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Wet-chemical etching of III-V semiconductors

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In recent years the electronics industry has shown growing interest in semiconductors consisting of elements from groups III and V of the Periodic Table. This is largely because multilayer structures of such semiconductors have interesting applications. A well-known example is the semiconductor laser in the Compact Disc player, an important product for consumer electronics. Device structures with the required patterns can be obtained by dissolving parts of the semiconductor materials by a wet-chemical etching technique. Until recently wet etching was a relatively empirical process. An extensive study at Philips Research Laboratories in Eindhoven has provided a much better understanding of the etching behaviour of III-V semiconductors. One result is that the methods and etchants used in present applications can now be optimized more effectively and appropriate etchants can be developed for new applications.

Introduction

For many years the most widely used basic material in the semiconductor industry has been silicon. Since the seventies, however, we have seen the growing emergence of III-V semiconductors such as GaP, GaAs and InP for applications including light-emitting diodes, microwave field-effect transistors [1] and semiconductor lasers [2]. For these applications multilayer structures of different III-V semiconductors are used, which are grown epitaxially on a III-V substrate. A well-known combination is that of GaAs and $Al_xGa_{1-x}As$ in lasers with an emission wavelength of about 0.8 μm for Compact Disc players and digital optical recording [3]. Another well-known combination is that of InP and $In_xGa_{1-x}As_yP_{1-y}$ in lasers emitting at wavelengths of 1.30 and 1.55 μm for fibre-optic communications [4].

Multilayer structures are made with extremely accurate patterns to give them the required characteristics. Besides the mastery of the technique of producing different III-V semiconductors by epitaxial growth, this also requires an accurate etching technique for removing material at the right places. This is usually done by wet-chemical etching, although dry etching methods like plasma etching are occasionally used. III-V semiconductors can be etched to the required shapes by wet-chemical methods because the materials are generally perfect single crystals and the etch rate depends on the crystal orientation. The structure may often consist of a combination of materials

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[1] P. Baudet, M. Binet and D. Boccon-Gibod, Low-noise microwave GaAs field-effect transistor, Philips Tech. Rev. **39**, 269-276, 1980.

[2] G. A. Acket, J. J. Daniele, W. Nijman, R. P. Tijburg and P. J. de Waard, Semiconductor lasers for optical communication, Philips Tech. Rev. **36**, 190-200, 1976;
J. C. J. Finck, H. J. M. van der Laak and J. T. Schrama, A semiconductor laser for information read-out, Philips Tech. Rev. **39**, 37-47, 1980.

[3] Special issue 'Compact Disc Digital Audio', Philips Tech. Rev. **40**, 149-180, 1982;
K. Bulthuis, M. G. Carasso, J. P. J. Heemskerk, P. J. Kivits, W. J. Kleuters and P. Zalm, Ten billion bits on a disk, IEEE Spectrum **16**, No. 8 (August), 26-33, 1979.

[4] G. A. Acket, Halfgeleiderlasers voor optische communicatie, Ned. T. Natuurk. B **51**, 13, 1985;
G. A. Acket and W. Nijman, Recente ontwikkelingen op het gebied van halfgeleiders, Ned. T. Natuurk. A **53**, 22-24, 1987.

which, though chemically closely related, are still sufficiently different for a suitable etchant to give a completely different etching behaviour.

In the investigation described in this article we made an extensive study of the etching behaviour of various III-V semiconductors in a variety of aqueous solutions. This was done for each of the three possible etching mechanisms: electrochemical oxidation with an external voltage source ('anodic etching'), electrochemical etching with an oxidizing agent but no external voltage source, known as 'electroless etching', and chemical etching with a reactive compound. The investigation has led to an improved understanding of the processes involved in the different mechanisms. As a result, some new etchants have been developed that can be used to improve the fabrication of the structures for certain applications.

In this article we shall first give a brief description of the three etching mechanisms. We shall then look at some kinetic and crystallographic aspects of etching that are relevant to the production of particular etch patterns. Finally we shall give some examples of wet-chemical etching of III-V semiconductors in practical applications.

Etching mechanisms

Anodic etching

For anodic etching of a III-V semiconductor in an electrolyte the semiconductor is connected to the positive terminal of a direct-voltage source and an inert counter-electrode is connected to the negative terminal. When the potential of the anode is made sufficiently positive a current starts to flow, and the constituent elements become oxidized at the surface of the semiconductor. The ions formed in this process dissolve. The occurrence of oxidation implies that electrons are withdrawn from the valence band of the semiconductor or — and this amounts to the same thing — that holes are supplied to the valence band. In general, the dissolution of a III-V semiconductor (e.g. GaAs) is found to require six holes (h^+) per formula unit [5]:

$$GaAs + 6h^+ \rightarrow Ga^{3+} + As^{3+}. \qquad (1)$$

The nature of the reaction products depends on the *p*H-value and composition of the electrolyte. The etching reaction of GaAs in acidic solutions can be represented as follows:

$$GaAs + 3H_2O + 6h^+ \rightarrow Ga^{3+} + H_3AsO_3 + 3H^+. \qquad (2)$$

The dependence of the anodic etch rate on the applied potential is determined by the potential distribution at the interface between the semiconductor and the electrolyte. As with a metal electrode, there is a potential difference across a region known as the Helmholtz double layer in the solution near the interface. There is an important difference from a metal electrode, however; the potential drop extends some way into the semiconductor material; see *fig. 1*. Because of this 'space-charge layer', which is formed below the surface as a result of the relatively low concentration of charge carriers in a semiconductor, the energy bands are curved.

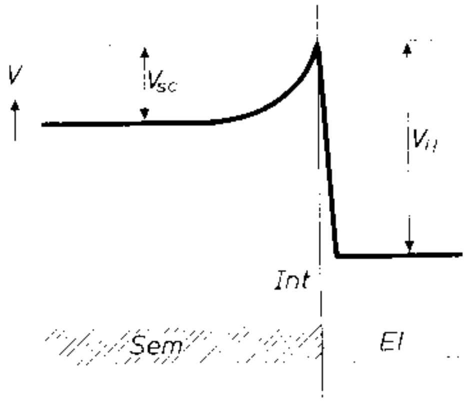

Fig. 1. The potential V at the interface *Int* of a semiconductor *Sem* and an electrolyte *El*. The potential distribution at a semiconductor electrode in an electrolyte differs from that of a metal electrode in that there is not only a potential difference, V_H, across the Helmholtz double layer but also a much more gradual fall in potential, V_{sc}, across the space-charge layer beneath the semiconductor surface.

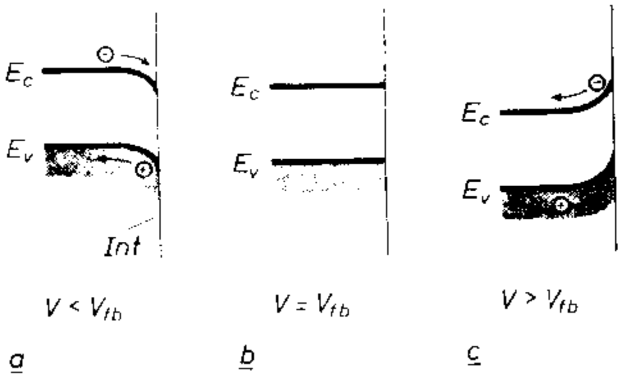

Fig. 2. Energy-level diagram for a semiconductor at the interface *Int* with an electrolyte for different values of the external potential V with respect to the flat-band potential V_{fb}, i.e. the potential at which the energy-band edges are flat right up to the surface. E_v top of the valence band. E_c bottom of the conduction band. The relative movements of electrons in the conduction band and holes in the valence band are also shown. At $V < V_{fb}$ (*a*) the bands are bent downwards; electrons tend to move to the surface and holes tend to move towards the bulk of the semiconductor. At $V = V_{fb}$ (*b*) the concentration of charge carriers at the surface is equal to the concentration in the bulk. At $V > V_{fb}$ (*c*) the bands are bent upwards, so that holes tend to go to the surface and electrons to the bulk. The location of E_v and E_c at the interface does not depend on the band-bending. The Fermi level (not shown) is assumed to be straight; in the bulk it is close to the conduction band if the semiconductor is n-doped and close to the valence band if the semiconductor is p-doped.

When the external potential is varied it is often found that only the potential difference across the space-charge layer changes, while that across the Helmholtz layer remains unchanged[6]. There is a particular potential at which the energy-band edges in the semiconductor go straight to the surface without bending. This potential, known as the 'flat-band potential', V_{fb}, depends not only on the semiconductor material but also on the doping and the nature of the electrolyte.

