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The Etching of InP in HCl Solutions: A Chemical Mechanism

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ABSTRACT

The etch rate of InP in solutions of high HCl concentration was shown to be independent of the applied potential in a wide potential range negative with respect to the flatband value. Dissolution of the solid led to the formation of PH₃. The etch rate, which was not mass-transport controlled, was first order in molecular HCl concentration. The results lead us to conclude that, in HCl etchants, InP is dissolved by a purely chemical mechanism. The influence of chemical etching on the anodic behavior of InP in these electrolytes is described.

Aqueous etching of III-V materials is often an important step in device technology (1, 2). While anodic etching is sometimes used (3), the necessity of making electrical contact to slices of small dimensions is invariably a disadvantage. Methods not involving an external current or voltage source are therefore favored (1, 2). Such methods can be divided into two classes: "electroless" and "chemical" dissolution. Electroless dissolution involves two separate potential-dependent electrochemical reactions: the oxidation of the solid and the reduction of an oxidizing agent. The principle is illustrated in Fig. 1 for the etching of a p-type III-V semiconductor (4). For these materials, holes in the valence band are required at the surface for bond breaking. As a result, the anodic dissolution current increases at potentials close to the flatband value (V_{fb}) as shown in curve (a). For electroless dissolution, holes must be supplied by an oxidizing agent in solution. If the distribution function of the oxidizing agent overlaps with the valence band of the semiconductor, then reduction via hole injection into the valence band is expected [curve (b)]. Here, we have assumed that the reduction reaction is diffusion controlled, i.e., the cathodic partial current is independent of potential. Curve (c) represents the total measured current-potential curve in the electrolyte containing the oxidizing agent. At the rest potential, the anodic and cathodic partial currents are equal. If the potential is changed from this value using an external source, then the etch rate of the semiconductor will, of course, also change.

Gerischer and co-workers (5, 6) have shown that semiconductors can be dissolved by a purely chemical mechanism, which is characterized by the absence of any influence of the surface carrier concentration on the etch rate. Such behavior is observed with bifunctional agents, such as halogen or H₂O₂ molecules, which are capable of forming two new bonds with the semiconductor surface more or less simultaneously. For GaAs dissolution in bromine solution, for example, they suggest a coordinated reaction sequence involving the breaking of Ga-As and Br-Br bonds and the simultaneous formation of Ga-Br and As-Br bonds.

Etchants based on HCl are widely used for InP semiconductor devices (7, 8). The presence of other acids in the HCl solution has a significant influence on the etch rate. However, InP does not dissolve in conventional etchants involving simple oxidizing agents. In order to resolve the question of the dissolution mechanism, we studied both the etching and electrochemistry of p-InP in various HCl solutions.

Experimental

The p-type InP slices used in this work were made from liquid-encapsulated Czochralski material with a carrier

density in the range $1-2 \times 10^{18} \text{ cm}^{-3}$. The (100) face was exposed to the solution. The diameter of the electrodes was 3 mm, with the exception of the InP rotating disk, which had a diameter of 4 mm.

The current-potential measurements were carried out under potentiostatic control in a conventional cell using a Pt counterelectrode and a saturated calomel electrode (SCE) as reference. All potentials are given with respect to this SCE. A Solartron 1172 Frequency Response Analyser was employed for determining the flatband potentials. All impedance measurements were carried out at a frequency of 10 kHz.

The total dissolution rate of InP at various potentials was determined analytically by measuring the indium concentration in the etching solution by induced-coupled-plasma (ICP) emission spectrometry. The etchant was passed over the InP electrode, which was mounted in a glass microelectrochemical flow cell as described by Haroutiounian *et al.* (9). Indium concentrations as low as 0.5 ppm could be determined with a relative accuracy of about 5%. An LKB Varioperpex peristaltic pump was used to pump the solution through the flow cell. The flow rate of the solution, mainly deter-

Fig. 1. Curve (a) represents the theoretical partial anodic dissolution current of a p-InP electrode in the dark, and curve (b) the diffusion-limited reduction current of an oxidizing agent as a function of the potential. Curve (c) gives the total current-potential curve.

mined by the lower limit of the indium detection, was in the range from 0.2 to 1.0 ml/min.

The gas was analyzed qualitatively using the color-detector tube method ("Dräger" tube), which in our case gave a color reaction specific for phosphine. A gas burette was used for the quantitative gas analysis.

Results

Flow-cell experiments.—In Fig. 2, results are given for the potentiostatic etching of p-InP in the dark in HCl solutions. Figure 2a shows the current-potential curves of this electrode in 3M and 6M HCl. At negative potentials the current is very low in both cases. In the vicinity of the flatband potential ($V_{FB} = 0.73V$ vs. SCE) the anodic current increases, as expected. It should be noted that the anodic curve for the 6M HCl solution is shifted slightly in the cathodic direction with respect to that for the 3M solution.

