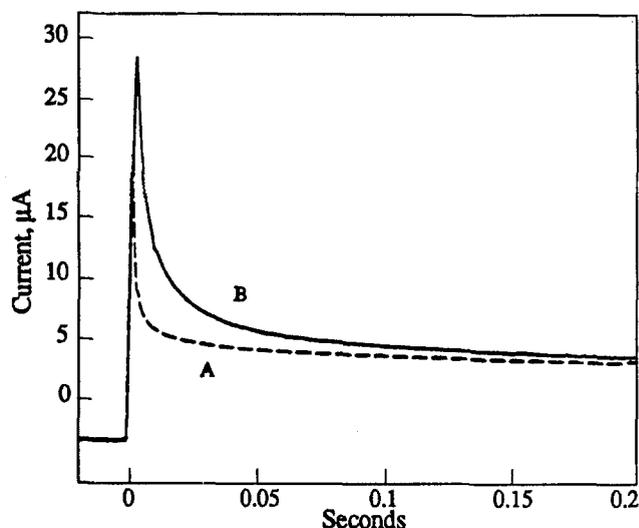

Fig. 2. Current time response for a potential step from -0.8 to 0.1 V vs. SCE for (100) p-InP in H_2SO_4 at 66°C. Curve (A) with no illumination and (B) illuminated for 0.1 seconds, 50 seconds prior to potential step.