The effect of the applied potential on the energy bands is shown schematically in *fig. 2*. When the potential is negative with respect to V_{fb} the bands bend downwards. This means that there are more electrons and fewer holes near the surface than in the bulk of the material. At a potential equal to V_{fb} the bands run completely straight: the charge-carrier concentration is the same at the surface as in the bulk. When the potential is positive with respect to V_{fb}, the bands bend upwards: there are then fewer electrons at the surface and more holes than in the bulk.

With n-type doping the value of V_{fb} is lower than with p-type doping. This is because V_{fb} is a measure of the position of the Fermi level in the flat-band situation, and because this level lies close to the conduction band for n-type doping and close to the valence band for p-type doping. The difference in V_{fb} is therefore approximately equal to E_g/e, where E_g is the band gap of the semiconductor and e the electronic charge.

For the oxidation of a III-V semiconductor to take place via the reaction with holes at the surface, there must be a sufficient number of holes in the valence band. This will be the case if the p-type doping is high enough as a result of the incorporation of a sufficient number of acceptor atoms. When there is equilibrium between the charge carriers at the surface and in the bulk the concentration of holes at the surface (p_s) is given by the Boltzmann equation:

$$p_s = p_b \exp(eV_{sc}/kT), \qquad (3)$$

where p_b is the concentration in the bulk, V_{sc} the potential drop across the space-charge layer in the semiconductor, k is the Boltzmann constant and T the absolute temperature. Assuming that the potential difference across the Helmholtz layer is constant, it follows from the definition of the flat-band potential that:

$$V_{sc} = V - V_{fb}, \qquad (4)$$

where V is the applied potential. It will be clear that the dissolution of a p-doped semiconductor requires a potential approximately equal to V_{fb} (fig. 2*b*) or, better still, positive with respect to V_{fb} (fig. 2*c*).

A measured current-potential curve for p-GaAs is shown in *fig. 3a*. As would be expected, the current and hence the etch rate in the vicinity of V_{fb} increases exponentially with the potential, as a result of the exponential increase in the concentration of holes at the surface; see eq. (3).

Undoped or n-doped semiconductors cannot be directly dissolved anodically, because of the absence of holes in the valence band. In this case, however, we can make use of the effect of illumination on semiconductors. Photons of sufficient energy can excite electrons from the valence band into the conduction band, so that holes are formed in the valence band. If the band-bending within the semiconductor is appropriate, the holes are able to reach the surface and the etching reaction can take place; this is referred to as photo-anodic etching.

Fig. 3*b* shows a current-potential curve for an illuminated n-GaAs electrode in an acidic solution. It

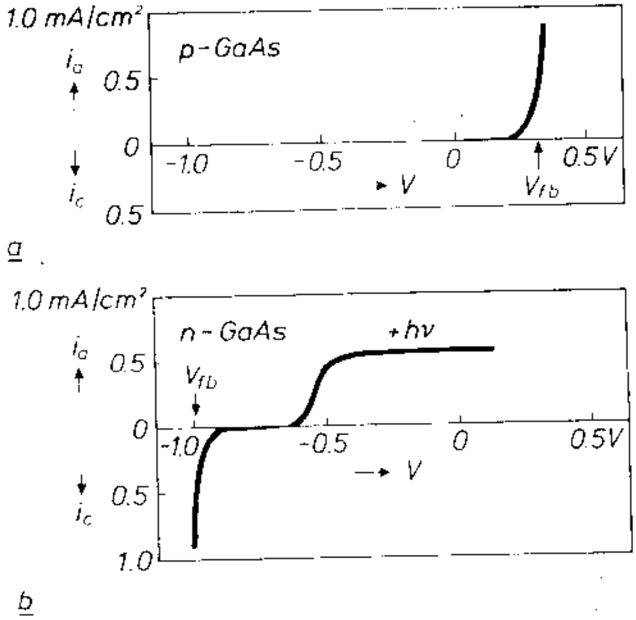

Fig. 3. Current-potential curves for p-GaAs (*a*) and n-GaAs (*b*) in 1N H_2SO_4. The anodic current density i_a and the cathodic current density i_c are plotted against the potential V of the semiconductor electrode with respect to a saturated calomel electrode. With p-GaAs a large potential-dependent anodic current flows as soon as the potential approaches the flat-band value V_{fb}. With n-GaAs a cathodic current flows at low potentials because electrons from the conduction band reduce H^+ ions in the solution to hydrogen gas. In the dark n-GaAs gives no anodic current. An anodic current (red) does flow upon illumination with photons of sufficient energy $h\nu$. This current only starts to flow at a potential that is substantially higher than the flat-band value for n-GaAs, and does not increase further at high potentials.

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[5] H. Gerischer, Über den Mechanismus der anodischen Auflösung von Galliumarsenid, Ber. Bunsenges. Phys. Chem. **69**, 578-583, 1965.

[6] R. Memming, Energy production by photoelectrochemical processes, Philips Tech. Rev. **38**, 160-177, 1978/79.

can be seen that the anodic current associated with the etching only occurs at a potential much higher than the V_{fb} value of n-GaAs. This is because the holes in an n-type semiconductor are the minority carriers. At a potential close to V_{fb}, the electron concentration at the surface is high and the holes recombine with electrons. At a higher potential the electrons and holes are effectively separated by the electric field (fig. 2*c*); the holes are now able to reach the surface and cause dissolution of the semiconductor. At a particular potential the anodic current saturates. In this case all the photo-generated holes take part in the etching process and the anodic current is proportional to the intensity of the incident light.

Anodic etching is not normally the most popular method for semiconductor technology. Working with a voltage source and a counter-electrode, with various electrical contacts, can be very inconvenient. Applying an electrical contact to a semiconductor material during the fabrication process can also be a problem and may even be undesirable for certain applications. There are however circumstances in which other etching methods give poor results and anodic etching may offer success. The study of anodic etching can also supply useful information about electroless etching.

Electroless etching

In electrochemical etching without an external voltage source, 'electroless etching', the etchant contains an oxidizing agent. The dissolution of the semiconductor is due to the oxidizing agent depleting the semiconductor of valence-band electrons and thus in fact supplying it with holes, so that it is itself reduced. A suitable oxidizing agent, e.g. for GaAs, is Ce^{4+}:

$$Ce^{4+} \rightarrow Ce^{3+} + h^{+}, \tag{5}$$

where the total reaction can be represented by

$$GaAs + 6\,Ce^{4+} \rightarrow Ga^{3+} + As^{3+} + 6\,Ce^{3+}. \tag{6}$$

A reaction of this kind is thermodynamically possible only if the redox potential, i.e. the equilibrium potential of the redox couple (in this case Ce^{4+}/Ce^{3+}), is higher than the potential of the solid (GaAs) in equilibrium with 'its ions' (Ga^{3+}, As^{3+}) in the solution. The rate of the reaction depends on the location of the energy bands of the semiconductor in relation to the energy levels of the redox couple in the solution.

Usually, the redox potential is related to the potential of a reference electrode, e.g. a saturated calomel electrode or a standard hydrogen electrode. In solid-state physics, however, the potential of an electron in vacuum is taken as the reference. If we take the same reference for an electrolyte, then the redox potential corresponds to the energy necessary for transferring an electron from the redox couple to vacuum. The energy of the electrons in the solution is then defined in the same way as for those in the solid, so that the redox potential can be considered as the Fermi level of the solution. Because of the interaction of the ions of the redox couple with the solvent, the electron energy of the reduced component is not the same as that of the oxidized component. The energy levels of the oxidized and reduced components are not discrete; they are broadened by the fluctuations of the solvation shell. This results in two Gaussian energy-distribution functions that are symmetrical with respect to the Fermi level, i.e. the redox potential; see *fig. 4*.