The total dissolution rate, according to the ICP analysis, is shown in Fig. 2b as a function of the potential. For the 3M HCl solution, the dissolution rate follows the current closely. At negative potentials the etch rate (r_t) is very low and increases considerably near the flatband potential. If we assume that in this case etching is due solely to anodic dissolution, then it can be easily shown that six holes are required to dissolve one InP entity. The total etch rate potential curve for the 6M HCl case differs markedly from that of the corresponding current-potential curve. This difference is most obvious at negative potentials, at which the InP dissolves at a rate essentially independent of applied potential. Since no cathodic reaction occurs in this range, we must conclude that InP is chemically dissolved by HCl. If we assume that anodic dissolution in 6M HCl here also requires six holes per InP, then the chemical etch rate can be calculated from the total etch rate and the measured anodic current. Figure 2c shows that the chemical etch rate (r_{chem}) remains

Fig. 2. Potentiostatically measured current-potential curves (a), total etch rate as a function of the electrode potential (b), and chemical etch rate as a function of the electrode potential (c) for a p-InP electrode in the dark in a 3M HCl (●) and 6M HCl (x) solution in water.

constant, even at potentials at which the electrode dissolves anodically.

A further example is shown in Fig. 3 for 1.5M HCl in concentrated acetic acid solution. Etchants based on HCl and acetic acid are often used in InP technology (7). Figure 3a shows the current-potential curve, and Fig. 3b the calculated chemical etch rate as a function of the electrode potential. The results in the cathodic region are similar to those found with 6M HCl solution; the current is low and a high chemical etch rate is found. The slow increase of the chemical etch rate with potential is probably due to a roughening of the electrode surface during the experiment. The increase in the anodic current at potentials near V_{FB} is considerably lower than that found in a HCl solution of the same concentration but without acetic acid. A dramatic decrease of the chemical dissolution rate is observed when the anodic dissolution starts. In this potential range, we observed the formation of an orange-colored film at the electrode surface. Phosphorus was found in this film by EDAX analysis. Obviously, a passivating film is formed during anodic dissolution. This film inhibits both the anodic and the chemical dissolution reactions.

It should be noted that the chemical dissolution rate depends markedly on the surface condition of the InP electrode. Since induction effects are observed, care must be taken to ensure a constant dissolution rate before measurements are made. This can be done by pre-etching the electrode in the same etching solution.

The results shown so far suggest that the chemical etch rate of InP is strongly dependent on HCl concentration. This dependence was studied by varying the HCl concentration over a wide range for two different systems. An InP crystal was chemically etched in these solutions in the flow cell (the measured current was zero), and the chemical dissolution rate was again analytically determined by ICP emission spectrometry. The results are shown in Fig. 4. For curve (a), the concentration was varied by diluting concentrated HCl with water. At 9M HCl, the chemical dissolution rate is high and decreases rapidly as the HCl concentration is lowered. For a 5M HCl

Fig. 3. Potentiostatically measured current-potential curve (a) and chemical etch rate as a function of the electrode potential (b) in the dark for a p-InP electrode in a solution of 1.5M HCl in concentrated acetic acid.

Fig. 4. Chemical etch rate as a function of the HCl concentration for a p-InP crystal in the dark. The HCl concentration was varied by diluting with water [curve (a)] and concentrated acetic acid [curve (b)].

concentration, the etch rate is less than 40 Å/min and even lower for more dilute solutions. For curve (b), concentrated HCl was diluted with concentrated acetic acid. It is striking that here a linear relationship between etch rate and HCl concentration is observed and that the etch rate is significantly higher than in the corresponding HCl-H₂O solutions.

To decide whether the dissolution is a diffusion or a kinetically controlled process, the etch rate was measured as a function of the rotation rate using a p-InP rotating disk electrode at open circuit. Figure 5 shows that the chemical etch rate measured in a 3M HCl in concentrated acetic acid solution is essentially independent of the rotation rate (N). This means that the rate of the dissolution reaction is kinetically controlled.

Gas analysis.—When an InP crystal was dissolved at the rest potential in a concentrated HCl solution, gas evolution was observed at the solid surface. Using the color-detector method, we showed that this gas was phosphine. A clear color change was indeed observed even with the most insensitive tubes. We determined the gas

Fig. 5. Chemical etch rate in the dark as a function of the rotation speed of a p-InP electrode in a solution of 3M HCl in concentrated acetic acid.

quantitatively with a gas burette and showed that the phosphorus is converted for 100% ($\pm 1\%$) as PH₃.

Electrochemical measurements.—The current-potential curves of p-InP in 1N H₂SO₄ and in different HCl solutions in the dark are shown in Fig. 6. In all cases, the blocking current in the cathodic region was very low ($< 0.02 \text{ mA}/\text{cm}^2$). The onset of the anodic current in the case of 1N H₂SO₄ [curve (a)] occurs near the flatband potential ($V_{FB} = 0.73 \text{ V}$), as expected. The anodic current for 1M HCl [curve (b)] is shifted some 150 mV in the negative potential direction with respect to the H₂SO₄ case. With an increase in the HCl concentration, this effect becomes more pronounced. For the 9M HCl solution, the shift amounts to about 350 mV. When the curve was measured again in 1N H₂SO₄ after the HCl experiments, exactly the same result was obtained as in the first measurement [curve (a)].