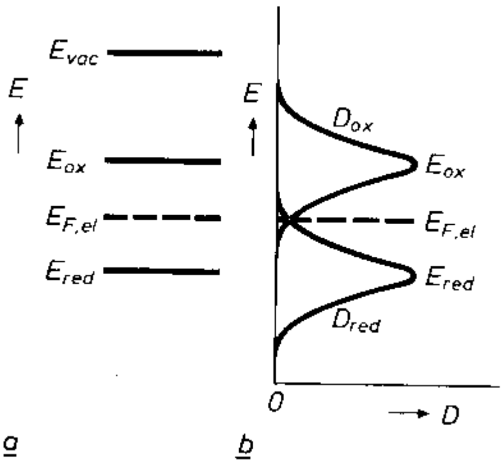


Fig. 4. *a*) Simplified diagram of the energy levels of the components of a redox couple in an electrolyte with respect to the potential energy E_{vac} of an electron in vacuum[6]. Because of the interaction with the solvent, the empty level E_{ox} of the oxidized component is higher than the filled level E_{red} of the reduced component. The Fermi level $E_{F,el}$, corresponding to the redox potential, lies halfway between E_{red} and E_{ox}. *b*) In reality the levels are broadened to energy-distribution functions D_{red} and D_{ox} owing to fluctuations of the solvation shell.

The dissolution reaction of eq. (6), where the redox couple causes the transfer of six holes to the valence band of the III-V semiconductor, is only possible if the energy-distribution function of the oxidized component corresponds approximately to the location of the valence band of the semiconductor. By measuring the electrode impedance, the potentials of the valence-band and conduction-band edges of the semiconductor can be determined with respect to the same reference potential in the solution. In *fig. 5* redox potentials of a number of redox couples in an acidic solution ($pH = 0$) are compared with the band-edge potentials of three widely used semiconductors: GaP, GaAs and InP. The couple Ce^{4+}/Ce^{3+} has a highly positive redox potential, so that holes can be injected into all three semiconductors. The redox potential of the couple Fe^{3+}/Fe^{2+} is less positive; this couple can

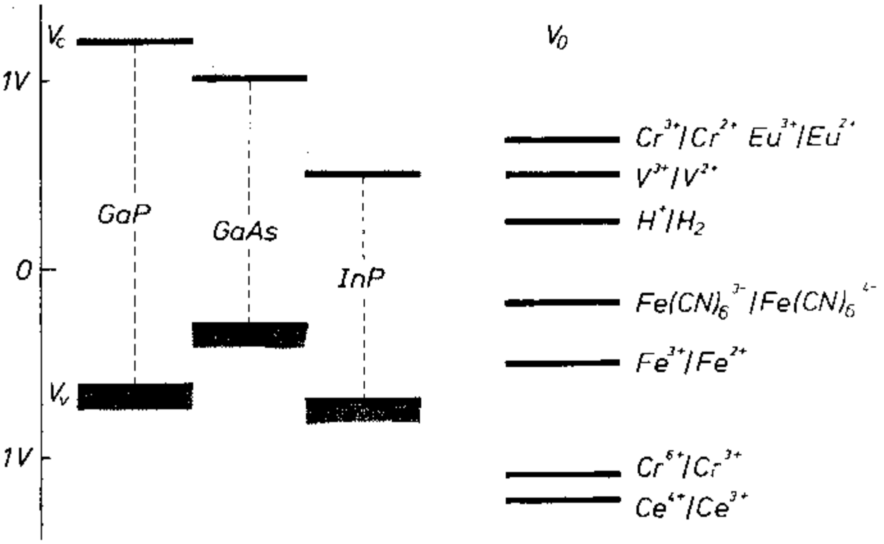


Fig. 5. Potentials of the energy bands of three semiconductors and the redox potentials of a number of redox couples in solutions with a pH of 0, measured with respect to a saturated calomel electrode. The potentials of the band edges of the semiconductors are indicated by V_v and V_c. The standard redox potential V_0 is shown for the redox couples; this is the redox potential measured when the concentration of the oxidized component in the solution is equal to that of the reduced component.

still inject holes into GaAs, but not into GaP and InP. The redox potential of the couple $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ is such that the injection of holes is no longer possible, not even into GaAs.

Oxidation with a redox couple can be thought of as the sum of an anodic process and a cathodic process, each with its own partial current-potential curve. *Fig. 6* shows these curves for the oxidation of p-GaAs with a Ce^{4+} solution. The anodic partial current increases steeply with the potential, but the cathodic partial current is practically independent of the potential in a wide range. This is because the rate at which the Ce^{4+} ions are reduced is determined entirely by the rate at which they diffuse to the semiconductor surface. Since there is no external current in electroless etching, the etching reaction takes place at the 'mixed potential', where the anodic and cathodic partial currents are equal. The value of the partial currents at the mixed potential determines the etch rate. In this case the etch rate is therefore completely controlled by the diffusion rate of the Ce^{4+} ions in the solution.

Since electroless etching depends on the transfer of electrons from the valence band to the oxidizing agent in the solution, both p-doped and n-doped semiconductors can be dissolved with the same etchants. The current-potential curves differ, however, because the injected holes in n-doped material are minority carriers. As an example, *fig. 7* gives the current-potential curves for n-GaAs in a Ce^{4+} solution. In the range of potentials from -1.0 V to -0.6 V the total current is still equal to the cathodic partial current because of the Ce^{4+} reduction. At these potentials there is not much band-bending, so that the electron concentration is relatively high at the surface and the injected holes recombine with the electrons supplied from the bulk. At higher potentials the electron concentration at the surface becomes negligible and the injected holes can no longer recombine with electrons. The holes then remain at the surface and oxidize the GaAs. Over the entire range of potentials the Ce^{4+} reduction gives the same cathodic partial current, which depends on the diffusion rate of the Ce^{4+} ions. Since at high potentials all the injected holes are used for oxidation, the anodic partial current at such potentials is equal to the cathodic partial current. At the mixed potential the rates of the GaAs oxidation and Ce^{4+} reduction are exactly equal and the recombination rate is zero. The etch rate of n-GaAs is thus determined by the diffusion rate of the Ce^{4+} ions and is the same as that of p-GaAs.

In fig. 5 the band-edge potentials of the semiconductors and the redox potentials of the redox couples apply to acidic solutions ($p\mathrm{H} = 0$). A change in the pH-value of the solution has no effect on the redox potential of a couple like $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$. The presence of H^+ ions or OH^- ions does however have a marked effect on the number of ions adsorbed at the semiconductor surface. This changes the potential difference across the Helmholtz layer (fig. 1), resulting in a different flat-band potential. It is known that the flat-band potential decreases by about 60 mV per unit increment in the pH. This means that at a pH of 14

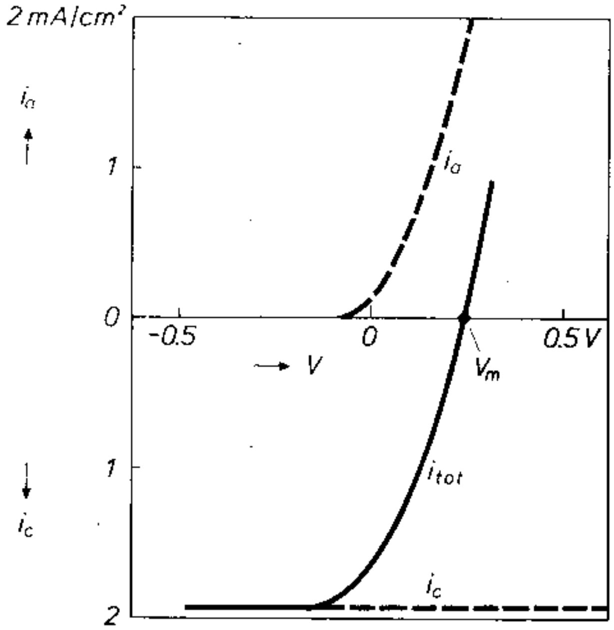


Fig. 6. Current-potential curves for p-GaAs in a Ce^{4+} solution. The anodic partial current density i_a due to the GaAs oxidation, the cathodic partial current density i_c due to the Ce^{4+} reduction, and the total current density i_{tot} are shown, plotted against the potential V with respect to a saturated calomel electrode. Whereas i_a at a particular potential increases steeply with V, the value of i_c is practically independent of the potential in a wide range. The electroless etching takes place at the mixed potential V_m, where $i_a = i_c$. In this case the etch rate, which is proportional to the value of i_a at V_m, is determined entirely by the constant cathodic partial current.

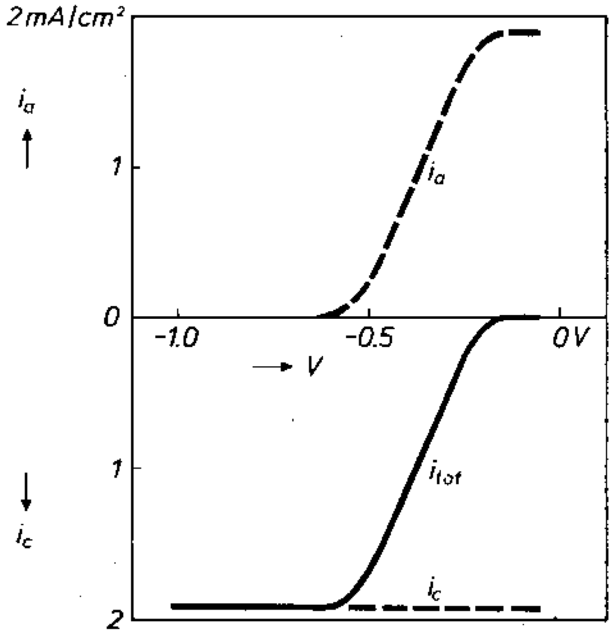


Fig. 7. Current-potential curves (as in fig. 6) for n-GaAs in a Ce^{4+} solution. Here again i_c is constant but i_a also becomes constant at high potentials and practically equal to i_c. The value of i_c again determines the etch rate.

the band-edge potentials of the semiconductors are shifted upwards by about 0.8 V with respect to those in fig. 5. The redox potential of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, for example, then comes to lie below the valence-band-edge potentials of GaP, GaAs and InP. The result is that this couple can inject holes into the valence band of all three semiconductors, so that etching is in fact possible at a *p*H of 14.

A redox potential that is well placed with respect to the valence-band-edge potential of the semiconductor is not always a guarantee of a satisfactory etching reaction. At the surface of InP, for instance, the reduction of Ce^{4+} is inhibited to such an extent, probably due to the formation of a thin oxide film, that there is hardly any etching. Etching GaAs with CrO_3/HF solutions is also less effective. In spite of the appropriate redox potential of the Cr^{6+}/Cr^{3+} couple, the dissolution rate of the GaAs is much lower than would be expected from the diffusion rate of Cr^{6+}. In this case the semiconductor surface is partly passivated by the adsorption of an intermediate formed during the etching reaction, probably a complex of hexavalent and trivalent chromium [7].

Besides the oxidizing agents that can give an etching reaction in the dark, there are other agents that can etch III-V semiconductors under illumination. This 'photo-etching' depends on both majority and minority carriers; see *fig. 8*. Photons with an energy equal to or greater than the band gap of the semiconductor generate electron-hole pairs. The holes that are formed oxidize the semiconductor, while the electrons reduce the oxidizing agent. A competing process is the recombination of electrons and holes. The couples that would appear to be useful for the photo-etching are those whose redox potential lies above the valence-band potential of the semiconductor and whose oxidized component has an energy-distribution function that corresponds to the conduction band. In the case of GaAs, for example, these are the couples V^{3+}/V^{2+},

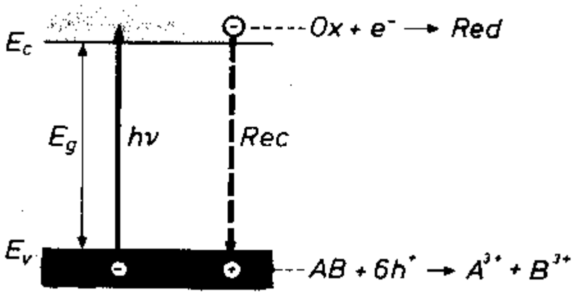


Fig. 8. Principle of electroless photo-etching of a III-V semiconductor AB. Photons of energy $h\nu$ equal to or greater than the band gap E_g excite electrons from the valence band to the conduction band. The holes formed oxidize the semiconductor while the electrons in the conduction band reduce the oxidizing agent Ox to Red. A competing process is the recombination *Rec* of electrons and holes.

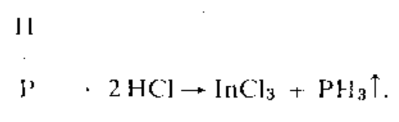
Cr^{3+}/Cr^{2+} and Eu^{3+}/Eu^{2+} (fig. 5). We have found however that these couples are unsuitable for photo-etching III-V semiconductors, because the electron transfer to the oxidizing agent cannot compete with the electron-hole recombination. There are some more complicated redox couples that do provide effective electron transfer [8], however. Acidic H_2O_2 solutions, for example, can be used to photo-etch both p-type and n-type GaAs [9]. We shall not consider the intricate mechanism of these etching reactions here.

Chemical etching

Chemical etching does not involve free charge carriers and cannot therefore be affected by an external potential. In chemical etching the surface of the semiconductor is attacked through the action of reactive molecules (e.g. HCl), with the result that bonds between the surface atoms are broken and at the same time new bonds are formed with the atoms of the reactive molecules. The compounds formed dissolve in the etchant or escape as gases.

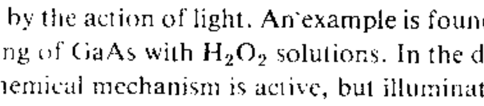
A mechanism of this type is found in the etching of InP with concentrated HCl solutions [10]. Since the dissolution of InP is due to the reaction with undissociated HCl molecules, the HCl concentration has to be fairly high — higher than 6 M at room temperature. The concentration can be lower in a solution containing a large amount of acetic acid, because the dissociation content of HCl is smaller in such a solution [11].

In the reaction between InP and HCl it is likely that a bond between In and P is broken at the same time as the bond between H and Cl, and that new bonds are then formed between In and Cl and between P and H:



$$\begin{array}{ccccc} \text{Cl} & \text{H} & & \text{Cl} & \text{H} \\ & & \rightarrow & & | \\ \text{In} & \text{P}- & & \text{In} & \text{P} \\ & & & & | \end{array} \qquad (7)$$

Since each surface atom is bonded to three atoms below it, two bonds then remain to be broken. Finally, the indium dissolves as $InCl_3$, while the phosphorus disappears as PH_3:



$$\begin{array}{cc} \text{Cl} & \text{H} \\ & \\ \text{In} & \text{P} \end{array} + 2\,\text{HCl} \rightarrow \text{InCl}_3 + \text{PH}_3\uparrow. \qquad (8)$$

In some cases the etching mechanism may be changed by the action of light. An example is found in the etching of GaAs with H_2O_2 solutions. In the dark only a chemical mechanism is active, but illumination gives rise to an electrochemical etching process, in which the holes formed in the valence band oxidize the GaAs [8].

Kinetic and crystallographic aspects

The rate at which III-V semiconductors are dissolved by a particular etching mechanism depends on a number of factors. The rate, for example, may be determined entirely by the kinetics of the reaction at the semiconductor surface. However, if the rate of this reaction is very high, the rate-determining parameter may be mass transfer in the solution. The etch rate may also be very dependent on the crystallographic orientation of the surface. Etching near the edges of masks may produce special effects. If a semiconductor is being etched in contact with another semiconductor or a metal, it might be expected that the rate of dissolution would be affected by the galvanic interaction between the materials. Since all these factors are relevant to the practical applications to be discussed, we shall first take a closer look at them.

Rate-determining step

In a kinetically controlled etching process, where the surface reaction is rate-determining, the concentration of the rate-determining species at the surface (c_s) will be equal to that in the bulk of the solution (c_b). In the simplest approximation the etch rate r_k is then given by

$$r_k = k\,c_b^n, \qquad (9)$$

where k is the reaction-rate constant and n the order of the reaction. The rate constant is given by:

$$k = A\exp(-E_a/RT), \qquad (10)$$

where A is a constant, E_a the activation energy for the reaction, R the gas constant and T the absolute temperature. A plot of log r_k against $1/T$ gives a straight line. The activation energy that can be derived from the slope of this line is of the order of 40 kJ/mol for most kinetically controlled etching reactions. This means that the activation energy per molecule is of the order of 0.4 eV.

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[7] J. van de Ven, J. E. A. M. van den Meerakker and J. J. Kelly, The mechanism of GaAs etching in CrO_3-HF solutions, I. Experimental results, J. Electrochem. Soc. 132, 3020-3026, 1985;
J. J. Kelly, J. van de Ven and J. E. A. M. van den Meerakker, The mechanism of GaAs etching in CrO_3-HF solutions, II. Model and discussion, J. Electrochem. Soc. 132, 3026-3033, 1985.

[8] J. J. Kelly, J. E. A. M. van den Meerakker and P. H. L. Notten, Electrochemistry of photo-etching and defect-revealing in III-V materials, in: Grundlagen von Elektrodenreaktionen, Dechema Monographien, Band 102, VCH Verlagsgesellschaft, Frankfurt am Main 1986, pp. 453-464.