We also measured the Mott-Schottky plots for each of the solutions used in Fig. 6. The flatband potential did not depend on the HCl concentration: $V_{FB} = 0.725 \pm 0.050 \text{ V}$ in all cases. The slope of the Mott-Schottky plots decreased somewhat as the HCl concentration was increased. This is probably due to an increase in the surface area of the electrode due to roughening as a result of etching. A similar effect can also be seen in Fig. 3b.

Discussion

From Fig. 2 and 4, it is obvious that chemical dissolution occurs in aqueous solution when the HCl concentration exceeds a certain critical value. The rate is strongly dependent on the HCl concentration and becomes very low at values lower than 5M [see Fig. 4, curve (a)]. This suggests that the etch rate depends on the degree of dissociation of HCl molecules. Although it is clear that at low concentrations the dissolution of HCl is complete, there is a considerable discrepancy in the literature with respect to higher concentrations (10). Calculations based on vapor pressure measurements and on Hammett functions show that the concentration of undissociated HCl begins to increase significantly above 5 mol/l (11, 12). In order to avoid the uncertainty involved when HCl is diluted with water, we studied the dissolution rate in HCl-acetic acid solutions. The dissociation constant of HCl in acetic acid ($K_a = 10^{-8.55}$) is much lower than in water ($K_a = 10^{-3}$) (13). Consequently, the degree of dissociation of HCl in acetic acid is negligible, even at low HCl concentrations. The chemical etch rate could therefore be studied as a function of the molecular HCl concentration. The linear dependence of the chemical dissolution rate on the HCl concentration in concentrated acetic acid [Fig. 4, curve (b)] indeed confirms that chemical dissolution is determined by the molecular HCl concentration. The

Fig. 6. Current-potential curves for a p-InP electrode in the dark in 1N H₂SO₄ (a), 1M HCl (b), 5M HCl (c), 7M HCl (d), and 9M HCl (e) in water. Scan rate: 10 mV/s.

high etch rate of HCl solutions diluted with concentrated acetic acid compared to that for aqueous solutions, also found by Adachi (7), can be understood in this way. Figure 5 shows that the etch rate is independent of the rotation rate of an InP electrode meaning that the chemical etch rate is kinetically determined by these HCl molecules.

The mechanism presented by Gerischer and Wallem-Mattes for the chemical dissolution of semiconductors involves symmetrical bifunctional etching agents such as H_2O_2 and halogen molecules (5, 6). Although we are, in the present work, dealing with an asymmetrical HCl molecule, we propose a reaction scheme similar to that for symmetrical agents. The first step involves a synchronous exchange of bonds: In-Cl and P-H bonds replace the original H-Cl and In-P bonds. This is very likely the rate-determining step

Since the indium and phosphorus atoms at the surface are triply bonded to neighboring atoms, two further bonds must be broken in an analogous manner to remove each atom from the lattice

Indium is therefore dissolved as hydrolyzed $InCl_3$ and PH_3 is evolved as a gas. Such a mechanism can account for the etching results observed.

The chemical etch rate of InP in HCl solution is independent of potential. At potentials near the flatband value (Fig. 2 and 3) the p-InP electrode dissolves anodically. The rate of the anodic etching increases as the surface hole concentration is increased, i.e., as the potential is made more positive. In aqueous HCl solutions, we have shown that six holes are required to dissolve one In-P entity. This means that both In and P are oxidized to the trivalent state, as is common for III-V materials (3-6). With a considerable concentration of acetic acid in the HCl solution, however, a film is formed on the electrode which inhibits both the chemical and anodic dissolution (Fig. 3). EDAX measurements have shown that this layer contains phosphorus but no indium or chlorine. We suspect that, in this case, phosphorus is not oxidized directly during anodic dissolution

A similar three-hole mechanism has been shown for GaP (14).

It is obvious from Fig. 6 that the chemical dissolution rate strongly influences the electrochemical behavior of InP. Anodic dissolution starts at a more negative potential as the HCl concentration is increased, although the flatband potential does not change. This must mean that the activation energy for electrochemical dissolution is lowered by chemical etching. A similar effect has been demonstrated by Gerischer and Wallem-Mattes (6) for the dissolution of GaAs in bromine solution. As in the GaAs case, this result can be explained if we assume that rup-

ture of the first In-P surface bond is rate determining for anodic dissolution

If this bond is broken during a chemical attack by HCl, then the remaining bonds are more easily attacked anodically and the onset potential for anodic dissolution is consequently lowered, indicating that it is, indeed, likely that the first step is the rate-determining dissolution step.

Conclusions

The dissolution of InP in concentrated HCl solutions follows a chemical mechanism in which undissociated HCl molecules play a decisive role. It seems likely that other etchants for InP, such as HBr and Br_2 (7, 8), are based on a similar mechanism. The reason why InP does not undergo electroless dissolution in conventional etchants containing oxidizing agents is probably related to the presence of a thin, highly resistant oxide layer on the semiconductor (15). Such a layer, which can inhibit either the dissolution of the solid or hole injection from the oxidizing agent, is unlikely to be present at the high HCl concentrations used here.

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