[9] D. V. Podlesnik, H. H. Gilgen and R. M. Osgood, Jr, Deep-ultraviolet induced wet etching of GaAs, Appl. Phys. Lett. 45, 563-565, 1984.

[10] P. H. L. Notten, The etching of InP in HCl solutions: a chemical mechanism, J. Electrochem. Soc. 131, 2641-2644, 1984.

[11] W. Huber, Titrations in non aqueous solvents, Academic Press, New York 1967, p. 215 and 226.

In an etching process with a very high rate constant the concentration of the reagent at the semiconductor surface may be so low that the diffusion of the reagent to the surface will be rate-determining. The rate of a diffusion-controlled etching process (r_d) is proportional to the concentration gradient at the surface. For one-dimensional diffusion with a linear concentration gradient it is given approximately by

$$r_d \approx \frac{D}{\delta}\,(c_b - c_s), \qquad (11)$$

where D is the diffusion coefficient and δ the thickness of the 'diffusion layer' at the surface. The temperature dependence of the etch rate is now mainly determined by that of the diffusion coefficient, which is inversely proportional to the viscosity of the solution. For the aqueous solutions normally used we can derive an 'activation energy' of about 18 kJ/mol from the curve of log r_d against $1/T$.

If the rate of the surface reaction is of the same order of magnitude as the rate of diffusion, there are various methods for influencing the rate-determining step. In the case where the surface reaction is not of the first order ($n > 1$), it follows from eq. (9) that increasing the concentration c_b will result in a greater increase in the reaction rate, so that the diffusion becomes more important. A change in the same direction is obtained by increasing the temperature; see *fig. 9*. The surface reaction, which is rate-determining at low temperatures, is much more temperature-dependent than the diffusion, so that at higher temperatures the diffusion becomes the rate-determining quantity. A change in the opposite direction can be obtained by reducing the thickness δ of the diffusion layer; see eq. (11). This can be done by rotating the semiconductor or by stirring the solution. It is then possible to change a diffusion-controlled process into a kinetically controlled process.

Diffusion in electroless etching

In the example given in fig. 6 the anodic partial current due to the oxidation of GaAs is kinetically controlled. The current depends only on the hole concentration at the surface. Near the mixed potential the reduction rate is determined by the diffusion of the oxidizing agent (Ce^{4+}) to the surface. This means that the rate of the total process is determined by diffusion via the reduction reaction. This situation is most frequently encountered in electroless etching.

We have been able to show that the etch rate can also be determined by diffusion via the oxidation reaction. This is illustrated in *fig. 10* for p-GaAs in a solution of 0.5 M $K_3Fe(CN)_6$ with a *p*H of 13. The total current-potential curve has three distinct plateaus. At low potentials the cathodic partial current due to the reduction of $Fe(CN)_6^{3-}$ is entirely determined by diffusion and does not depend on the potential. The reduction stops as soon as the potential approaches the redox potential of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple. The anodic partial current due to the GaAs oxidation becomes important at the flat-band potential. At higher potentials, however, the anodic partial current also becomes constant. We have found that the etching process then depends on the transfer of OH^- ions to the semiconductor surface. The intermediate plateau in the total curve is the result of the difference between the potential-independent sections of the anodic and cathodic partial curves.

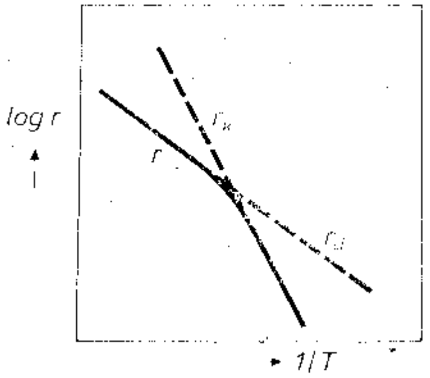

Fig. 9. Diagram showing the effect of the temperature T on the rate r and the kinetics of the etching process, where r_k is the etch rate when the surface reaction is kinetically controlled and r_d is the etch rate when the surface reaction is diffusion-controlled. Both log r_k and log r_d decrease linearly with $1/T$. At low temperatures, however, r_k is much smaller than r_d, so that the surface reaction determines the etch rate ($r \approx r_k$). At high temperatures r_k is much larger than r_d, and diffusion is then rate-determining ($r \approx r_d$).

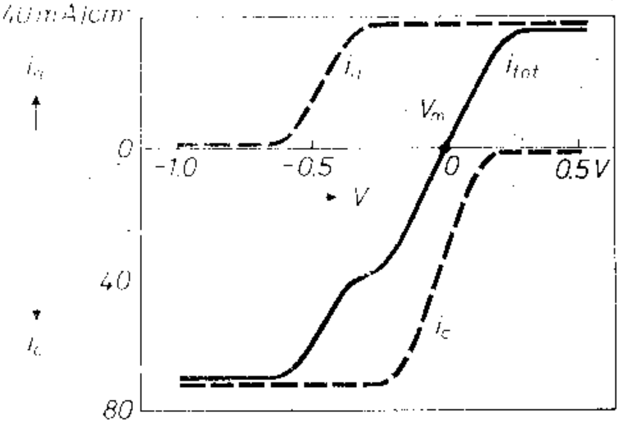

Fig. 10. Current-potential curves (as in figs 6 and 7) for p-GaAs in an 0.5M $K_3Fe(CN)_6$ solution with a *p*H of 13. The anodic and cathodic partial current densities i_a and i_c are such that the curve for the total current density i_{tot} has three plateaus, corresponding to the constant value of i_c at low V, the constant value of i_a at high V and the difference between these two values. The etch rate, which is proportional to i_a at the mixed potential V_m, is not determined by a constant cathodic current in this case, but by a constant anodic current.

The constant cathodic current in fig. 10 is much higher than the constant anodic current. At the mixed potential it is not the cathodic current that is constant, but the anodic current, so that the etch rate is diffusion-controlled via the oxidation reaction. If the $K_3Fe(CN)_6$ concentration is decreased so as to make the constant cathodic current lower than the constant anodic current, the result, just as in fig. 6, is an etch rate that is diffusion-controlled via the reduction reaction.

Effect of the crystal planes

Semiconductors like GaAs, GaP and InP are normally used in single-crystal form. Their crystal structure corresponds to the zinc-blende structure of ZnS. The A atoms (Ga, In) form a face-centred cubic structure in which half the tetrahedral interstices are periodically filled with B atoms (As, P). Crystal planes such as the {100} and {111} planes can be distinguished from each other by a different density and arrangement of the atoms, which can affect the etch rate. Because of the polarity in the ⟨111⟩ directions, an A{111} plane, i.e. a {111} plane occupied only by A atoms, will behave differently from a B{111} plane[12].

The arrangement of the atoms in the surface crystal plane can have a considerable effect on the flat-band potential V_{fb}. *Table I* gives the values of V_{fb} for the {100}, As{111} and Ga{111} planes of n-type and p-type GaAs. The difference in V_{fb} between corresponding crystal planes of n-type and p-type GaAs is approximately equal to E_g/e, where E_g is the band gap of GaAs (see p. 63). The {100} and As{111} planes have almost the same V_{fb}-value, but that of a Ga{111} plane is much higher. Partly because of this the anodic dissolution of a Ga{111} surface only starts at a potential more than 100 mV higher than the onset potential for dissolution of an As{111} surface.

Table I. Flat-band potential V_{fb} with respect to a saturated calomel electrode for three kinds of crystal planes of n- and p-GaAs in an NaOH solution with a pH of 14.

Crystal planes	V_{fb}	
	n-GaAs	p-GaAs
{100}	− 1.80 V	− 0.50 V
As{111}	− 1.75	− 0.45
Ga{111}	− 1.55	− 0.25

In the literature various examples are given of the effect of the crystal planes on the rate of chemical etching, when this is not determined by mass transfer in the solution. It was found, for example, in the etching of InP[13] that the rate varies in the sequence P{111} ≥ {100} ≫ In{111}. The explanation for this goes beyond the scope of this article[12].

Etching at mask edges

If the etch rate is determined by diffusion for all crystal planes, isotropic etching would be expected at mask edges. Chemical etching does indeed give rounded profiles in this case. At a mask edge the etch depth is relatively large, because there is mass transfer both from the solution above the etched surface and from the solution beside the mask aperture. *Fig. 11* shows a profile produced at a mask edge after a diffusion-controlled chemical etching process. It agrees well with the theoretical profile calculated from a two-dimensional model[14].

If the etch rate of one of the crystal planes is determined by the rate of the surface reaction, facets are found at mask edges. The shape of the etch profile is then usually determined by the plane etched most slowly, which is usually an A{111} plane.

In electroless etching processes, profiles with facets may be observed even though the etch rate of all the

Fig. 11. Scanning electron-microscope photograph (scale divisions 1 µm) of GaAs at a mask edge after a diffusion-controlled etching process with an H_2O_2/HCl solution. The etching results in a rounded profile, in good agreement with a profile calculated for this case[14].

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[12] See for example H. C. Gatos, Crystalline structure and surface reactivity, Science 137, 311-322, 1962.

[13] R. Becker, Sperrfreie Kontakte an Indiumphosphid, Solid State Electron. 16, 1241-1249, 1973.

[14] H. K. Kuiken, J. J. Kelly and P. H. L. Notten, Etching profiles at resist edges, I. Mathematical models for diffusion-controlled cases, J. Electrochem. Soc. 133, 1217-1226, 1986;
P. H. L. Notten, J. J. Kelly and H. K. Kuiken, Etching profiles at resist edges, II. Experimental confirmation of models using GaAs, J. Electrochem. Soc. 133, 1226-1232, 1986.

individual planes is determined entirely by diffusion. This is related to the effect of cathodic protection, which we shall now briefly discuss.

Cathodic protection

When a metal is in contact with another metal during etching, the etch rates of the individual metals may be changed considerably by galvanic effects[15]. The etch rate of the less-noble metal tends to increase, while the more-noble metal is etched more slowly. The more-noble metal is then said to be 'cathodically protected'.

This effect is also found in the electroless etching of different semiconductors or semiconductor regions in contact with each other[16]. *Fig. 12* gives a schematic representation of the current-potential curves for two p-doped III-V semiconductors, A_1B_1 and A_2B_2, of equal area. Owing to the difference in 'nobility' the anodic partial curves of A_1B_1 and A_2B_2 are different. On the other hand the cathodic partial curves coincide, because the reduction rate is assumed to be determined by the diffusion rate of the oxidizing agent in the solution. Consequently the separate semiconductors are etched at the same rate, A_1B_1 at the mixed potential V_1 and A_2B_2 at the mixed potential V_2. If A_1B_1 and A_2B_2 are in electrical contact, their partial current-potential curves have to be added together. This results in a new curve for the anodic process and in a cathodic current that is twice as large, because the areas of A_1B_1 and A_2B_2 are combined. This gives a new mixed potential ($V_{1,2}$), with a value higher than V_1 and lower than V_2, which means that the etch rate of A_1B_1 is higher and that of A_2B_2 lower.

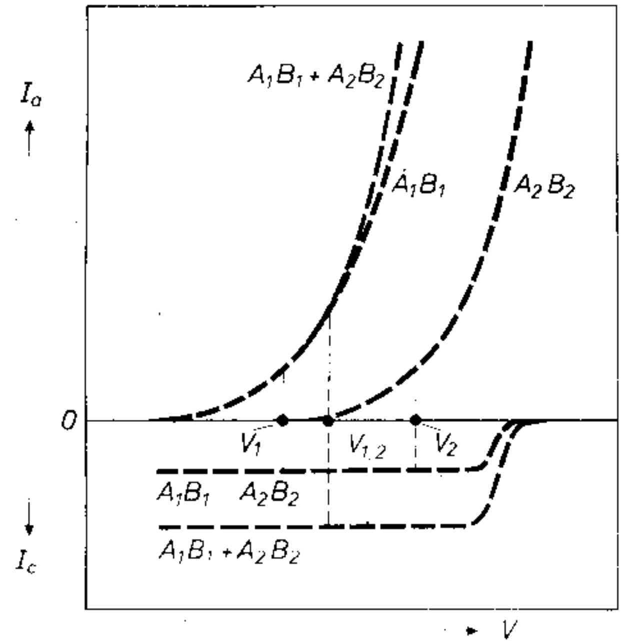

Fig. 12. Schematic current-potential curves illustrating the occurrence of cathodic protection in the etching of two semiconductors in electrical contact. Electroless etching of the individual semiconductors A_1B_1 and A_2B_2 at the mixed potentials V_1 and V_2 takes place at the same rate, determined by the constant value of the cathodic partial current. If there is electrical contact the partial currents of A_1B_1 and A_2B_2 have to be added together (red). Etching then takes place at an intermediate mixed potential, $V_{1,2}$, so that the 'less-noble' A_1B_1 is dissolved faster and the 'nobler' A_2B_2 more slowly.

Cathodic protection can be useful for selectively etching semiconductors in multilayer structures: while there is little or no difference in the etching behaviour of the separate materials, there can be a considerable difference in etch rate because of the electrical contact between them.

Practical examples

The applications of wet-chemical etching of III-V semiconductors are much too numerous for a detailed description of each. We shall therefore confine ourselves to a few interesting applications that we have investigated.

Material quality control

Although the semiconductors used for making electronic devices are true single crystals, they always have some crystallographic defects. These defects, which may decide the quality and life of a component, can be revealed by a treatment with a defect-selective etchant. Defects usually correspond to crystallographically perturbed areas such as dislocations and stacking faults. Since these areas will behave less 'nobly' than their environment, they can be selectively etched in the dark. The higher etch rate at defects leads to the formation of etch pits. The sensitivity of etchants based on this principle is in general low: to make all the defects visible it is necessary to etch away more than 10 μm. Obviously this cannot be done for thin films.

Crystallographic defects can also be revealed by photo-etching, since it is known that effective recombination of free electrons and holes often takes place at such defects. Since the photo-etch rate depends on the surface concentration of both types of charge carrier, the increased recombination at crystal defects produces a local decrease in the etch rate. Photo-etching therefore makes the sites with defects stand out from their environment ('hillocks'). The high sensitivity that can be achieved in this way is demonstrated in *fig. 13*, which shows a photomicrograph of n-GaAs after photo-etching with an H_2O_2/H_2SO_4 solution. Many defects are visible after removal of 0.4 μm of the surface. Striations due to areas of different doping concentration also appear, as parallel lines.

Fig. 13. Photomicrograph (interference contrast) of n-GaAs after photo-etching with an H_2O_2/H_2SO_4 solution for revealing crystal defects[8].

The CrO_3/HF solutions mentioned earlier are also suitable etchants for the quality control of III-V semiconductors. In these etchants the crystallographic defects are revealed by the formation in the dark of a thin passivating film, which is slightly thicker at the defects than on a perfect surface[7]. The defects are thus preferentially passivated, so that they are etched away more slowly. In n-GaAs and n-InP the sensitivity can be increased further by illumination; this effect can again be attributed to increased recombination of electrons and holes at the defects.

Profile etching

The etching of special shapes and profiles with the aid of a resist is a very important process in III-V semiconductor technology. To take a particular example, structures with symmetrically rounded edges or grooves with a V-shaped cross-section are frequently used for semiconductor lasers. Good use can often be made here of etching kinetics. As we have shown, etching processes with a rate-determining surface reaction give structures with facets, whereas the diffusion-controlled chemical etching processes are isotropic. We have also shown that the etching kinetics can be changed, for example by raising the temperature (fig. 9). This makes it possible to influence the etching profile fairly easily. *Fig. 14* shows an example in which the profiles were made in GaAs by chemical etching at different temperatures. At 0 °C the surface reaction is still rate-determining and a V-groove is produced. At 20 °C diffusion becomes important, with the result that the profile is slightly rounded. At 40 °C diffusion is rate-determining and the result is an almost completely rounded profile.

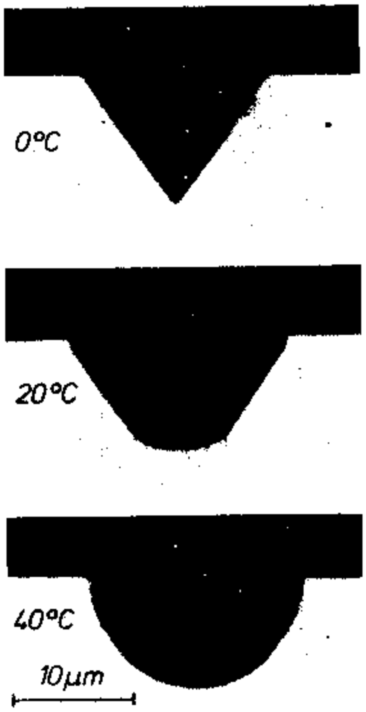

Fig. 14. Photomicrographs of profiles in GaAs after chemical etching with a Br_2/KBr solution at different temperatures. A change in temperature has a pronounced effect on the etching kinetics and gives a completely different etching profile: from a V-groove at 0 °C to an almost completely rounded profile at 40 °C.

Another factor that has an important bearing on the shape of the etching profile is the orientation of the mask in relation to the crystal orientation. If for example a narrow track in the $[\bar{1}10]$ direction is etched into a (001) surface, the result is a channel with a V-shaped cross-section, formed by two {111} planes

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[15] J. J. Kelly and C. H. de Minjer, An electrochemical study of undercutting during etching of duplex metal films, J. Electrochem. Soc. **122**, 931-936, 1975;
J. J. Kelly and G. J. Koel, Galvanic effects in the wet-chemical etching of metal films, Philips Tech. Rev. **38**, 149-157, 1978/79.

[16] H. Löwe and I. Barry, Zur Kinetik der Germaniumauflösung in alkalischen Hexacyanoferrat-III-Lösungen, Z. Phys. Chem., Leipzig **249**, 73-80, 1972.

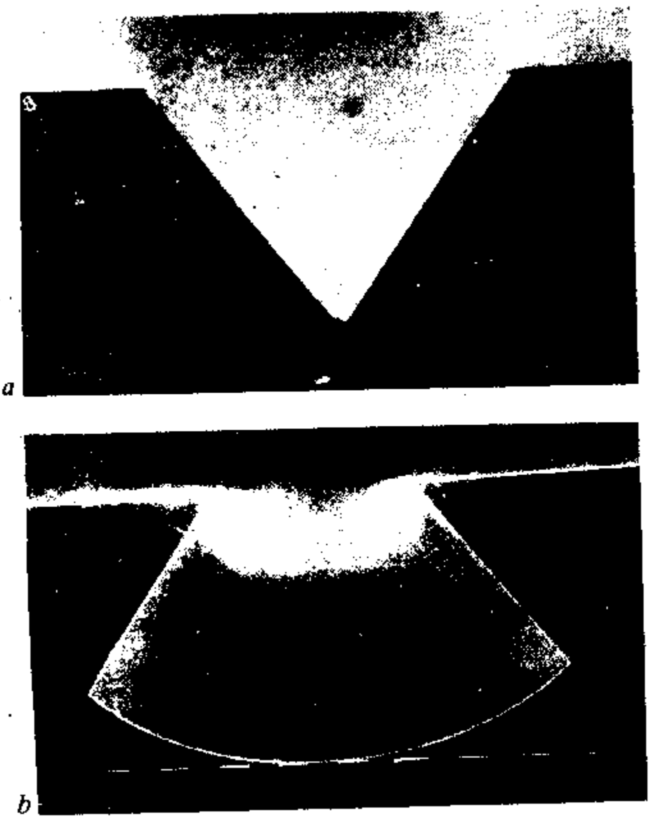

Fig. 15. Scanning electron-microscope photographs (scale divisions 1 μm) of GaAs after chemical etching with a Br_2/HBr solution for two different mask orientations. When a narrow track is etched in the [$\bar{1}$10] direction a V-groove is formed (*a*). When this is done in the [110] direction, the result is a 'dovetail' (*b*).

with A atoms; see *fig. 15a.* The characteristic etching angle between the side planes and the surface is 55°, corresponding to the angle between the (001) plane and the {111} planes. If on the other hand a narrow track is etched in the [110] direction (i.e. perpendicular to the [$\bar{1}$10] direction), then the etching spreads outwards with a characteristic angle of 125°, corresponding to the supplement of the angle between the (001) plane and the {111} planes. This results in a channel with a 'dovetail' cross-section (fig. 15*b*).

In electroless etching the etch rates for the various crystal planes are clearly often diffusion-controlled, and yet profiles with facets are obtained. In these cases the etch rate is determined by the cathodic partial current due to the reduction reaction (figs 6 and 7). During etching at a mask edge various crystal planes are exposed to the etchant. As we have shown, these have different V_{fb}-values (Table I) and the anodic-current-potential curve depends on the crystal plane. This means that galvanic effects can occur between the planes of *the same* crystal. In an analogous way to that shown in fig. 12, the most-noble plane is cathodically protected by the rest of the surface, and this results in the formation of a facet.

This effect does not occur when, as in fig. 10, the etch rate is determined by a diffusion-controlled anodic current. This situation is shown schematically in *fig. 16.* In this case the diffusion-controlled cathodic current (not shown) is very high and there are two planes of quite different nobility. It can be seen from the anodic current at the mixed potential that the electrical contact between the planes has no effect on their etch rate. There is no cathodic protection, so that the planes dissolve at the same diffusion-controlled rate and a rounded profile is obtained.

In the photo-etching of III-V semiconductors using light of very short wavelength (e.g. 350 nm) an exceptionally high anisotropy can be achieved[9]. The strong absorption of the light induces a relatively high concentration of holes in the exposed part of the semiconductor surface, resulting in a highly direction-dependent etching process. Since the etched cavity acts as a waveguide for the incident light, and dissolution only occurs at the bottom of the cavity, structures with very deep holes or grooves can be produced. Structures of this type offer interesting prospects for practical application.

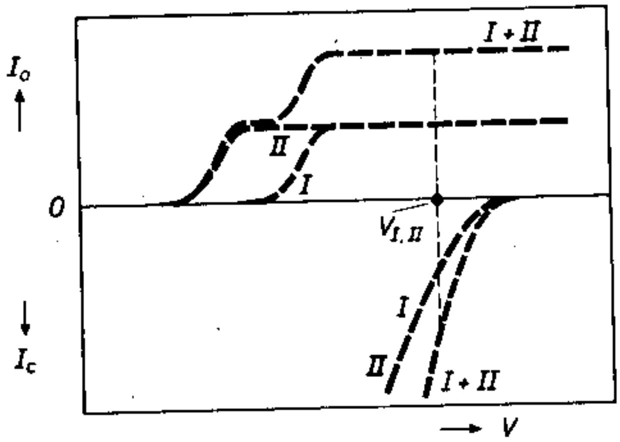

Fig. 16. Schematic current-potential curves for the etching of two crystal planes *I* and *II*, of dissimilar 'nobility', with no cathodic protection. Both planes give the same diffusion-controlled constant anodic current, which is much lower than the diffusion-controlled cathodic current (not shown here). At the mixed potential $V_{I,II}$ the total anodic current (red) is equal to the sum of the constant anodic currents of *I* and *II*, so that the electrical contact between *I* and *II* has no effect on their etch rates.

Selective etching

In III-V semiconductor technology there is a need for selective etchants that are highly sensitive to the composition of the material. High selectivity is particularly important for etching thin-film structures, as in semiconductor lasers, in which the active layer is no thicker than 0.1 μm. To illustrate what can be achieved in this field we shall discuss a few typical examples.

With chemically dissimilar materials the required selectivity can often be obtained by using the appropriate etchant. For instance, InP can be dissolved selectively with respect to $In_xGa_{1-x}As_yP_{1-y}$ by chemical etching in a concentrated HCl solution, in which the $In_xGa_{1-x}As_yP_{1-y}$ is hardly attacked at all. *Fig. 17* shows a multilayer structure with these semiconductors, in which the InP has been partly removed by selective etching. The opposite selectivity can be obtained in electroless etching, e.g. with a Ce^{4+}/H_2SO_4 solution. The $In_xGa_{1-x}As_yP_{1-y}$ readily dissolves in this solution, while the InP is passivated, probably because of the formation of an oxide film on the surface. An example of a multilayer structure etched in this way is shown in *fig. 18*.

Both forms of selectivity are also possible with GaAs and $Al_xGa_{1-x}As$. In etching multilayer structures with these materials the $Al_xGa_{1-x}As$ is passivated to such an extent in some solutions, by the formation of an oxide film, that virtually only the GaAs is attacked; see *fig. 19*. A suitable method for selectively dissolving $Al_xGa_{1-x}As$ with respect to GaAs is based on the difference in the nobility of these compounds in electroless etching. *Fig. 20* shows a multilayer structure treated by this method. Etching through a mask first produces a narrow hole in the upper GaAs layer, and then a much wider hole in the $Al_xGa_{1-x}As$ layer beneath it. The bottom GaAs layer is not attacked, however, because of its greater nobility and the cathodic protection.

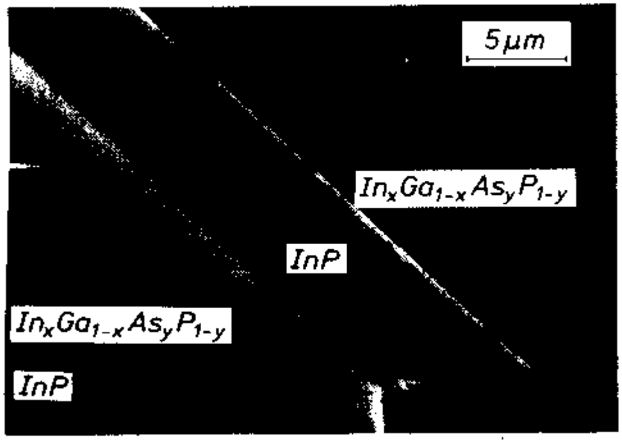

Fig. 17. Scanning electron-microscope photograph of a multilayer structure of InP and $In_xGa_{1-x}As_yP_{1-y}$, after chemical etching with a concentrated HCl solution. Only the InP layers have been partly etched away.

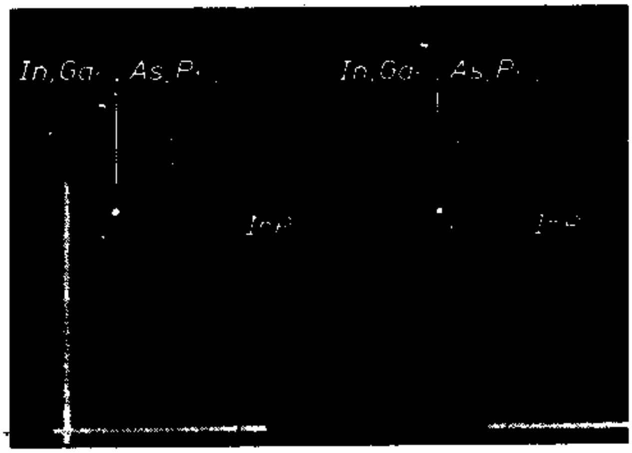

Fig. 18. Scanning electron-microscope photograph (scale divisions 1 μm) of a multilayer structure of InP and $In_xGa_{1-x}As_yP_{1-y}$, in which electroless etching with a Ce^{4+}/H_2SO_4 solution has only affected the $In_xGa_{1-x}As_yP_{1-y}$.

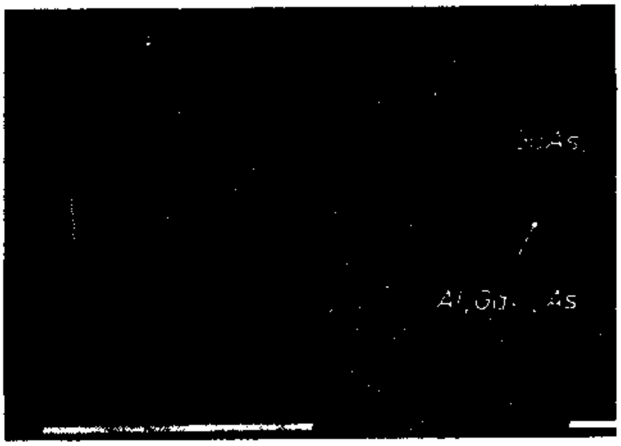

Fig. 19. Scanning electron-microscope photograph (scale divisions 1 μm) of a multilayer structure of GaAs and $Al_xGa_{1-x}As$, in which only GaAs has been partly removed by chemical etching with an H_2O_2 solution.

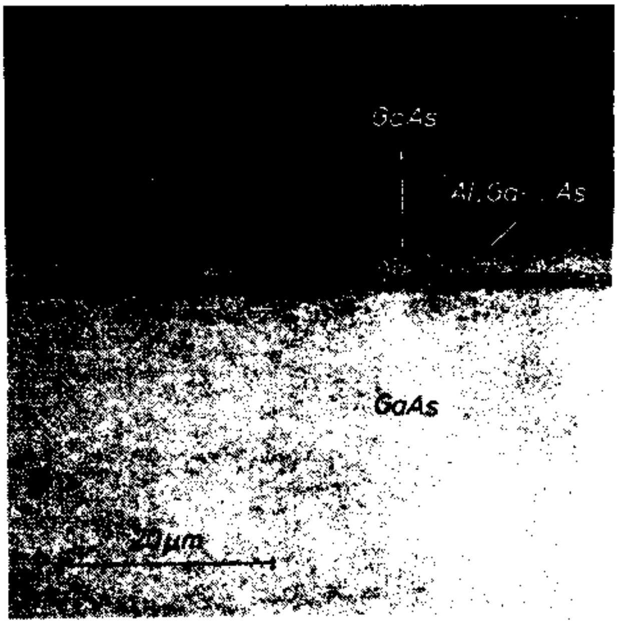

Fig. 20. Photomicrograph of a multilayer structure of GaAs and $Al_xGa_{1-x}As$. Electroless etching through a mask has produced a relatively small hole in the top GaAs layer and a much wider hole in the underlying $Al_xGa_{1-x}As$ layer. The bottom GaAs layer has not been attacked, however.

The selective etching of semiconductor materials that differ only in the type of doping is in general not possible by electroless or chemical etching. Although some selectivity may be obtained with electroless photo-etching, the most reliable method is based on anodic etching. The principle can be simply illustrated with reference to fig. 3. The p-GaAs is selectively dissolved in the dark at a potential near its flat-band potential (about 0.3 V), whereas on exposure to light and with a lower potential only the n-GaAs is dissolved. In this way regions on either side of a pn-junction in GaAs can be etched selectively. A p-doped InP layer can also be completely removed from an n-InP layer beneath it by anodic etching.

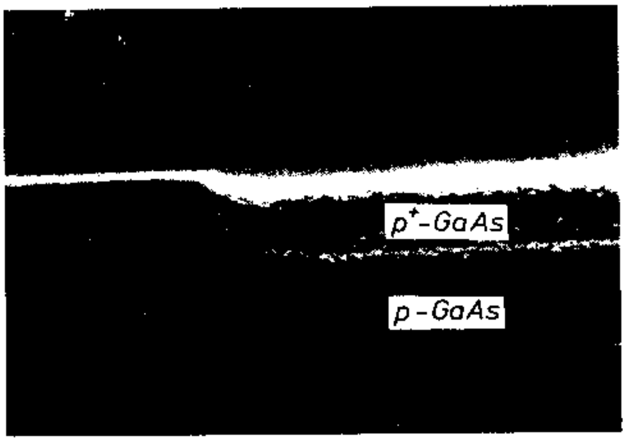

Fig. 21. Scanning electron-microscope photograph (scale divisions 1 μm) of a GaAs layer in which the heavily doped p^+ region has been etched away with a $K_3Fe(CN)_6$ solution; the less heavily doped p region has hardly been attacked.

By using a difference in potential distribution, with cathodic protection, we have succeeded in selectively etching semiconductor materials that differ only in doping concentration. Such combinations of materials are found in laser structures with a top layer of p-GaAs that is heavily doped (p^+) locally to give good electrical contact. The contact region can be revealed by selective etching with a solution of 0.1 M $K_3Fe(CN)_6$ at a *p*H of 14; see *fig. 21*. The only difference between the p and p^+ regions shown here is the doping concentration: 10^{18} and 10^{20} cm^{-3}. Because of the near-metallic nature of the p^+ region, the potential distribution at the interface with the solution is quite different from that for a conventional p-type semiconductor. The p^+ region is less noble and is more rapidly dissolved when in contact with a large p-type area.

Summary. III-V semiconductors like GaAs can be wet-chemically etched by three mechanisms: electrochemically with an external voltage source, electrochemically using an oxidizing agent (electroless), and chemically with a reactive compound. In some cases the etching process only proceeds when the semiconductor is exposed to light. The etch rate depends on the relative reaction rate at the semiconductor surface and the mass transfer in the solution. Other important factors are the effect of the crystal planes, the orientation of a mask with respect to these planes, and the electrical contact with other materials. Wet-chemical etching of III-V semiconductors can be used on a large scale for various applications, including the detection of crystallographic defects, the fabrication of special profiles and the selective dissolution of closely related materials in multilayer structures.